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Edited by Angelo Basile, Alfredo Cassano
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Preface

Water is the most abundant and renewable resource in the world. Unfortunately, only a small quantity is fit for use to sustain human life. In addition, population growth coupled with industrialization and urbanization has led to the increased pollution of existing freshwater resources, resulting in an increased demand for fresh water. At the same time, challenges related to water systems are expected to increase in the near future, requiring further investment and technological innovation to meet global needs.

Currently, water recycling is widely accepted as a sustainable option in response to the general increase in the demand for fresh water and to water shortages and environmental protection. According to this view, industrial companies are increasingly interested in recycling wastewater to reach an ideal zero-discharge condition.

Membrane technology has become a significant separation technology in the field of water filtration over the past two decades, providing effective alternatives to related technologies such as adsorption, extraction, distillation, ion exchangers, and sand filters. It enables desalination, or obtaining drinking water from saltwater, as well as purification of groundwater or wastewater.

Low-energy consumption, continuous separation, easy scale-up, modularity, remote control, and no phase separation are well-recognized key advantages of membrane processes over conventional separation technologies.

The growth of the global membranes market is mainly the result of the impressive development of materials used for membrane fabrication and modification, improvements in membrane modules, and the evolution of different related systems, plants, and equipment.

This book covers the most recent and applicable achievements regarding materials, processes, and applications of membranes for water treatment.

The book is split into three parts. The first is related to both novel membrane materials and advances in membrane operations. The second part considers how to improve membrane performance, and the last part illustrates selected applications in water treatment. In the following section, each chapter is briefly introduced.

Chapter 1 (Madeani, Ghaemi, and Rajabi) illustrates the recent development of new materials and methods for the fabrication and modification of polymeric membranes for water treatment. Chapter 2 (Lee, Wu, and Li) provides an extensive analysis concerning recent progress in ceramic membranes for drinking water production and in the treatment of municipal and industrial wastewater, produced water (waste stream generated from oil and gas operations), and wastewater generated in the food and beverage industry. In Chapter 3 (Koyuncu, Sengur, Turken, Guclu, and Pasaoglu), after a general overview of the global membrane market and various membrane fabrication techniques, advances in water treatment by membrane processes such as ultrafiltration, microfiltration, and nanofiltration are extensively illustrated. Water treatment by both reverse and forward osmosis for the desalination of water is described in Chapter 4 (Rastogi, Cassano, and Basile). Differences among various membrane processes and the fundamentals of water treatment by reverse osmosis and forward osmosis are also considered. Chapter 5 (Deowan, Bouhadjar, and Hoinkis) introduces membrane bioreactor technology, with particular attention to water treatment. Both aerobic and anaerobic reactors are described. The various factors affecting membrane performance in both reactors (membrane fouling, hydraulic residence time, water flux decline, and so on, in aerobic reactors, and temperature, organic loading rate, membrane properties, and so on, in anaerobic reactors) are seen as important issues in this application of technology. For each reactor, a case study is also proposed. The state of the art in the use of electrodialysis and electrodialysis with bipolar membranes for water treatment is reported in Chapter 6 (Van der Bruggen). In particular, after a general description of the operational mechanisms of electrodialysis, progress in anion and cation exchange membranes and new developments in module configurations and process integration are described. Finally, a brief overview of applications of electrodialysis for water treatment is given. Chapter 7 (Molinari, Argurio, Palmisano, and Grillone) discusses both the basic principles of photocatalysis and advantages related to its coupling with membrane separation in so-called photocatalytic membrane reactors (PMRs). Important aspects for appropriate large-scale implementation are the types of membranes used, their criteria of selection, PMR configuration, and membrane operation. Some case studies in water treatment are also discussed, evidencing possibilities, drawbacks, and future trends. Chapter 8 (Arribas, Khayet, García-Payo, and Gil) describes pressure-driven membrane processes and significant progress achieved over the past few years regarding the fabrication of novel membranes and their modification. In particular, the chapter focuses on novel flat-sheet and hollow-fiber membranes made with innovative materials and with improved properties suitable for specific applications. In Chapter 9 (Arribas, Khayet, García-Payo, and Gil), the authors of the previous chapter extend consideration to the electric potential and concentration gradient membrane processes. In particular, in this chapter the authors focus on water treatment, by electrodialysis, with forward osmosis. Also, special attention is dedicated to alternative technologies of emerging interests used to produce power, such as reverse electrodialysis and pressure-retarded osmosis, able to generate electricity from salinity gradients. Some critical challenges (e.g., concentration polarization, membrane fouling, reverse solute diffusion, and draw solute design) are also discussed.

Chapter 10 (Frenkel) introduces the importance of membrane technologies when the water supply is considered for the community, industry, or agricultural user. In fact, membrane technologies have entered every aspect of water and wastewater treatment, such as municipal and industrial water, advanced wastewater treatment and reuse, and seawater and brackish water desalination. This chapter pays attention to the design of both low- and high-pressure membrane systems for water treatment.

Finally, integrated membrane systems and a combination of membrane treatment and other technological processes are briefly considered. After distinguishing between membrane ageing and failure, Chapter 11 (Tng, Antony, Wang, and Leslie) describes membrane ageing during water treatment with particular attention to the modes and mechanisms of failure. The authors review possible monitoring and control techniques necessary for the early detection of membrane ageing. They also suggest some measures for mitigating membrane failure caused by ageing. Chapter 12 shows the importance of mathematical modeling in membrane operations for water treatment (Ang and Mohammad). In particular, this chapter provides useful data on designing the plant and helpful prediction of the performance of the membrane water treatment plant. Different transport mechanisms are involved in pressure-driven membrane operations. Thus, the mathematical models necessary to predict their performance are also different. The authors show that the selection of a particular model of membrane water treatment plant is crucial because it leads to a better understanding of its long-term performance. Chapter 13 (Curcio, Di Profio, Fontananova, and Drioli) provides a general overview of membrane operations currently in use in seawater and brackish water desalination for potable water production. In this chapter, reverse osmosis, novel salinity gradient power technologies (with emphasis on pressure-retarded osmosis and reverse electrodialysis) and membrane distillation are treated as viable options in the logic of zero liquid discharge. After introducing a section on drivers and barriers to membrane technologies for municipal wastewater treatment, Chapter 14 (Sadr and Saroj) describes various membrane-assisted processes and technologies in wastewater treatment. Another important part of the chapter is related to both applications of nanofiltration/reverse osmosis after biological treatment and the design, operation, and control of membrane processes in municipal wastewater treatment. The optimization of membrane processes in municipal wastewater treatment is also well described, taking into consideration cost assessment, energy efficiencies, and operational costs. In Chapter 15 (Bodzek), an analysis of the main organic and inorganic micropollutants of water sources is presented. Membrane processes such as reverse osmosis and nanofiltration, ultrafiltration, and microfiltration in integrated systems, Donnan dialysis, and electrodialysis, as well as membrane bioreactors and liquid membranes are presented as alternative technologies for producing high-quality drinking water as well as purified wastewater that can be drained off into natural water sources. Chapter 16 (Yang) highlights key advantages of pressure-driven membrane operations and their integration into existing systems for water treatment and reuse in the gas and petrochemical industries. Methods to reduce concentration polarization and membrane fouling phenomena, which mainly affect membrane system performance and directly determine the capital and operational costs of membrane systems in this field, are also presented and discussed. Membrane technologies for water treatment and reuse in the textile industry are described in Chapter 17 (Petrinić, Bajraktari, and Hélix-Nielsen). The authors present various examples of reverse osmosis/nanofiltration/ultrafiltration-based systems and membrane bioreactor technology that have been investigated for textile wastewater remediation. Forward osmosis, used to concentrate textile dyes, is also presented. Chapter 18 (Cassano, Rastogi, and Basile) presents an overview of membrane-based processes for water reuse and the environmental control in the treatment of wastewaters from food-processing industries. Various applications involving the use of pressure-driven membrane operations, electrodialysis, membrane bioreactors, and integrated membrane systems are shown and discussed. In particular, the authors illustrate typical applications for the treatment of process waters from the fruit and vegetables, dairy, fish, meat, soya, and wine industries, highlighting their advantages and drawbacks with respect to conventional technologies. Chapter 19 (Mänttäri, Kallioinen, and Nyström) focuses on the use of membrane technologies to purify raw water and wastewaters, circulate process waters, and recover valuable materials in the pulp and paper industry. The driving forces to use membranes and barriers, as well as their challenges, are discussed in the introduction. Chapter 20 (Daal) focuses on water treatment required for the production of demineralized water employed for the water/steam cycle in industrial plants. Water purification technologies including membrane technologies and operational experiences with membranes are presented and discussed.

The editors wish to take this opportunity to thank all of the authors of the chapters for preparing, developing, and improving their text. Special thanks to all of the staff of Woodhead for their excellent help to both the authors and the editors.

Angelo Basile
Alfredo Cassano
Navin K. Rastogi

Part One

Novel membrane materials and advances in membrane operations

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Advances in polymeric membranes for water treatment

1

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1.1 Introduction

As the most precious and renewable resource in the world, water is an important aspect of life. The world's population tripled in the twentieth century and it will increase by another 40% to 50% within the next 50 years. Population growth coupled with industrialization and urbanization has resulted in the rapidly increasing demand for fresh water. Furthermore, some existing fresh water resources have gradually become polluted because of human or industrial activities. Problems with water are expected to grow in the coming decades, with water scarcity occurring globally, even in regions currently considered water-rich. Therefore, many researchers have focused on suitable methods to obtain fresh water by purifying and reusing water to support future generations. Water purification is the process of removing unpleasant agents such as chemicals, organic and biological contaminants, and suspended solids from water to obtain satisfactory water.

Owing to its low cost and high efficiency, membrane technology has dominated water purification technologies. Compared with the other types of membranes, polymeric membranes lead the membrane separation industries and markets because they are economically and practically beneficial. However, limited chemical, mechanical, and thermal resistance restricts their application. Extensive efforts have been implemented to improve both flux and selectivity and reduce membrane fouling as the most important problem in application of membranes. To eliminate obstacles and decrease the problems in membrane use, much research and numerous studies have been conducted to develop new materials and methods for fabricating and modifying polymeric membranes. This chapter covers the most recent and applicable achievements regarding the preparation, modification, and performance of polymeric membranes for water treatment.

1.2 Advances in polymeric membranes

1.2.1 Composite (mixed matrix) membranes

Sometimes when fabricating membranes, structural modification is necessary to enhance overall performance as well as the mechanical, chemical, and thermal stability

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of the membrane. Methods to overcome the challenges of membrane modification have been well established for polymeric membranes. Much research on membrane science and technology has focused on the development of new membrane preparation techniques and material. An alternate way to improve membrane performance including permeability and selectivity involves introducing second phases into the membrane matrix. Polymers and some nanofillers were mostly introduced as a second phase into polymeric membranes to prepare different kinds of composite membranes.

1.2.1.1 Composite membranes prepared via blending of polymers

Blending of additives into the casting solution is one of the most applicable methods to change the phase separation process and, consequently, membrane characteristics. Polymeric materials are applied considerably as additives into the dope solution (Musale, Kumar, & Pleizier, 1999; Ochoa et al., 2001). Although certain polymers such as polyethersulfone (PES) and poly(vinylidenefluoride) (PVDF) possess excellent thermal and mechanical stability as well as acceptable film-forming properties that make them ideal materials for membrane preparation, their application is often restricted because of their hydrophobic nature, which results in low water permeation and high fouling. On the other hand, the membranes made of hydrophilic polymers such as poly(vinyl alcohol) (PVA), cellulose acetate (CAc), and polyacrylonitrile (PAN) are also applied for the fabrication of liquid separation membranes; however, the thermal and mechanical resistance and chemical stability of these membrane are low. Blending of polymers in membrane fabrication has been widely investigated because of the simplicity of procedure and high efficiency in developing new membranes with elevated properties and performance.

The main focus in blending polymers is to increase hydrophilicity and decrease membrane fouling. Rahimpour and Madaeni (2007) prepared PES membrane by blending different concentrations of CAP (20, 30, and 40 wt%) and PVP (2, 4, and 8 wt%) as a pore former. Contact angle measurements showed that the hydrophilicity of membranes was enhanced for all compositions because of numerous acidic and carbonyl functional groups in the CAP structure. Pure water flux, milk water permeation, and protein rejection also increased with an increase in PES/CAP compositions up to 80/20. Moreover, the antifouling property of PES membranes was improved by adding even small amounts of CAP into the casting solution. In another study (Masuelli, Marchese, & Ochoa, 2009), a PVDF ultrafiltration membrane was modified by blending PVDF with PVP and sulfonated polycarbonate to enhance permeation flux and reduce fouling. Surprisingly, the hydraulic permeability of the membrane was reduced and fouling increased for composite membranes (Masuelli et al., 2009). Composite polysulfone (PSf) membranes were synthesized by Adams, Nxumalo, Krause, Hoek, and Mamba (2012) by blending PSf with different concentrations of β-CPU (0−10%) using a phase inversion technique. Addition of 5% β-CPU to PSf membrane greatly improved the hydrophilicity of composite membranes compared with higher amounts because fewer pores were created on the membrane surface and owing to the chemical interaction between OH/NH and the sulfonyl backbone of PSf. Moreover, it was revealed that a low concentration of β-CPU was effective in improving flux without compromising membrane rejection (Adams et al., 2012). Table 1.1 summarizes some studies on composite membranes and the main properties of blending polymers.

Table 1.1 Studies on composite polymeric membranes

Materials	Feed solution	Properties of composite versus nascent membrane	References
CA/SPSf	—	Larger pore size	Malaisamy, Mahendran, and Mohan (2002)
PVDF/PMMA	Effluent from engine factory	Larger macrovoides, higher hydrophilicity, lower fouling	Ochoa, Masuelli, and Marchese (2003)
PS/PA	Solution of CN^-, Zn^{2+}, $Zn(CN_4^{2-})$	Good chemical stability, less mechanical resistance, good selectivity	Amado, Gondran, Ferreira, Rodrigues, and Ferreira (2004)
PES/CAP/PVP	Milk	Higher hydrophilicity, more pure water flux, milk water permeation, and protein rejection	Rahimpour and Madaeni (2007)
PES/PI/PVP	Salt solution	Higher hydrophilicity, more pure water flux, more salt rejection	Mansourpanah, Madaeni, Adeli, and Rahimpour (2009)
SPC/PVDF	Oil–water emulsion	Lower fouling	Masuelli et al. (2009)
PSf/PAN	Aqueous solution of heavy metals	Decrease in mean surface-pore size, overall porosity, and permeability, high lead, cadmium, and chromium rejection	Mbareck, Nguyen, Alaoui, and Barillier (2009)

Continued

Table 1.1 Continued

Materials	Feed solution	Properties of composite versus nascent membrane	References
CA/PU	Aqueous solutions containing textile dye	Lower thermal stability	Zavastin et al. (2010)
HPAA/PSf	BSA solution, aqueous solution containing heavy metal	Higher water flux, higher rejection of BSA and Cd (II)	Han, Yu, et al. (2012)
CNC/PSf	Papermaking effluent	Decreasing mechanical strength by increasing CNC content, higher permeation, good ability in papermaking effluent filtration	Zhou, Zhao, Bai, Zhang, and Tang (2012)
PVDF/SPPO	Ionic solution	Higher water content and ion-exchange capacity, superior performance by 60% SPPO and 40% PVDF	Khodabakhshi et al. (2012)
PSf/β-CPU	Solution of heavy metal	Higher hydrophilicity, more water flux and rejection, lower porosity, less mechanical strength	Adams et al. (2012)

1.2.1.2 Thin-film composite membranes

Dense membranes generally have low flux but high selectivity, whereas porous membranes have low selectivity but high permeability. To increase flux through a dense membrane with high selectivity, the thickness of the membrane should be reduced as much as practically possible. However, the membrane should be defect-free and possess adequate mechanical strength. This may be achieved with the use of thin-film composite (TFC) membranes.

Such composite membranes often consist of two layers: a thin, dense, selective top layer supported by a porous substrate. The main role of the porous support is to provide mechanical strength, whereas the thin skin layer is responsible for permselectivity. A TFC membrane is usually formed by a two-step process: formation of a thick, porous, and nonselective substrate followed by coating with an ultrathin skin layer. Among different methods for forming the top layer, dip-coating (Lang, Sourirajan, Matsuura, & Chowdhury, 1996; Peng, Huang, Jawor, & Hoek, 2010; Susanto & Ulbricht, 2008) and interfacial polymerization (Kim, Kim, Yu, & Deng, 2009; Prakash Rao, Desai, & Rangarajan, 1997; Rahimpour, Jahanshahi, Mortazavian, Madaeni, & Mansourpanah, 2010; Reddy et al., 2005; Shao et al., 2013; Verissimo, Peinemann, & Bordado, 2005; Wu et al., 2006) were widely used. Of these, interfacial polymerization is particularly interesting, taking into account the considerable amount of research in this field.

TFC membranes have had remarkable development since the concept of interfacial polymerization was introduced by Mogan in 1965 (Lau, Ismail, Misdan, & Kassim, 2012). In this technique, polymerization reaction takes place between two reactive monomers at the interface of two immiscible solvents. First, the pores of a membrane used as the support are filled with liquid A; then, the support is immersed in a bath containing a reactant for liquid A. As the result of interfacial polymerization reaction, a dense, highly cross-linked polymer layer is formed on the surface of the membrane at the interface of two solutions. Heat, ultraviolet (UV), and plasma treatment are often applied to control and complete interfacial polymerization. The top skin layer is extremely thin (0.1 μm or less), so TFC membrane permeability is high. Also, membrane selectivity is high as a result of the high cross-linking of polymers.

Commonly used reactive monomers are aliphatic/aromatic diamines such as piperazine (PIP), *m*-phenylenediamine (MPDA), and *p*-phenylenediamine (PPD), and acid chloride monomers such as trimesoyl chloride (TMC), isophthaloyl chloride (IPC), and 5-isocyanatoisophthaloyl chloride (ICIC). Among these materials and prepared TFC membranes, polyaniline (PA) membranes prepared by interfacial polymerization of multifunctional amine and acyl chloride monomers (Han, Chung, et al., 2012; Kim, Hwang, Gamal El-Din, & Liu, 2012; Kim et al., 2009; Maurya, Parashuram, Singh, Ray, & Reddy, 2012; Rahimpour et al., 2010; Shao et al., 2013; Verissimo et al., 2005; Yu, Liu, Liu, and Gao, 2009; Wu et al., 2006) are the most typical and successful TFC membranes. Rahimpour et al. (2010) prepared a TFC PA nanofiltration membrane using interfacial polymerization of PDA with TMC. The TFC polyamide membranes displayed a higher ability to soften water. The composite membrane exhibited water permeability of 7 and 21 kg/m^2 h for salt solution containing NaCl (1 g/l) and $MgSO_4$ (1 g/l) at 5 and 10 bar, respectively. Also, rejection of the divalent salt $MgSO_4$ (85% and 90%) was high compared with the monovalent salt NaCl (64% and 67%) at 5 and 10 bar, respectively. In other research, Han, chang, et al. (2012) demonstrated that blending a certain amount of sulphonated poly(ether ketone) (SPEK) material into the PSf substrate of TFC forward osmosis (TFC-FO) membranes not only has a key role in forming a fully spongelike structure, but also enhances membrane hydrophilicity and reduces structure parameters. In this study, MPDA and 1,3,5-TMC were employed as monomers for the interfacial polymerization reaction to form a thin aromatic polyamide selective layer. The TFC-FO membranes with the most hydrophilic SPEK (50 wt%) in the substrates exhibited the lowest membrane thickness, a fully spongelike structure, and the highest water flux of 50 and 35 l/m^2 h when deionized water and 2 M NaCl were used as the feed and draw solution, respectively.

New synthesized monomers were also employed to prepare TFC membranes with notable properties. Li and Kim (2008) synthesized a series of isomeric tetra-functional biphenyl acid chloride (mm-BTEC, om-BTEC, and op-BTEC) to prepare TFC reverse osmosis membranes through an interfacial polymerization technique with MPDA as the amine monomer in aqueous solution. According to this study, the organic phase reactants had a considerable impact on membrane performance compared with the aqueous phase reactant. Experimental results showed that the membrane prepared from op-BTEC revealed the highest permeability (54.2 l/m^2 h) followed by membranes prepared from om-BTEC (50.0 l/m^2 h) and mm-BTEC (31.7 l/m^2 h) when tested using a 2000 ppm NaCl solution at 2 MPa. The rougher and larger surface area of the op-BTEC membrane, which led to greater contact with water molecules, was reported as the reason for the flux enhancement of this membrane (Li , Zhang, Zhang, & Zheng, 2008). In another study, Chen, Li, Zhang, and Zhang (2008) synthesized a new class of polymeric amine, named SPES-NH_2, which was applied for the preparation of TFC reverse osmosis membranes. Polysulfone was used as substrate and TFC membrane was prepared through interfacial polymerization of TMC solutions and amine solutions containing SPES-NH_2 and m-Phenylenediamine (MPDA). The salt rejection and water flux of the composite membrane prepared under the optimum condition (acyl chloride monomer = 1.0%; ratio of MPDA to SPES-NH_2 = 2:1; 4 min contact time with organic solution) reached 97.3% and 51.2 l/m^2 h, respectively. The improvement in water flux was due to the incorporation of hydrophilic SPES-NH_2 to polyamides. On the other hand, the high salt rejection was related to the chain stiffness of the copolymer and the high degree of cross-linking. A novel amine monomer, β-cyclodextrin polyurethane (DABA), with three amino groups was synthesized and applied along with MPDA in TFC membrane preparation by Wang Li, Zhang, and Zhang (2010) to increase the hydrophilicity of a PAN nanofibrous substrate. With an increase in the DABA content in the aqueous phase from 0% to 0.25% (w/v), the TFC membranes showed an increment in water flux from 37.5 to 55.4 l/m^2 h while maintaining high salt rejection (~98%) in the filtration of a salt solution containing 2000 ppm NaCl at 2 MPa.

With respect to the fouling resistance, Abu Seman, Khayet, and Hilal (2010, 2011) reported on the preparation of TFC membranes with improved antifouling tendency by means of interfacial polymerization between BPA and/or TMBPA with TMC. Irreversible fouling of modified polyester TFC PES membranes decreased during filtration of solutions containing humic acid at different pH values. The highly uniform top polyester layer coupled with the negative charge of the composite membrane was introduced as the main reason for the lower fouling of the TFC membrane.

Furthermore, An, Li, Ji, and Chen (2011) incorporated PVA into composite nanofiltration membranes by adding different amounts of PVA into PIP during interfacial polymerization with TMC to improve the antifouling performance of composite membranes. The incorporation of a hydrophilic PVA chain into the PA active layer had beneficial effects on developing a smoother surface and increasing membrane hydrophilicity that were effective in diminishing the fouling of protein over the long run.

The application of additives such as synthesized hydrophilic surface modifying macromolecules (Abu Tarboush, Rana, Matsuura, Arafat, & Narbaitz, 2008; Rana, Kim, Matsuura, & Arafat, 2011) was shown to be effective in altering TFC membrane performance. Abu Tarboush et al. (2008) prepared a TFC membrane with a more hydrophilic surface by incorporating the synthesized additive hydrophilic surface modifying macromolecules (LSMM) into the active PA thin top layer. It was observed that during in situ polymerization, LSSMs could migrate toward the top air–polymer interface, rendering the membrane hydrophilic and producing a composite membrane with improved flux stability over an extended operational period compared with an LSMM-free composite membrane. Another important development in TFC membrane technology was the incorporation of nanoparticles into the TFC membrane structure (Kim, Kwak, Sohn, & Park, 2003; Lee, Im, Kim, Kim, & Min, 2008). Kim et al. (2003) prepared a hybrid TFC reverse osmosis membrane by the self-assembly of anatase TiO_2 nanoparticles through coordination and H-bonding interaction with the COOH functional groups of an aromatic polyamide thin-film layer to reduce membrane biofouling. The photocatalytic bactericidal ability of the hybrid TFC membrane was examined by determining the survival ratios of *Escherichia coli* cells with and without UV light illumination. Photocatalytic bactericidal efficiency was remarkably higher for the hybrid TFC membrane under UV light illumination than that without illumination and the neat TFC membranes. Lee et al. (2008) also reported on a preparation of PA nanocomposite membrane containing TiO_2 nanoparticles synthesized via in situ interfacial polymerization under various curing temperatures and curing times. The interfacial reaction occurred between the aqueous phase of MPDA and the organic phase of TMC in which TiO_2 nanoparticles were homogeneously dispersed. The incorporation of TiO_2 nanoparticles into PA resulted in an increase in water flux owing to the enhancement of hydrophilicity in the membranes. When the concentration of TiO_2 nanoparticles was 5.0 wt%, the optimum membrane performance was obtained together with strong mechanical properties. In more concentration of TiO_2, the permeation flux increased and salt rejection decreased significantly. Moreover, the decrease in mechanical strength of the membranes resulted in easier peeling-off of the PA-TiO_2 layer from PES substrate after the filtration experiment. These results were attributed to the fact that a lower degree of polymerization of PA occurs at high TiO_2 concentrations because of an increase in the interference of interfacial polymerization by TiO_2 nanoparticles. The incorporation of zeolite-A nanoparticles (Jeong et al., 2007) and multi-walled nanotubes (MWNTs) (Wu, Tang, & Wu, 2010) throughout the thin-film layer were also explored as a facile approach to produce superior hydrophilic membranes with improved performance.

The addition of co-solvent into the organic phase is another alternative to improve TFC membrane performance (Kim, Kwak, & Suzuki, 2005; Kong, Kanezashi, Yamomoto, Shintani, & Tsuru, 2010). Kong et al. (2010) applied this method and added acetone as the co-solvent into the organic phase to synthesize TFC nanofiltration membranes with controllable active layer thickness and effective nanopores. The presence of acetone could eliminate the large immiscibility gap between water and hexane; therefore, it caused the interfacial polymerization reaction zone to be controllable. Consequently, the permeation flux increased noticeably from 2.1×10^{-12} m^3/m^2 Pa s for membranes prepared by conventional interfacial polymerization to 8.0×10^{-12} m^3/m^2 Pa s for TFC membranes prepared by adding co-solvent.

1.2.2 Nanocomposite membranes (nano-enhanced membranes)

In another approach to membrane development processes, researchers focused on incorporating inorganic nanoparticles into polymeric materials, which resulted in the formation of nanocomposite (nano-enhanced) membranes with improved mechanical and physicochemical properties. Various nanomaterials have been employed as filler, such as carbon nanotubes (CNTs), nanoclay, nanosilver, and nanosized TiO_2, ZnO, Al_2O_3, Fe_3O_4, SiO_2, and ZrO_2. More details about developments in nanocomposite membranes and their performance in water treatment are presented in the following sections.

1.2.2.1 Carbon nanotubes

Among the various nanomaterials studied, CNTs have received a great deal of attention. With high hydrophilicity, good chemical stability, and high surface area, CNTs induce highly antibacterial properties and increase the porosity of nanocomposite membranes. They are ideal for reinforcing membranes because of their high aspect ratio and high axis strength (Daraei, Madaeni, Ghaemi, et al., 2013). The wide range of possible applications for CNTs has been a driving force for the production of high-quality single-walled (SW), double-walled (DW), and MW CNTs for incorporation into CNT—polymer composites (Vatanpour, Madaeni, Moradian, et al., 2012).

Several methods have been applied to produce inorganic-polymer membranes, such as filtration of the solvent containing dispersed CNTs through the membrane and then in situ polymerization onto the membrane surface (Madaeni, Zinadini, & Vatanpour, 2011a), dispersion of CNTs in the monomer solution and then interfacial polymerization onto a membrane as substrate (Roy, Addo Ntim, Mitra, & Sirkar, 2011), and blending nanoparticles into the casting solution followed by immersion into the coagulation bath (Celik, Park, Choi, & Choi, 2011; Choi, Jegal, & Kimb, 2006; Mansourpanah et al., 2011) or evaporation (Tang, Zhang, Wang, Fu, and Zhang, 2009).

Blending has some advantages over other methods. The method is simple and has mild conditions, reproducibility, and capability for industrialization. Also, preparation through polymer solution casting permits the use of polymers, which were previously found not to be suitable for in situ polymerization (Vatanpour, Madaeni, Moradian, et al., 2012). Previous studies by Choi et al. (2006) showed that MWCNT-blended PSf microfiltration membranes had slightly higher flux and rejection rates than nascent PSf membrane. Also, those authors found that MWCNT-blended membranes were more hydrophilic than PSf ones. In a related work, Qui et al. (2009) showed that MWCNT-blended PSf ultrafiltration membranes had higher flux and lower rejection as well as lower protein adsorption compared with nascent PSf membrane.

Although CNTs have excellent separation characteristics and electrical and mechanical properties, there are problems in preparing mixed matrix membranes using this material, such as no suitable dispersion of synthesized CNTs in organic solvents and different polymers (Celik et al., 2011; Shirazi, Ahmadzadeh Tofighy, and Mohammadi, 2011; Vatanpour, Madaeni, Moradian, et al., 2012). Thus, surface modification of this material is necessary to fabricate a homogeneous nanocomposite membrane. Recent studies showed that surface modification can increase the dispersing properties of CNTs. Chemical modification and functionalization of CNTs, surfactant treatment, and polymer wrapping are several methods that have been widely used for uniform dispersion of nanotubes in a polymer matrix and for enhancing CNT adhesion to the polymer (Choi et al., 2006; Eitan, Jiang, Dukes, Andrews, & Schadler, 2003; Islam, Rojas, Bergey, Johnson, & Yodh, 2003; O'Connell et al., 2001; Qu et al., 2004; Yang, Chen, et al., 2007). In this regard, Shawky, Chae, Lin, and Wiesner (2011) added different concentrations of MWCNTs to the PA membrane casting solution to form a nanocomposite structure, improve the mechanical properties of these membranes, and increase their ability to reject salts. The MWCNTs were dispersed into a mixture of dimethylacetamide (DMAc) (solvent) and lithium chloride salts. Benzoyl peroxide (BPO) initiator was added into the casting solution with the goal of forming free-radicals on both CNTs and PA. This process resulted in polymer-grafted nanotubes that dispersed better throughout the casting solution, and a more homogeneous MWCNTs–PA composite membrane was formed. Investigation of the hydrophilicity and mechanical strength of nanocomposite membranes revealed a decrease in hydrophilicity owing to the hydrophobic nature of nanomaterials and an increase in the mechanical strength of the membranes because of the strong interactions between the PA matrix and MWCNTs and homogeneous dispersion of CNTs.

The decrease in permeability from 32 to 28 l/m^2 h and increase in salt rejection from 24% to 76%, respectively, for the PA and MWCNTs/PA (15 mg/g) composite membrane were attributed to this network structure. In addition, humic acid removal by MWCNT composite membranes increased from 54% to 90% as the MWCNT loading increased from 0 to 10 mg/g (Shawky, Chae, Lin, and Wiesner, 2011).

The introduction of hydrophilic functional groups onto the surface of the CNTs using chemical modification, especially acid, is one of the simplest, most widely used, and least expensive methods for uniform dispersion of nanotubes in the polymer matrix (Balasubramanian, & Burghard, 2005; Celik et al., 2011; Eitan et al., 2003; Shirazi et al., 2011; Vatanpour, Madaeni, Moradian, Zinadini, & Astinchap, 2011). Vatanpour et al. (2011) fabricated nanocomposite membranes composed of PES and acid-treated functionalized MWCNTs using a solution of 3 M HNO_3/H_2SO_4 (1/3, v/v). Functionalized MWCNTs were embedded in PES matrix using the phase inversion method. The treated MWCNTs exhibited good dispersion and compatibility with the polymer matrix. The blending of MWCNTs into PES matrix resulted in an increase in hydrophilicity and water flux along with a decrease in fouling of the nanocomposite membrane caused by Bovine Serum Albomin (BSA) filtration.

In another work, the same author (Vatanpour, Madaeni, Moradian, et al., 2012) fabricated an anti-bifouling nanofiltration membrane by mixing PES with TiO_2-coated functionalized MWCNTs. They coated MWCNTs with TiO_2 nanoparticles to enhance the dispersion of CNTs in organic solvent and polymer and improve the interaction between the CNTs and the polymer matrix. To purify and functionalize CNTs, the MWCNTs were dispersed into a mixture of H_2SO_4 and HNO_3 with a ratio of 3:1. The functionalized MWCNTs could participate in a reaction with other reagents as a result of the formation of carboxylic acid groups on the surface of MWCNTs (Vatanpour, Madaeni, Moradian, et al., 2012). To better deposit TiO_2 nanoparticles onto the surface of oxidized MWCNTs, dendrimer polycitric acid was grafted onto functionalized CNTs. At the final step, MWCNTs were coated with TiO_2 nanoparticles. A schematic of the preparation of TiO_2-coated MWCNTs is presented in Figure 1.1.

The TiO_2-coated MWCNTs showed suitable compatibility with polymeric matrix, resulting in a low agglomeration of MWCNTs. Addition of the modified MWCNTs influenced the surface mean pore size and porosity of the nanocomposite membranes.

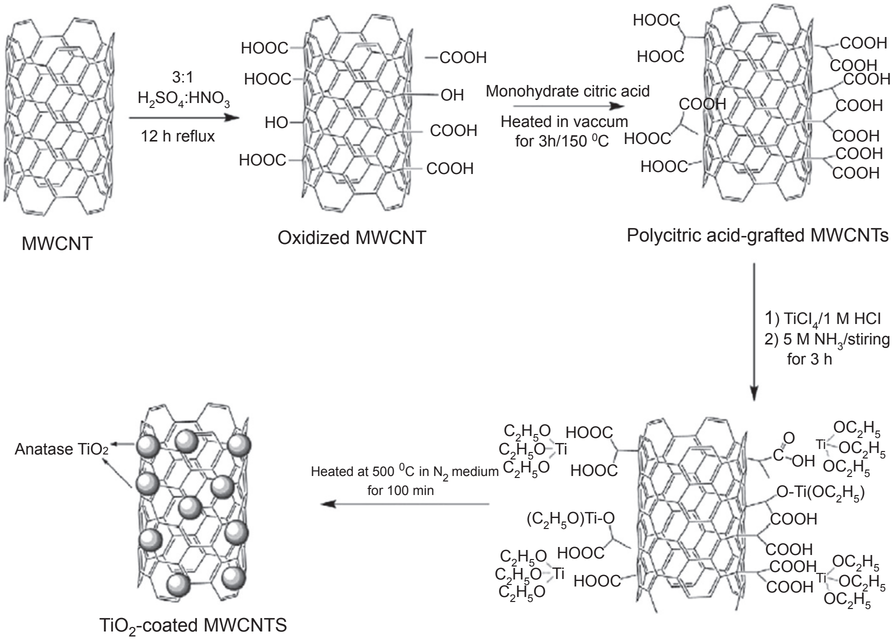

Figure 1.1 Schematic showing coating of multi-walled carbon nanotubes (MWCNTs) with TiO_2 nanoparticles.
Reprinted from Vatanpour, Madaeni, Moradian, et al. (2012), with permission from Elsevier.

The prepared mixed matrix membranes showed higher hydrophilicity compared with nascent PES membrane, which resulted in an increase in pure water flux. Also, the anti-biofouling characteristics of the nanoparticle-embedded membranes improved as a result of increased hydrophilicity and decreased membrane surface roughness (Vatanpour, Madaeni, Moradian, et al., 2012). Daraei, Madaeni, Ghaemi, Ahmadi, et al. (2013) and Daraei, Madaeni, Ghaemi, Khadivi, et al. (2013) studied the effects of blending polymer-modified MWCNTs and PES membranes and compared the results with acid-functionalized MWCNTs. They modified acid functionalized MWCNTs using three hydrophilic polymers through an in situ polymerization reaction. Citric acid, acrylic acid, and acryl amide were polymerized on acid-functionalized MWCNTs to achieve a higher number of functional groups on MWCNTs (Daraei, Madaeni, Ghaemi, Khadivi, et al., 2013). The CNT-mixed membranes were fabricated using the phase inversion precipitation method. Although this treatment process caused a higher pure water flux with unchanged protein retention by adding a constant amount of PAA and PAAm-modified MWCNT into the membrane matrix, the best antifouling performance was shown by the membrane containing PCA-modified MWCNT. The hyperbranched PCA caused an efficient dispersion of MWCNTs because of good compatibility with PES. This membrane also showed acceptable reusability and durability during three cycles of fouling–washing steps.

1.2.2.2 Clay nanoparticles

Clay nanoparticles are another inorganic additive for enhancing membrane performance. Unmodified montmorillonites (Na^+–MMT) and Cloisite grades (modified MMT) are widely used nanofillers in the preparation of polymer nanocomposites. Montmorillonite contains phyllosilicate groups and possesses an octahedral sheet sandwiched between two tetrahedral sheets, forming a plate-shaped structure (with the average diameter around 1 mm) (Abdollahi, Rahmatpour, Aalaie, & Khanbabae, 2008; Xie, Tan, Liao, and Liu, 2010). The layered structure of silicate has attractive hydrophilic properties and good thermal stability at high temperature (Bebin, Caravanier, & Galiano, 2006). The most common methods used to prepare polymer clay nanocomposite technology are: in situ polymerization, melt intercalation, and solution dispersion. In the latter method, the clay mineral is exfoliated in single layers in the solvent medium, and polymer chains are intercalated into these clay mineral layers. The clay mineral platelets are joined by weak van der Waals forces and can easily be dispersed in the solvent because of the increase in entropy caused by their disorganization. Then, polymer is adsorbed onto the delaminated clay mineral layers and the layers are reassembled after evaporation of the solvent and filled with polymer chains, forming an intercalated nanocomposite (Anadão, Sato, Wiebeck, Rolando, & Diaz, 2010; Ghaemi, Madaeni, Alizadeh, Rajabi, & Daraei, 2011).

The clays most applied in polymer clay nanocomposite materials are generally those containing clay minerals of the smectic group, especially those containing MMT, which are often employed for several innovative uses: for example, as absorbers in the retention of pollutant gases, in acid catalysis, in sensors, and as nanofillers in nanocomposite preparation.

Many researchers have investigated the effects of adding clay particles on the morphology and thermal, mechanical, and hydrophilic properties as well as on the performance of composite polymeric membranes. Bebin et al. (2006) prepared a composite membrane containing clay particles. Membranes were prepared by a recasting procedure using a Nafion solution mixed with Laponite particles comprising sulfonic acid groups bonded to its surface. The surface of clay particles was modified using plasma activation to bond styrenesulfonic moieties at their surface. The dispersion of modified clay particles had a significant effect on the behavior of the Nafion membrane and enhanced both the water retention and proton conductivity of nanocomposite membranes. Monticelli, Bottino, Scandale, Capannelli, and Russo (2007) reported on improving water permeability for PSf membranes blended with cationically modified clays. The cationic clay—PSf membranes showed the most flux and the least water contact angle (most hydrophilicity), resulting in the enhancement of membrane performance. Anadão et al. (2010) also used modified clay as a PSf dopant and reported significant changes to the membrane morphology and thermal, mechanical, and hydrophilic properties.

Another typical polymer used to prepare polymer clay composites is PVDF. Li and Kim (2008) investigated the effect of adding modified clay (Closite Na^+) on the thermal properties of microporous PVDF membranes. The authors reported that the thermal properties of PVDF nanocomposite membrane diminished after adding modified clay nanoparticles. In another work, various kinds of clay particles (Closite Na^+, Closite 15A, Closite 20A, and Closite 30B) were incorporated into PVDF membrane by a solution mixing method and PVDF—clay nanocomposite membranes were prepared by the phase inversion method (Hwang, Kim, Kim, Hong, & Nam, 2011). Improved mechanical properties and thermal stability against shrinkage were obtained by incorporating clay particles into the PVDF matrix. In contrast, Koh et al. (2010) did not find considerable improvement in the mechanical properties of PVDF—hexafluoropropylene (PVDF—HFP)—clay nanocomposite membranes because of the increased porosity of the nanocomposite membranes.

Ghaemi et al. (2011) synthesized PES—organically modified montmorillonite (OMMT) nanocomposites using Closite 15A and reported significant changes to the membrane skin layer and sublayer with increasing clay concentration in the casting solution. They declared that the addition of OMMT can be effective in considerably improving membrane hydrophilicity and thermal and mechanical resistance as well as pesticide retention capability at different solution conditions (acidic and neutral). In similar work, Mierzwa, Arieta, Verlage, Carvalho, and Vecitis (2013) investigated the effect of incorporating unmodified clay nanoparticles (single platelet MMT) with and without sodium hexametaphosphate as a clay nanoparticle dispersant into the casting solution on the morphology and performance of PES ultrafiltration membranes. They showed that clay additives have the ability to increase membrane permeability as a result of changes induced on the structure of the internal and surface pores of the membrane. The addition of clay nanoparticles resulted in a reduction in hydrophilicity and the negative charge of the membrane surface. Surprisingly, it was revealed that although the clay membranes were more prone to fouling, membrane permeability in the filtration of alginate solution was still greater than the nascent membrane (Mierzwa et al., 2013).

Wan Ngah, Teong, and Hanafiah (2011) used chitosan-based composites containing MMT, clay, bentonite, etc., for dye removal from effluents. Improvement of chitosan properties and performance was considered the main achievement of fabricating such nanocomposites. An increase in mechanical and thermal strength as well as higher plasticity of chitosan−OMMT nanocomposite was also reported by researchers (Abdollahi et al., 2008; Casariego et al., 2009; Han, Lee, Choi, & Park, 2010). Moreover, many studies were conducted on the adsorption of pollutants onto the chitosan−clay composites in which the increment of the adsorption capacity of chitosan membranes was proved as a result of adding clay nanoparticles (An & Dultz, 2007; Bleiman & Mishael, 2010; Celis, Adelino, Hermosin, & Cornejo, 2012; Chang & Juang, 2004; Nesic, Velickovic, & Antonovic, 2012; Pandey & Mishra, 2011). For example, Nesic et al. (2012) tested the adsorption capability of chitosan/MMT (Closite Na^+) with Bezactiv Orange V-3RBO (BO) solution. The effect of different amounts of MMT on the adsorption of BO was evaluated under different pHs and temperatures. It was revealed that chitosan in combination with clays produced a reliable adsorbent. The main advantage of these membranes compared with similar systems is that these membranes possessed significantly higher adsorption capacity at low acidic conditions (pH above 6). Therefore, the pretreatment of wastewater is not needed in real applications. Despite relatively long adsorption tests, these membranes were applicable as the result of a high adsorption capacity. Thin-film composite membranes using chitosan−nanoclay (Closite 15A and 30B) coated onto the PVDF microfiltration membrane was fabricated by Daraei et al. (2013). Insertion of organoclays with various percentages into the chitosan made it more efficient for fabricating TFC membranes with the valuable ability to remove dye (methylene blue and acid orange 7) from effluents.

1.2.2.3 Silver nanoparticles

Compared with other nanoparticles, silver (Ag) is one of the first nanomaterials that gained attention for fabricating composite membranes. The bactericidal nature of silver nanoparticles brought them into the field of mixed matrix membranes. Silver nanoparticles have a large surface-to-volume ratio; thus, they are used as a sustained local supply for Ag^+ ions and provide a prolonged prevention of bacterial adhesion (Cao, Tang, Liu, Nie, & Zhao, 2010; Martinez-Gutierrez et al., 2012; Mollahosseini, Rahimpour, Jahamshahi, Peyravi, & Khavarpour, 2012). Silver is believed by some researchers (Danilczuk, Lund, Saldo, Yamada, & Michalik, 2006) to be nonallergic, nontoxic, and environmentally friendly. Other researchers believe that silver is less harmful to human cells compared with bacteria (Taurozzi et al., 2008). Research has shown that incorporation of Ag nanoparticles onto the surface or in the matrix of membranes is effective against the bacteria *E. coli*, *Pseudomonas mendocina* KR1, *P. aeruginosa*, and *Staphylococcus aureus* (Li, Shao, Zhou, Li, & Zhang, 2013; Liu, Zhang, He, Zhao, & Bai, 2010; Liu, Rosenfield, Hu, & Mi, 2013; Mollahosseini et al., 2012; Zhang, Zhang, Gusseme, & Verstraete, 2012; Zodrow et al., 2009). Also, it was proved that the addition of Ag nanoparticles into the membrane matrix not only makes the membranes bactericidal, but also results in a significant improvement in virus removal (Zhang et al., 2012; Zodrow et al., 2009). Chamakura, Perez-Ballestero, Luo, Bashir, and Liu (2011) described in detail the steps of the antibacterial mechanism including (1) generation of reactive oxygen species indirectly, (2) direct interaction of Ag with proteins and lipids in the cell wall and also proteins in the cytoplasmic membrane, and (3) interaction with deoxyribonucleic acid. Some investigators (Koseoglu-Imer, Kose, Altinbas, & Koyuncu, 2013) suggested that Ag nanoparticles might pass through cell barriers and then release Ag^+ ions. Then, Ag^+ ions interact with the thiol groups of enzymes and cell proteins, damage bacterial respiration, and transport systems across the cell membrane.

Silver ions were employed in membrane fabrication because of their low toxicity toward humans and their antibacterial ability. In this regard, researchers prepared membranes with silver ions to obtain a superior antifouling performance (Basri et al., 2010; Chou, Yu, & Yang, 2005). In contrast with silver ions, silver nanoparticles induced long-lasting antibacterial and anti-adhesive effects, and consequently considerable resistance to biofouling in the membranes (Li et al., 2013; Zodrow et al., 2009). To take advantage of Ag nanoparticles, Ag does not necessarily need to be embedded into the membrane structure during preparation. It can be added to a commercial membrane and regenerated if needed. However, loss of antimicrobial and antiviral activity of Ag-coated membranes might occur as a result of depleting silver particles from the membrane surface and ineffectiveness against silver-resistant bacterial strains (Zodrow et al., 2009). For this reason, silver nanoparticles have received more attention in lessening biofouling through embedding into the membrane backbone; so far, most studies on antifouling nanocomposite membranes have focused on incorporating silver nanoparticles inside the membranes (Gusseme et al., 2011; Li et al., 2008; Sawada et al., 2012; Thomas et al., 2009; Travan et al., 2009; Zhang et al., 2012; Zodrow et al., 2009). This way, silver nanoparticles were added into the PAN (Yu et al., 2003), poly (2-ethyl-2-oxazoline) (Kang, Kim, Char, Won, & Kang, 2006), PA (Lee et al., 2007), polyimide (PI) (Deng, Dang, Zhou, Rao, & Chen, 2008), PES (Basri, Ismail, & Aziz, 2011; Basri et al., 2010; Cao et al., 2010; Huang, Arthanareeswaran, et al., 2012), CA (Barud et al., 2011; Chou et al., 2005), chitosan (Liu et al., 2010; Zhu, Bai, Wee, Liu, & Tang, 2010), PVDF (Li et al., 2013), and PSf (Zodrow et al., 2009) composite membranes. Antibacterial experiments confirmed that bacterial growth was effectively inhibited and anti-biofouling performance rose in these kind of nanocomposite membranes.

An increase in the hydrophilicity and selectivity of membranes blended with Ag nanoparticles was also reported apart from the antibactericidal and antifouling properties of silver (Basri et al., 2011; Koseoglu-Imer et al., 2013; Yong et al., 2010; Zodrow et al., 2009). Silver nanoparticles can be used as a suitable candidate for the simultaneously improvement of membrane surface hydrophilicity and antifouling performance under proper conditions. This phenomenon occurs because Ag particles diminish the surface tension of a pristine membrane and so water can easily spread onto membrane surfaces (Li et al., 2013).

1.2.2.4 Titanium dioxide nanoparticles

Titanium dioxide (TiO_2) is a special semiconductor that has been the focus of numerous investigations because of its excellent photocatalytic and hydrophilicity properties in absorbing UV rays and its stability, cheapness, and commercial availability. Therefore, many researchers have prepared TiO_2-mixed matrix membranes to improve membrane performance by increasing hydrophilicity and reducing fouling (Madaeni & Ghaemi, 2007; Vatanpour, Madaeni, Khataee, et al., 2012; Yang & Wang, 2006; Yang, Zhang, et al., 2007).

Ebert, Fritsch, Koll, and Tjahjawiguna (2004) investigated the influence of incorporating TiO_2 particles on the performance of PVDF and PAI membranes at elevated pressures and temperatures. Membranes fabricated by the phase inversion method revealed considerable thermal and mechanical stability. In another work, Yang and Wang (2006) prepared a PS/TiO_2 organic—inorganic hybrid ultrafiltration membrane with high hydrophilicity and permeability and mechanical and thermal stability using a sol-gel and phase inversion process. The hybrid membranes exhibited extraordinary hydrophilicity, increased porosity, and superior permeability without changing retention.

The main benefit of using TiO_2 nanoparticles in a mixture with polymeric membranes is the reduction of membrane fouling. Much work has been conducted in blending TiO_2 nanoparticles with different polymeric membranes to prepare composite membranes with antifouling properties. Table 1.2 lists some prepared polymeric/TiO_2 composite membranes with antifouling properties.

Regarding the photocatalytic bactericidal ability of TiO_2 nanoparticles, in recent years, heterogeneous photocatalysis UV—TiO_2 systems have been also applied to solve a variety of important environmental problems such as detoxifying water and producing self-cleaning materials. Damodar et al. (2009) prepared PVDF—TiO_2 composite membranes via the phase inversion method by mixing different amounts of TiO_2 nanoparticles (0—4 wt%) into the PVDF casting solution. The photocatalytic bactericidal ability of composite PVDF—TiO_2 membranes was tested using *E. coli* (initial concentration $= 6.6 \times 10^{+07}$ colony-forming units/ml) with and without the presence of UV light (Figure 1.2).

These results were compared with a reference *E. coli* solution that was kept in darkness. Result showed that almost all *E. coli* cells survived in the dark whereas about 58% of cells survived on pristine PVDF membrane exposed to UV light for 1 min. The number of surviving *E. coli* cells decreased by adding TiO_2 particles and increasing their content in the PVDF—TiO_2 composite membrane, and almost complete removal of *E. coli* occurred with a 4% TiO_2—PVDF membrane during 1 min (Damodar et al., 2009). In similar work with similar results, Rahimpour Jahanshahi, Rajaeian, and Rahimnejad (2012) induced bactericidal ability into a PVDF—SPES-blend membrane by incorporating TiO_2 nanoparticles into the membrane to remove *E. coli.*

To increase homogeneous dispersion, reduce agglomeration, enhance nanofiller—polymer interaction, and improve the stability of TiO_2 nanoparticles, chemical approaches have been applied to modify TiO_2 nanoparticles (Li, Zhu, & Zheng, 2007; Madaeni, Zinadini, & Vatanpour, 2011b; Razmjou et al., 2011). Li et al. (2007) organically modified TiO_2 nanoparticles with silane couple to overcome aggregation and improve the dispersion of TiO_2 nanoparticles in organic solvent. The morphology and structure of PPESK ultrafiltration membrane indicated that the addition of TiO_2 nanoparticles increased the thickness and porosity of the skin

Table 1.2 Some prepared polymeric–TiO_2 composite membranes with antifouling properties

Polymer	TiO_2 (type)	TiO_2 (size, nm)	Reference
PSf-PVDF-PAN	Degussa P25	20	Bae and Tak (2005)
PVDF	Rutile	26–30	Cao et al. (2010)
PVB	Anatase	180	Fu, Matsuyama, and Nagai (2008)
PES	Degussa P25	20	Rahimpour, Madaeni, Taheri, and Mansourpanah (2008)
PES	Rutile	30	Wu, Gan, Cui, and Xu (2008)
PVDF	Degussa P25	20	Damodar, You, and Chou (2009)
PVDF	Degussa P25	20	Oh, Kimb, and Lee (2009)
PES	Degussa P25	20	Li et al. (2009)
PVDF	Degussa P25	20	Yu, Shen, et al. (2009)
PES	Degussa P25	20	Hamid et al. (2011)
CA	Anatase	62	Abedini, Mousavi, and Aminzadeh (2011)
PVDF/SPES	Degussa P25	20	Rahimpour et al. (2011)
PVDF	Degussa P25	25	Wei et al. (2011)
PVDF	Degussa (80% anatase and 20% rutile)	20	Madaeni, Zinadini, and Vatanpour (2011b)
PES	Degussa P25, anatase	20, 8, 15–25	Vatanpour, Madaeni, Khataee, et al. (2012)
PVDF	Anatase	20	Shi, Ma, Ma, Wang, and Sun (2012)

Reprinted from Vatanpour, Madaeni, Khataee, et al. (2012), with permission from Elsevier.

layer as well as the surface wettability and hydrophilicity of the membrane. The tensile mechanical strength of the membrane was also enhanced after the addition of TiO_2. Moreover, permeability and rejection tests showed that the pure water flux and solute rejection of composite membranes were remarkably elevated when a small amount of TiO_2 nanoparticles was added into the membrane structure.

In other research, Razmjou et al. (2011) employed mechanical and chemical modifications of TiO_2 nanoparticles to improve their dispersion into the PES membrane matrix. For mechanical modification, TiO_2 nanoparticles with a volume of 50 cm^3

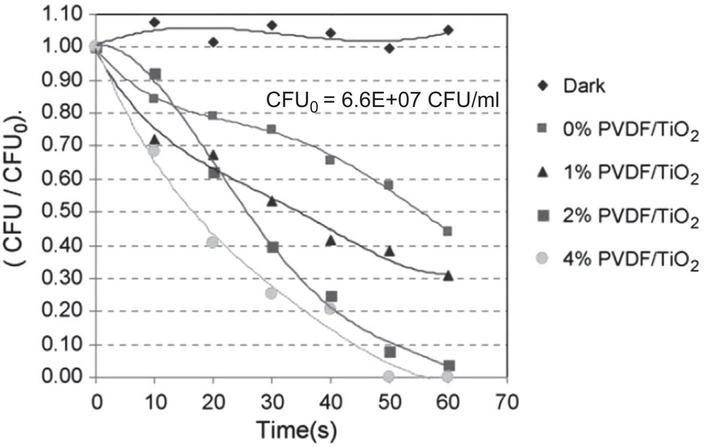

Figure 1.2 Removal efficiency of *Escherichia coli* in water on the surface of different poly(vinylidenefluoride) (PVDF)/TiO_2 membranes with and without the radiation of UV light. Reprinted from Damodar, You, and Chou (2009), with permission from Elsevier.

were ground into fine powder until the volume decreased to 12.5 cm^3. Afterward, the powder was dispersed in DMAc by sonication in a bath for 15 min followed by 10 min sonication by probe at an amplitude of 20 kHz. The chemical modification of TiO_2 was also carried out by surface modification of TiO_2 nanoparticles with aminopropyltriethoxysilane (APTES) as silane coupling agent. First, 2.5 g of mechanically modified TiO_2 nanoparticles was added into pure ethanol under nitrogen purging; this was followed by 30 and 10 min sonication in bath and by probe, respectively. Different amounts of APTES (2, 20, 50, and 80 wt%) were added drop-wise to the mixture under an N_2 atmosphere. After stirring for 2 h at 65 °C, the particles were separated from the solution by centrifuging at 10,000 RPM for 10 min. Finally, the TiO_2 particles were dried in an oven for 24 h at 50 °C and then were ground into fine powder. The combination of chemical and mechanical modifications was significantly effective for the free energy and roughness of the surface, pore size, and protein absorption resistance of the membrane surface as well as improved hydrophilicity of the membrane. Although most researchers reported that an increase in hydrophilicity is the most likely reason for decreased fouling, Razmjou et al. (2011) believed that the other parameters such as changes in the membrane morphology and local surface modifications might have a similar effect on the higher fouling resistance of TiO_2-embedded membranes.

1.2.2.5 Zinc oxide nanoparticles

Another applicable nanoparticle used in modifying membranes is nano-zinc oxide (ZnO). As a multifunctional inorganic nanoparticle, ZnO nanoparticles have recently drawn increasing attention owing to their prominent physical and chemical properties, such as high catalytic activity and effective antibacterial and bactericide capabilities (Balta et al., 2012; Hong & He, 2012). Moreover, ZnO nanoparticles are more economical than some other nanoparticles such as TiO_2 and Al_2O_3 nanoparticles.

On the other hand, ZnO nanoparticles are easily able to absorb hydrophilic hydroxyl groups (−OH) (Shen et al., 2012). Thus, the supplementation of ZnO nanoparticles can improve the hydrophilicity and mechanical and chemical properties of the polymer matrix (Hong & He, 2012; Lin et al., 2009; Shen et al., 2012).

Balta et al. (2012) significantly reduced fouling of PES nanofiltration membranes after blending with different concentrations of ZnO nanoparticles (0.035, 0.07, 0.085, 0.125, 0.250, 0375, 0.500, 0.750, 1, 2, and 4 wt%). The ZnO-blended membranes showed a lower decline in flux and better permeability compared with pristine membrane owing to the significantly higher hydrophilicity of nanocomposite membranes even at ultra-low concentrations of ZnO nanoparticles. Also, raising the nanoparticle concentration to 0.125 wt% increased the relative flux of nanocomposite membranes, but at higher concentrations no further increment was observed. Furthermore, the addition of ZnO nanoparticles considerably improved the fouling resistance of composite membranes during filtration of solutions containing humic acid. This was attributed to the reduction of adsorption of organic pollutants within the membrane structure as a result of increments of membrane hydrophilicity after the addition of ZnO nanoparticles. Shen et al. (2012) obtained similar results in fabricating a PES−ZnO composite membrane. Hydrophilicity, thermal resistance, porosity, water flux, and antifouling capability of the nanocomposite membrane improved after adding ZnO nanoparticles (Shen et al., 2012).

In other work (Leo, Cathie Lee, Ahmad, & Mohammad, 2012), ZnO nanoparticles were added into a PSf ultrafiltration membrane to create antifouling properties not only on the membrane surface but also inside the pores. Based on the results, the addition of ZnO nanoparticles significantly increased the membrane hydrophilicity. As a result of increasing the mean pore size and membrane hydrophilicity, an increase as much as 100% was observed in permeability. The PSf membranes blended with ZnO nanoparticles also exhibited less fouling compared with nascent PSf membranes during filtration of an aqueous solution containing oleic acid. Moreover, the composite membranes showed improved thermal stability.

In a study conducted by Liang, Xiao, Mo, and Huang (2012), ZnO nanoparticles with different concentrations were blended with PVDF polymer and applied for the fabrication of a composite PVDF−ZnO membrane using the wet phase separation method. Multi-cycle filtration tests demonstrated significant anti-irreversible fouling of the modified PVDF membrane. Specifically, all modified membranes reached almost 100% water flux recovery and maintained the initial fluxes constant in multi-cycle tests. Similar to much other research, this change was attributed to an increase in the surface hydrophilicity of the membrane.

1.2.2.6 Aluminum oxide nanoparticles

The stability, availability, hydrophilicity, and suitable mechanical strength of aluminum oxide (Al_2O_3) nanoparticles make this inorganic material another option for preparing of nanocomposite membranes. By the aid of Al_2O_3 blending, the membrane can combine the basic properties of these materials and display specific benefits with respect to thermal and chemical resistance, separation performance, and adaptability to the severe water and wastewater conditions. Much research has been done in applying Al_2O_3 nanoparticles blending with a PVDF membrane to determine the effect of Al_2O_3 particles on the hydrophilicity, permeation flux, morphology, mechanical properties, and antifouling performance of membranes.

Various mixed matrix membranes of alumina (Al_2O_3) with CAc (Wara, Francis, and Velamakkani, 1995), CAP (Mukherjee & De, 2013), PA (Saleh & Gupt, 2012), and PVDF (Yan, Li, & Xiang, 2005; Yan, Li, Xiang, & Xianda, 2006; Yan, Hong, Li, & Li, 2009) were prepared to change membrane properties such as hydrophilicity, permeability, and fouling resistance. Yan et al. (2005, 2006) prepared a PVDF—Al_2O_3 nanocomposite membrane with different concentrations of Al_2O_3 (1 nm) using the phase inversion method. The addition of nanosized Al_2O_3 particles increased membrane permeability with no change in the membrane pore size and number, just by improving the surface hydrophilicity of the membrane. The improvement in the hydrophilicity of the nanocomposite membrane also increased its antifouling performance in filtering oil—wastewater solution from the oil field (Yan et al., 2005). In another work, the same authors prepared the phase inversion method using a nanocomposite tubular ultrafiltration PVDF—Al_2O_3 membrane (Yan et al., 2009). The flux of the modified membranes was always higher (about twice) than that of the unmodified membranes owing to the improvement of membrane hydrophilicity caused by adding nanosized alumina particles into the PVDF. Interestingly, the permeation performance of the modified membrane increased significantly without sacrificing its retention properties. All of these studies indicate that the permeability and antifouling performance of the modified PVDF membranes were considerably changed by incorporating Al_2O_3 nanoparticles into the membrane matrix (Yan et al., 2009; Yi et al., 2011).

On the other hand, Liu, Moghareh Abed, and Li (2011) used γ-Al_2O_3 nanoparticles. The authors tried to modify PVDF chains and impede segregation of nanoparticles by a grafting reaction between γ-Al_2O_3 nanoparticles (containing a substantial amount of hydroxyl groups [—OH]) and the PVDF polymer catalyzed by some acid (H_2SO_4). The authors presented a mechanism for the reaction between γ-Al_2O_3 and PVDF, shown in Figure 1.3. The PVDF—γ-Al_2O_3 nanocomposite membranes revealed high hydrophilicity and fouling resistance owing to their surface activity, high adsorptive ability, and surface enrichment of reactive functional hydroxyl groups.

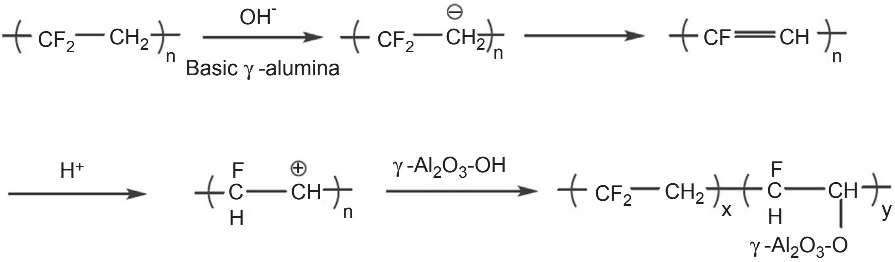

Figure 1.3 Schematic of the reaction between γ-Al_2O_3 and poly(vinylidenefluoride) polymer. Reprinted from Liu, Moghareh Abed, and Li (2011), with permission from Elsevier.

In studies conducted by Maximous, Nakhla, Wan, and Wong (2009) and Maximous, Nakhla, Wan, et al. (2010), PES membranes were modified by inserting different concentrations of nanosized alumina (48 nm) particles inside the polymer matrix. The increase in porosity and decrease in the hydrophobic interaction between membrane surface and foulants changed the performance of the PES membrane after adding Al_2O_3 nanoparticles into the casting solution. As a result of the induced changes on the membrane after adding Al_2O_3 nanoparticles, the nanocomposite membrane showed less flux decline compared with a pristine PES polymeric membrane (Maximous, Nakhla, Wan, et al., 2010; Maximous et al., 2009).

1.2.2.7 Iron oxide nanoparticles

Magnetic nanoparticles have gained much attention by researchers in recent years. Because of their inherent super paramagnetic properties, magnetic nanoparticles have been studied for various applications including drug and gene targeting, cell separation, and hyperthermia (Ye, Liu, Wang, Huang, & Xu, 2009). Iron oxide (Fe_3O_4) has excellent thermal and chemical stability and good magnetic performance, but also good biocompatibility and biodegradation ability (Dudek et al., 2012; Huang et al., 2008). In this regard, a PSf—Fe_3O_4 composite ultrafiltration membrane was fabricated by Fe_3O_4 nanoparticles (8—12 nm in size) wrapped in the oleic acid using the phase inversion method, and the membrane performance in retaining lysozyme was inspected under the magnetic field (Jian, Yahui, Yang, & Linlin, 2006). Although the thermal stability and porosity of the PSf membrane increased after adding Fe_3O_4, membrane hydrophilicity declined as the result of the hydrophobicity of Fe_3O_4 nanoparticles, which were wrapped in the oleic acid. The rejection of lysozyme using PSf membrane remained constant within and without the presence of the magnetic field. However, the rejection of the nanocomposite membrane was clearly reduced under the magnetic field; the retention recovered quickly when the magnetic field was removed. On the other hand, with the increase in magnetic intensity, the decline in rejection was more noticeable. The authors concluded that it is possible to separate some substances using a PSf—Fe_3O_4 nanocomposite membrane by altering the magnetic intensity.

In various studies, Huang, Guo, Guo, and Zhang (2006), Huang, Chen, Chen, Zhang, and Xu (2010), and Huang, Zheng, et al. (2012) investigated the effects of incorporating Fe_3O_4 nanoparticles on the performance of polymeric membranes. The authors showed that magnetization of a PAN membrane using Fe_3O_4 nanoparticles led to an increment of membrane permeation and antifouling performance in the ultrafiltration of pig blood (Huang et al., 2006). Moreover, Fe_3O_4 nanoparticles with different concentrations were applied in fabricating PSf—Fe_3O_4 (Huang et al., 2010) and PVDF— Fe_3O_4 (Huang, Zheng, et al., 2012) nanocomposite membranes. The composite membranes showed the best performance in terms of pure water flux, rejection, and fouling resistance.

Apart from improvements in membrane characteristics, obvious benefits of iron oxide nanoparticles in the removal of arsenic (Sabbatini et al., 2010; Sabbatini, Rossi, Thern, & Marajofsky, 2009; Park & Choi, 2011) and adsorption of heavy metals

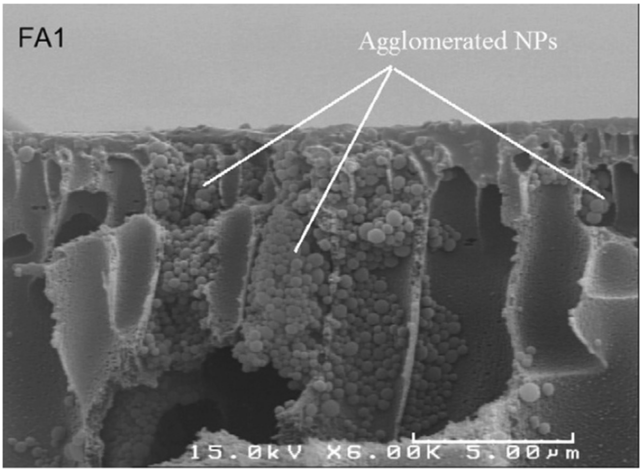

Figure 1.4 Field emission scanning electron microscopic image of cross-section of membrane prepared with 1 wt% polyacrylonitrile (PAN)/Fe_3O_4 nanoparticles.
Reprinted from Daraei et al. (2012), with permission from Elsevier.

(Daraei et al., 2012; Gholami, Moghadassi, Hosseini, Shabani, & Gholami, 2013; Mansour, Ossman, & Farag, 2011) were proved in some research. Daraei et al. (2012) prepared Fe_3O_4—PA nanoparticles as adsorbent and used them in the PES matrix to obtain a nanocomposite membrane with enhanced affinity for the removal of copper ions. According to the experiments, nanocomposite membranes indicated higher Cu(II) ion removal but lower pure water flux compared with pristine PES membrane. This was due to the surface pore blockage as a result of the presence of nanoparticles in the superficial pores of the membrane during preparation (Figure 1.4). In other research conducted by Gholami et al. (2013), iron oxide nanoparticles were blended with polyvinyl chloride-blend cellulose membrane to apply the adsorbent properties of Fe_3O_4 nanoparticles in the removal of lead from aqueous solution. As expected, the permeability and rejection of lead rose in nanocomposite membranes compared with pristine membrane.

1.2.2.8 Silicon dioxide nanoparticles

Silicon dioxide (SiO_2) is another convenient nanoparticle widely used in fabricating nanocomposite membranes because of the mild reactivity and distinguished ability in increasing hydrophilicity and improving the thermal and mechanical stability and fouling resistance of membranes (Jin, Shi, et al., 2012; Jin, Yu, et al., 2012; Ogoshi & Chujo, 2005; Wu, Xu, & Yang, 2003). Silica was widely used with polymeric membranes such as PMMA (Zulfikar, Mohammad, & Hilal, 2006), PES (Shen, Ruan, Wu, & Gao, 2011; Wu et al., 2003), PSf (Zhang, Liu, Lu, Zhao, & Song, 2013), PA (Jin, Shi, et al., 2012; Kim & Lee, 2001), PVA (Nagarale, Shahi, & Rangarajan, 2005; Thanganathan, Nishina, Kimura, Hayakawa, & Bobba, 2012; Yang, James Li, & Liou, 2011), and PVDF (Cho & Sul, 2001; Cui, Liu, Xiao, &

Zhang, 2010; Liao, Zhao, Yu, Tong, & Luo, 2012; Yu, Xu, et al., 2009; Zhang, Ma, Cao, Li, & Zhu, 2014) using sol-gel (Thanganathan et al., 2012; Wu et al., 2003), phase inversion (Cui, Liu, Xiao, & Zhang, 2010; Liao, Zhao, Yu, Tong, & Luo, 2012; Shen et al., 2011; Zhang et al., 2013), and interfacial polymerization (Jin, Shi, et al., 2012; Namvar-Mahboub & Pakizeh, 2013). The sol-gel technique allows the formation of an inorganic framework under mild conditions, and incorporation of minerals into the polymers results in increased chemical, mechanical, and thermal stability without obviously decreasing the properties of the polymers (Kim and Lee, 2001; Wu et al., 2003; Yu, Xu, et al., 2009). Furthermore, the hydrogen bond clusters remaining at the surface of the materials after the sol-gel reaction improved membrane hydrophilicity and enhanced the stability of composite materials (Cho & Sul, 2001; Nagarale et al., 2005; Yu, Xu, et al., 2009). A simple method to obtain an organic—SiO_2 hybrid is to mix an organic polymer with a metal alkoxide such as tetraethoxysilane (TEOS), followed by a sol-gel process involving hydrolysis and polycondensation of TEOS (Wu et al., 2003; Yu, Xu, et al., 2009). Yu, Xu, et al. (2009) synthesized organic—inorganic PVDF—SiO_2 composite hollow fiber ultrafiltration membranes using a sol-gel and wet-spinning process. The microstructure, mechanical property, thermal stability, hydrophilicity, permeability, and fouling resistance of composite membranes improved significantly by an appropriate choice of TEOS concentration (3 wt%).

The phase inversion process was also used by researchers as a simple and applicable technique to prepare polymer—silica-mixed matrix membranes. The addition of hydrophilic SiO_2 nanoparticles into the casting solution enhanced membrane hydrophilicity (Cui et al., 2010; Shen et al., 2011). On the other hand, the permeability and antifouling ability of nanocomposite membranes also improved as the result of increased hydrophilicity and the decreased adsorption of foulants on the membrane surface.

Interfacial polymerization is another valuable method because the characteristics of the skin layer as a key factor in determining membrane performance can be optimized separately (Jin, Shi, et al., 2012). Jin, Yu, et al. (2012) and Jin, Shi, et al. (2012) prepared a nanofiltration membrane with poly(amidoamine) (PAMAM) dendrimer and TMC containing SiO_2 nanoparticles through an interfacial polymerization reaction on PSf ultrafiltration membrane. The addition of nano-SiO_2 in the skin layer improved thermal stability and membrane hydrophilicity. The results of raw water filtration by pristine PA membrane and PA-SiO_2 membrane (1 wt% SiO_2 nanoparticles) are shown in Figure 1.5.

As shown in the figure, the flux of both PA and PA-SiO_2 membranes was reduced during the filtration time; however, the pristine PA membrane showed a greater amount of flux decline compared with the hydrophilic PA-SiO_2 membrane. Surface water typically contains three potential groups of foulants, including microbial (bacteria, viruses, etc.), organic, and inorganic (humic acid and minerals) compounds. The addition of SiO_2 nanoparticles to the membrane significantly increased the antifouling ability of the PA membrane as the result of the presence of a huge number of hydroxyl groups on the surface of SiO_2 nanoparticles. This increased the negative charge on the membrane surface, weakening the force between the negatively charged micelles and the surface of the membrane (Jin, Shi, et al., 2012).

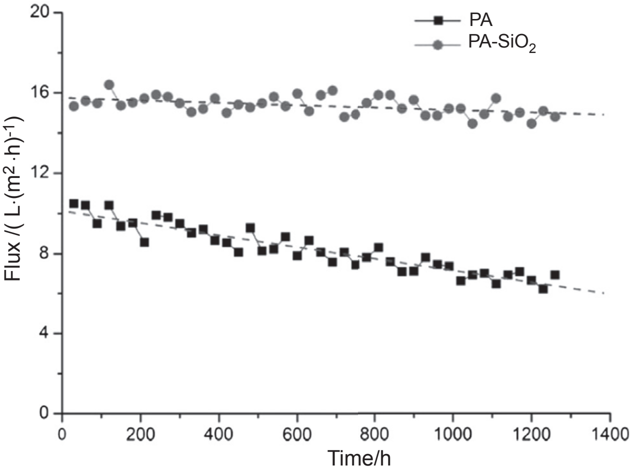

Figure 1.5 Flux of polyaniline (PA) and PA-SiO_2 membranes versus filtration time. Reprinted from Jin, Shi, et al. (2012), with permission from Elsevier.

1.2.2.9 Zirconium oxide nanoparticles

Polymer—zirconium dioxide (ZrO_2) composite membranes are known to be chemically more stable than titanium dioxide and aluminum oxide membranes and are more suitable for liquid phase applications under rough conditions (Maximous, Nakhla, Wan, et al., 2010), although a few studies have investigated the incorporation of ZrO_2 into the membrane matrix. Bottino, Capannelli, and Comite (2002) prepared ZrO_2—PVDF membranes using the phase inversion method. Membrane performance depended on the PVDF solvent (NMP or TEP) or ZrO_2 concentration. Other work conducted by Zheng, Zou, Nadeeshani Nanayakkara, Matsuura, and Paul Chen (2011) found that the addition of zirconia nanoparticles in PVDF membrane increased the hydrophilicity and surface porosity of the membrane and resulted in an increment of flux in the composite membrane. It was proved that the ZrO_2/PVDF-blend membrane could be applied effectively to remove arsenate from an aqueous solution in a wide range of pHs; the optimal pH was 3.0—8.0.

Furthermore, Maximous, Nakhla, Wan, et al. (2010) found that ZrO_2—PES membrane was stronger than pristine membrane, and membranes blended with ZrO_2 showed less flux decline and fouling resistance compared with unmodified PES membrane. On the other hand, Pang et al. (2014) prepared ZrO_2—PES hybrid ultrafiltration membranes by combining the ion-exchange process with the immersion precipitation technique to increase membrane hydrophilicity and decrease membrane fouling. The authors reported that the adsorption of foulants on the membrane surface decreased considerably compared with pristine membranes because of an increase in membrane hydrophilicity.

1.2.3 Nanostructured membranes

Based on the ISO definition, membranes with pores in the range of 1—100 nm would evidently be considered nanostructured materials. Hence, ultrafiltration and most nanofiltration membranes that reject particles about 0.2–200 kDa corresponding to a nanoscale diameter of around 1–100 nm should be classified as nanostructured membranes (Bhadra & Mitra, 2013; Muellera et al., 2012). Generally, membranes are defined on the basis of the size of the particles that are rejected; therefore, the term "nano" in "nanofiltration" does not refer to structural elements of the membrane such as pore size (Bhadra & Mitra, 2013).

Rahimpour, Madaeni, Shockravi, and Ghorbani (2009) added different concentrations of PSAm (2, 5, 10, and 15 wt%) into the PES casting solution to prepare nanostructured ultrafiltration membranes. Addition of PSAm not only resulted in the formation of an ultrafiltration membrane with nanopores, it improved the hydrophilicity, mechanical strength, permeability, and protein rejection of PES membranes. Moreover, Mansourpanah and Momeni Habili (2013) employed the interfacial polymerization technique to prepare a PA skin layer on the PES support using TMC and PIP as reagents. Acrylic acid as a hydrophilic monomer and UV irradiation as a physical procedure were used to modify the obtained thin layers. The effect of UV irradiation times (30, 60, and 120 s) and acrylic acid concentration (1%, 5%, and 10 wt%) on the performance and morphology of modified TFC membranes was investigated by the authors. This modification technique resulted in the fabrication of a nanoporous membrane by reducing the membrane pore size from 110 to 30 nm. Meanwhile, the hydrophilicity, permeation flux, rejection, and antifouling ability of the modified membranes improved considerably.

1.2.4 Bio-inspired membranes

Bio-inspired studies have drawn much attention as a potentially feasible approach to improve current technologies. In this method, nature is considered a large database to which its scientific rules might be applied in engineering applications as efficient solutions for difficult problems. In this way, biological materials or natural biopolymers are considered for the fabrication of bio-inspired membranes because of their well-controlled structures and superior properties, and the improvement of any aspect of biological materials has the possibility of improving the structure and function of bio-inspired membranes. Moreover, the conditions under which the membrane is fabricated are mild: an aqueous solution, controlled temperature, moderate pressure, and neutral or near neutral pH. As a result of numerous advantages, wide areas of application, and high efficiency, bio-inspired membranes have the chance to be the next generation of membranes (Morones-Ramırez, 2013; Rawlings, Bramble, & Staniland, 2012).

Several bio-inspired platform methods such as bio-adhesion and bio-mimetic adhesion have been created (Li, Liu, et al., 2009; Pan et al., 2009). In addition, a platform called bio-mineralization or bio-mimetic mineralization was developed from the formation process of bio-silica (Pan, Jia, Cheng, & Jiang, 2010). Bio-inspired membranes have great benefits such as high permeability, catalytic reactivity, and fouling resistance, and hence have the potential to be employed in water treatment processes. Pan et al. (2010) proposed an innovative procedure to fabricate a polymer–inorganic skin layer of a composite membrane by combining bio-mimetic mineralization and polymer network structure manipulation. In this work, the silica nanoparticles showed uniform size and homogeneous distribution within the PVA structure. The composite membrane consisting of a PVA–silica skin layer and PSf hollow fiber support layer showed appropriate free volume properties.

Inspired by the hierarchical structures in biology, Xu et al. (2011) proposed the concept of vertically aligned nanotubes to emulate the biological channels within a membrane matrix. As a result of the presence of nanopores inside the membrane matrix, the permeability, selectivity, and durability of bio-inspired membrane increased. Furthermore, Balme et al. (2011) conducted a research project focusing on bio-inspired membranes with biological ion channels. These channels were confined inside the nanopores of solid-state materials. The solvent had an effective role on membrane performance in terms of ion permeability and selectivity.

Aside from the transport properties and membrane structure, the development of intelligent properties such as self-cleaning, self-healing, and stimulus–response in bio-inspired membranes are other concerns that have drawn the attention of some researchers (Capadona, Shanmuganathan, Tyler, Rowan, & Weder, 2008; Madaeni & Ghaemi, 2007; Wang, Janout, & Regen, 2011).

1.3 Applications for water treatment

Polymeric membranes are employed extensively for water treatment applications such as desalination, water softening, purification of industrial and municipal wastewaters, production of ultra-pure water, and the food, chemical, and pharmaceutical industries. Membrane processes offer significant advantages such as operational simplicity and flexibility, cost-effectiveness, reliability, low energy consumption, good stability, environment compatibility, and easy control, handling, and scale-up under a wide spectrum of operating conditions such as temperature, pressure, and pH. However, there are still unresolved problems regarding the employment of polymeric membranes under more stringent applications. Membrane fouling, insufficient separation and rejection, treatment of concentrates, membrane lifetime, and resistance to some chemicals are the most important and well-known problems related to polymeric membranes.

Fouling is the most important and well-known problem in membrane separation processes. The urgent need for pretreatment, cleaning, limited recovery, and short lifetime are some negative results of fouling problems. Membrane lifetime and chemical resistance are also related to fouling and consequent cleaning as well as the conditions under which the membranes are employed. Many researchers have concentrated on proposing efficient solutions and strategies to prolong the lifetime and chemical resistance of membranes, improve membrane morphology, increase hydrophilicity, decrease surface roughness, and increase the degree of cross-linking of the polymeric top layer to decrease membrane fouling and increase the chemical resistance and lifetime of the membrane.

Another inherent problem for pressure-driven membranes is the concentrate stream. Concentrate is usually an unwanted by-product of water treatment using membrane technologies and needs to be further treated. This treatment may include reuse, further treatment by removal of contaminants, and direct or indirect discharge into the surface water or groundwater and landfills.

1.4 Concluding remarks and future trends

One of the most crucial problems facing the world in this century is the provision of clean water with adequate quality from water resources. Given the numerous privileges of membranes such as relatively high selectivity and permeability, low energy consumption, operational simplicity, control, scale-up, and adaptability, as well as satisfactory stability under various conditions, over the years membranes have been the dominant technology in the water treatment industry. Hence, many studies have been conducted and much progress has been achieved in optimizing membrane characteristics and performance. However, some challenges still need to be addressed, such as decreasing membrane fouling; increasing the membrane lifetime, selectivity, and permeability; improving thermal, mechanical, and chemical resistance; and reducing energy consumption.

Some important incentives for the further development of polymeric membranes in water treatment are fabrication of antifouling and self-cleaning membranes, enhancement of membrane permselectivity, an increase in membrane stability at extreme operational conditions, the production of new polymers with special properties for use in composite membranes, synthesis of novel nanomaterials for application in nanocomposite membranes, and the expansion of applications of bio-inspired and environmentally responsive membranes.

Abbreviations

AA	Acrylic acid
AAm	Acryl amide
APTES	Aminopropyltriethoxysilane
BPA	Bisphenol A
BO	Bezactiv Orange V-3R
CA	Citric acid
CAc	Cellulose acetate
CAP	Cellulose acetate phthalate
CNC	Cellulose nanocrystalline
CNTs	Carbon nanotubes
DABA	β-Cyclodextrin polyurethane
DMAc	Dimethylacetamide
DW	Double-walled
HPAA	Hyperbranched poly(amidoamine)
ICIC	5-Isocyanatoisophthaloyl chloride
IPC	Isophthaloyl chloride

LSMM	Hydrophilic surface modifying macromolecules
mm-BTEC	3,3′,5,5′-biphenyl tetra acyl chloride
MMT	Montmorillonite
MPDA	*m*-Phenylenediamine
MWCNT	Multi-walled carbon nanotube
MWNTs	Multi-walled nanotubes
NMP	*N*-methyl-2-pyrrolidone
om-BTEC	2,2′,4,4′-biphenyl tetra acyl chloride
OMMT	Organically modified montmorillonites
op-BTEC	2,2′,5,5′-biphenyl tetra acyl chloride
PA	Polyaniline
PAA	Poly acrylic acid
PAAm	Poly acryl amide
PAm	Polyamide
PAMAM	Poly(amidoamine)
PAI	Poly(amide-imide)
PAN	Polyacrylonitrile
PCA	Polycitric acid
PDA	1,3-Phenylenediamine
PES	Polyethersulfone
PI	Polyimide
PIP	Piperazine
PMMA	Poly(methyl methacrylate)
PPD	*p*-Phenylenediamine
PPESK	Poly(phthalazine ether sulfone ketone)
PS	Polystyrene
PSAm	Poly(sulfoxide-amide)
PSf	Polysulfone
PU	Polyurethane
PVA	Poly(vinyl alcohol)
PVB	Poly(vinyl butyral)
PVDF	Poly(vinylidenefluoride)
PVP	Polyvinylpyrrolidone
SEM	Scanning electron microscope
SPC	Sulfonated polycarbonate
SPEK	Sulphonated poly(ether ketone)
SPES	Sulfonated poly(ether sulfone)
SPES-NH$_2$	Sulfonated cardo poly(arylene ether sulfone)
SPPO	Sulfonated poly(2,6-dimethyl-1,4-phenylene oxide)
SPSf	Sulfonated polysulfone
SW	Single-walled
TEOS	Tetraethoxysilane
TEP	Triethylphosphate
TFC	Thin-film composite
TFC-FO	TFC forward osmosis
TMBPA	Tetramethyl bisphenol A
TMC	Trimesoyl chloride
TiO$_2$	Titanium dioxide

Greek symbol

β-CPU	β-Cyclodextrin polyurethane

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Advances in ceramic membranes for water treatment

2

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2.1 Introduction

2.1.1 Water treatment

Water is the most abundant natural resource on our planet but only a small percentage is accessible and fit for use in sustaining human life. Many areas of the world have no access to safe and clean drinking water and are in urgent need of economical, reliable and effective methods of treating local raw water sources. In addition, the global water consumption rate continues to increase because of the rapid rise in population and increased industrialization and agricultural needs. The strain placed on the limited clean water supply will lead to rises in water price, which can significantly increase the operating costs in many industries where water is used extensively and in large volumes. Furthermore, regulations on the quality of drinking ground, surface and wastewater qualities are becoming increasingly stringent, and thus effective water management is of paramount importance more than ever. Many industries' ideal state would be to recycle all of their wastewater and reach a 'zero-discharge' condition. Significant developments have been made over the past half-century in the water treatment field: in particular, in the development of cost-effective low-pressure membrane processes such as microfiltration (MF) and ultrafiltration (UF) (Judd, 2010; Staff, 2011; Van Der Bruggen et al., 2003).

2.1.2 Micro- and ultrafiltration processes in water treatment

The commercialization of cost-effective MF/UF membranes may be of the most significant changes in water and wastewater treatment since the 1960s. MF and UF are low pressure-driven separation processes that are less energy-intensive than traditional treatment methods. The two processes can separate components by a sieving mechanism without the need for chemical or physical pre- or post-treatment. Hence they are widely used in many applications for a range of different purposes, such as removing suspended solids, bacteria and viruses, and heavy metals, achieving oil and water separation, and pretreating desalination (Lens et al., 2001; Mallada & Menéndez, 2008). MF/UF membranes are porous with pore sizes ranging from microns to nanometres; they can be easily incorporated into existing processes as a standalone unit or combined with other technologies.

A hybrid system that has broadened the use of MF/UF in wastewater treatment is the membrane bioreactor (MBR). It combines the biological treatment of wastewater

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with a membrane filtration process and is commonly used to treat industrial and municipal wastewater (Judd, 2008, 2010; Meng et al., 2009). However, fouling and replacement costs of polymeric membranes still challenge the widening and large-scale use of MBRs. Although the capital costs of ceramic membranes are higher, their robustness, higher resistance to microorganisms and ease of cleaning lead to lower maintenance and replacement requirements, cutting down long-term operating costs and offering a competitive alternative to polymeric systems (Gander, Jefferson, & Judd, 2000; Judd, 2008).

2.1.3 Ceramic membranes in water treatment

Ceramic membranes may be an alternative material for use in MF/UF applications in the place of polymeric membranes. Because of their superior chemical, thermal and mechanical properties, they can be backwashed, cleaned with harsh cleaning agents and sterilized at high temperatures, offering reliable performance over longer periods of time. Ceramic membranes have found commercial success in applications in which the operating conditions are harsh, such as at high temperatures and in aggressive chemicals (solvents and highly acidic or caustic solutions). Examples of successful commercial-scale plants that use MF/UF ceramic membranes include purifying and concentrating valuable components such as enzymes and (Krstić et al., 2007) clarifying fermentation broths in biotechnology industries (Finley, 2005; Sondhi, Bhave, & Jung, 2003), clarification of fruit or sugar cane juices (Daufin et al., 2001; Girard, Fukumoto, & Sefa Koseoglu, 2000; Sondhi et al., 2003) and treatment of highly oily wastewater and degreasing baths (Cheryan & Rajagopalan, 1998; Majewska-Nowak, 2010).

In contrast, ceramic membranes are much less commonly used in water and wastewater treatment, such as for the production of drinking water and treatment of municipal wastewater. This has historically been because of their high fabrication costs compared with commercially available polymeric membranes. Common configurations of ceramic membranes include flat-sheet, tubular and monolith elements, as shown in Table 2.1. They are normally thicker than polymeric hollow-fibre membranes, leading to lower packing densities. They are also intrinsically brittle and therefore more expensive to pack and seal.

However, as the result of sustainable developments in ceramic membranes, cheaper, more effective, higher-performing and more compact ceramic systems can be formed, potentially allowing the widening of their applications. Table 2.1 lists some current major international ceramic MF/UF membrane suppliers. Tubular, monolithic and flat-sheet ceramic membranes currently dominate over hollow-fibre membranes, with great water permeation fluxes.

2.2 Development in ceramic membranes and their fabrication processes

A membrane can be defined as a semi-permeable active or passive barrier, which when placed under a certain driving force separates one or more selected species or

Table 2.1 **List of commercially available ceramic membranes for MF/UF**

				Technical specifications			
	Company	**Product**	**Material**	**Pore size (μm)**	**Channel diameter/ outer diameter (mm)**	**Packing density (m^2/m^3)**	**Pure water flux ($L/(m^2.h.bar)$)**
Flat sheet	ItN Nanovation AG	CFM Systems® (Itn-nanovation water filtration; Itn-nanovation Filtration rack; Itn-nanovation T-series)	Substrate: α-Al_2O_3 Selective layer: α-Al_2O_3/ZrO_2	0.2	3.0/—	91.8	—
	Meidensha Corporation	Ceramic membrane unit (Ceramic membrane unit, 2013)	α-Al_2O_3	0.1	—	36.1	1670
	LiqTech International, Inc.	Silicon carbide flat sheet membrane (Liqtech)	SiC	0.2	—	37.7	—
Flat disc	LiqTech International, Inc.	Silicon carbide Flat disc membrane (Liqtech Dynamic)	SiC	0.04, 0.1, 1.0	—	—	3000, 4000, 10,000
Tubular/ monolith	Tami Industries	CéRAM (Inside céram™) ISOFLUX (Isoflux™)	—	MF: 0.14−1.4 UF MWCO: 1 kDa−150 kDa	—	—	—
	Atech Innovations GmbH	Ceramic membranes (Atech-innovations)	MF: α-Al_2O_3 UF: TiO_2	MF: 0.1−1.2 UF: up to 0.05 and MWCO: 5 kDa	2.5−8.0/ 10.0−52.0	—	—

Continued

Table 2.1 **Continued**

				Technical specifications			
	Company	**Product**	**Material**	**Pore size (μm)**	**Channel diameter/ outer diameter (mm)**	**Packing density (m^2/m^3)**	**Pure water flux ($L/(m^2.h.bar)$)**
	LiqTech International, Inc.	SteriMem® (LiqTech SiC SteriMem®), CoMem (COMEM®), CoMem Conduit (COMEM® CONDUIT) and Aquasolution (AQUASOLUTION®)	SiC	0.04, 0.1, 1.0	3.0–17.0/ 25.0–146.0	–	–
	Pall Corporation	Membralox® (Pall® Membralox®; Membralox®)	Substrate: Al_2O_3 Selective layer MF: Al_2O_3 or ZrO_2 UF: TiO_2	MF: 0.1–5.0 UF: 0.02–0.1 and MWCO: 1–5 kDa	3.0–6.0/–	285	–
	Veolia Water, Ltd	Ceramem® (Tundrasolutions; CeraMem® Full-size membrane modules, 2013; Veoliawaterst & CERAMEM®)	MF: α-Al_2O_3, SiC, TiO_2 UF: SiC, SiO_2, TiO_2	MF: 0.1–0.5 UF: 0.005–0.05	2.0–5.0/142.0	782	MF: 400–1200 UF: 200–800
Hollow fibre	Hyflux, Ltd	InoCep® (Inocep membrane; InoCep)	α-Al_2O_3	0.02–1.4	3.0/4.0	157	250–4500
	Media and Process Technology, Inc.	MPT hollow-fibre membranes (Media and process)	α-Al_2O_3	0.004–0.2	1.0–3.5/–	502	–

components of a liquid mixture whilst the rest is rejected (Mulder, 1996). Micro- and ultrafiltration are low pressure-driven processes in which physical separation of the different-sized feed components is achieved via a sieving mechanism across the membrane with a specific pore size.

In 1989, the Membrane Technology and Research, Inc. (MTR) performed a study addressing the research priorities in the membrane separation industry (Ruutenhuch, 1992). For MF and UF, the highest priority research topics include: fouling-resistant long-life membranes that are high temperature, solvent, wide pH and oxidant resistant, low-cost membrane modules and low energy module designs. Although the study was performed more than 20 years ago, many of the issues still remain as important research areas today. The development of cheap asymmetric inorganic membranes with high packing densities can be seen as a possible solution to most of the challenges listed above. Significant progresses have been made in recent years regarding the ceramic membranes and their fabrication processes.

2.2.1 Desirable membrane characteristics and their design

To understand the type of membrane properties desired for pressure-driven membrane processes, it is important to understand the membrane transport mechanisms. Transport models can help identify the structural parameters that affect the membrane performance. Different pore geometries exist depending on the fabrication processes, and hence different models can be used to describe the transport through these different geometries. For example, the pores can be depicted as parallel cylinders or a network of tightly packed spheres. For pores formed from voids between tightly packed spheres, the Carman–Kozeny relationship can be used to describe membrane flux assuming no interaction exists between the fluids and surface of the membrane (Mulder, 1996):

$$J = \frac{\varepsilon^3}{\kappa \eta S^2 (1-\varepsilon)^2} \frac{\Delta p}{\Delta x} \tag{2.1}$$

where J is the membrane flux (m^3/(m^2 s)), κ is the Carman–Kozeny constant (depending on pore shape and tortuosity), ε is the porosity, S is the specific surface area (m^2/m^3), η is the permeate viscosity (N s/m^2), Δp is the pressure difference (N/m^2) and Δx is the membrane thickness (m). Membrane selectivity and permeation flux are major indicators of membrane performance; Eqn (2.1) shows that structural parameters such as high porosity, narrow pore size distribution and thin membrane thickness are always desirable for improved membrane performance. The different characteristics of the membrane can be designed and tailored using different fabrication techniques and controlling the related fabricating parameters during the course of production.

2.2.2 Material and microstructure

Various membrane materials are available for MF/UF processes. The choice of the membrane material affects the practicality and sustainability of the filtration operation, and hence can be chosen based on the specific application requirements.

Examples of ceramic materials include alumina (γ-Al_2O_3 and α-Al_2O_3), zirconia (ZrO_2), titania (TiO_2), glass (SiO_2) and silicon carbide (SiC). Ceramic membranes offer superior temperature and chemical tolerances, leading to an extensive range of applications across many industries. They can be an important and environmentally friendly component in helping companies achieve a 'zero-discharge' state. However, the main drawback of using ceramic membranes for water treatment is their high capital cost; hence, large-scale membrane applications or less challenging water purification processes are still dominated by polymeric membranes. As shown in Table 2.1, commercial ceramic membranes for MF/UF processes consist mainly of α-Al_2O_3 as the substrate and α-Al_2O_3, TiO_2 or ZrO_2 as the selective separation layer. According to experiments in the literature, there is a general consensus that chemical stability (in highly acidic or basic environments) decreases with the following trend: $TiO_2 > ZrO_2 > \alpha\text{-}Al_2O_3 > \gamma\text{-}Al_2O_3 > SiO_2$ (Hofman-Züter, 1995; Mallada & Menéndez, 2008; Van Gestel et al., 2003). Generally, inorganic membranes can withstand organic solvents, chlorine and other oxidants, are less susceptible to microbial attack than polymeric membranes and can be used at pH values close to 0 and up to 14 (TiO_2 and α-Al_2O_3) (Hsieh, 1996; Mallada & Menéndez, 2008).

Ceramic membranes are generally accepted to have high mechanical strength. Because of this they can be backwashed at elevated pressures and operated over a longer period of time compared with polymer membranes (Guerra, Pellegrino, & Drewes, 2012; Sondhi & Bhave, 2001). However, a disadvantage of ceramic membranes is their brittleness; hence, they must be handled with care and the choice of housing and sealing should be carefully considered. The pressure required to drive MF is 0.1–2 bar and much higher for UF (Van Der Bruggen et al., 2003). The maximum operating pressure specified by a hollow-fibre ceramic membrane manufacturer is 6 bar (Hyfluxmembranes InoCep®), much higher than the 2.5-bar maximum allowable for polyethersulphone (PESf) membranes (Hyfluxmembranes Kristal®).

As mentioned in Section 2.1, the microstructure across the membrane cross-section and surfaces is a key property that dictates the performance and usability of a membrane for a certain applications. A membrane can be categorized into symmetric and asymmetric structures. A symmetric membrane has a uniform cross-section throughout whereas an asymmetric membrane does not, as shown in Figure 2.1(a) and (b) (or Figure 2.1(c)), respectively.

For MF and UF processes, asymmetric membranes consisting of a thin skin layer on top of a porous sub-layer are desired. The top layers of UF membranes are much denser than MF membranes; hence, they require higher trans-membrane pressures and generally have lower permeability. The asymmetric structures are associated with higher permeation flux, because the effective membrane thickness can be much thinner than in symmetric membranes. The porous sub-layer acts to provide adequate mechanical strength. This type of structure combines high selectivity of the skin layer with good permeation fluxes.

An asymmetric membrane can be integral or made of several layers, known as a composite. The top and porous layers of an integral asymmetric membrane are normally made of the same material (Figure 2.1(c)), and for composite membranes the top skin layer and the porous sub-layer can be made of different materials (Figure 2.1(b)).

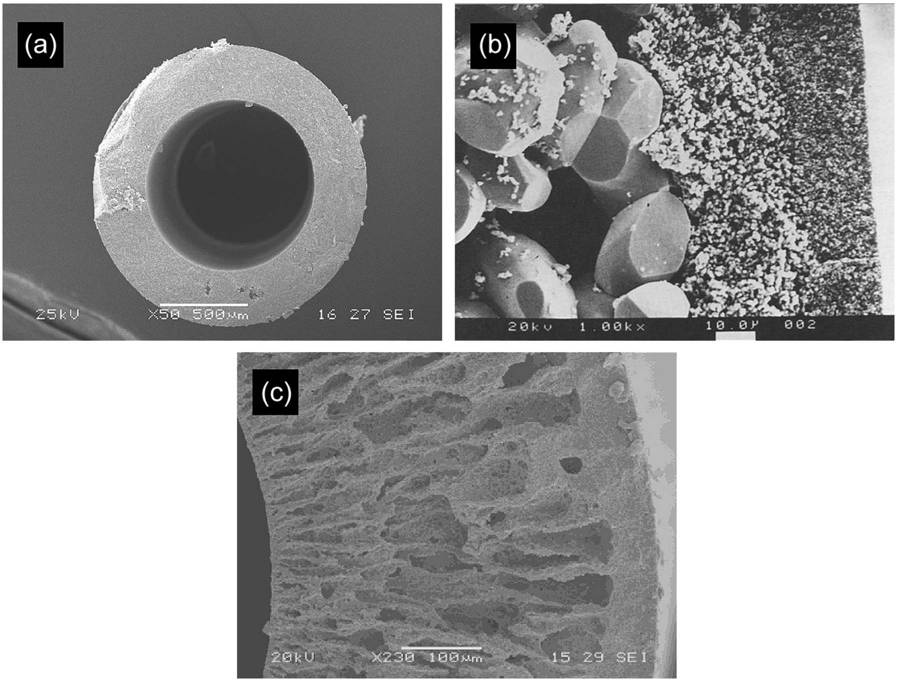

Figure 2.1 Scanning electron micrograph of the cross-section of (a) a symmetric alumina substrate (Reprinted from Kingsbury and Li (2009), with permission from Elsevier), (b) a three-layered alumina membrane/support composite (Reprinted from Hsieh, Bhave, and Fleming (1988), with permission from Elsevier) and (c) an asymmetric integral alumina membrane (Reprinted from Kingsbury et al. (2010), with permission from Elsevier).

A composite membrane's properties and performance can be tailored using different materials in different layers. Some disadvantages of composite membranes include the high complexity of the membrane fabrication process, which requires many steps, and the possibility of membrane failure owing to delamination of the separation layer, which occurs during sintering or variations in filtration pressures (wang, Jerome, Morris, & Kesting, 1999). Integral membranes are homogeneous in composition but can also be highly structurally varied in layers or distinct regions, depending on their fabrication methods.

As shown in Figure 2.1(c) and (b), the cross-sectional microstructure of the integral membrane and the composite membrane vary significantly even though both are asymmetric membranes. The integral membrane in Figure 2.1(c) is normally achieved via the combined phase inversion/sintering method (Li, 2007) whereas the composite in Figure 2.1(b) is made by skin deposition on top of a multi-layer substrate support. The integral membrane consists of two different types of sub-structures: sponge-like and finger-like. The sponge-like structure can provide the membrane with the desired selectivity and the finger-like structures can reduce the overall membrane resistance to permeate flow. On the other hand, the composite membrane consists of pores formed by voids between the particle packing only and the membrane selectivity is provided by the finer particles at the top layer and at a lower magnification the entire cross-section will appear to have a sponge-like structure.

Integral and composite ceramic membranes can be made via different fabrication methods; the choice of method will largely depend on the membrane configuration and microstructures that are desired.

2.2.3 Membrane configurations

There is a wide variety of membrane geometries available, depending on the shape formation technique chosen in the fabrication process. Ceramic membranes exist in two main types of element configurations, i.e. flat and cylindrical. The choice of membrane configuration depends largely on the application, such as the required operating and feed conditions.

2.2.3.1 Flat membranes

Flat ceramic membranes can come in a disc or sheet form. The packing density of disc membranes is generally low and hence they are limited to use in small-scale industrial, medical and laboratory applications. Commercial ceramic flat-sheet membranes may have thicknesses of around 6 mm and can be multi-channelled across their cross-section, as shown in Table 2.1 and Figure 2.2. Flat-sheet membranes are easy to replace when packed in modules and can handle high-turbidity feeds. Mechanical cleaning of ceramic flat-sheet membranes is also versatile; it can withstand air scrubbing, backwashing and high-pressure water jet cleaning.

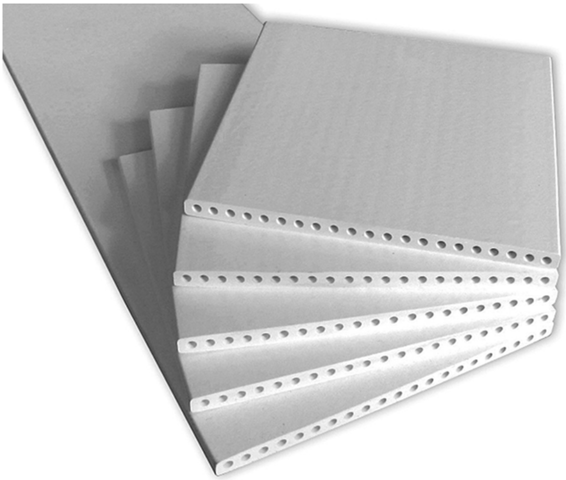

Figure 2.2 Product photograph of a commercial multi-channelled alumina flat-sheet membrane (CFM Systems®)
From ItN Nanovation AG (CFM-Flyer) (Reproduced by permission of ItN Nanovation AG).

2.2.3.2 Cylindrical membranes

Single-channel tubular membranes generally have diameters of between 10 and 25 mm, shown in Table 2.1 and Figure 2.3. They are more suitable for separating feeds that have high turbidity and large amounts of suspended solids. Because of their larger diameters and robustness they can be more easily cleaned mechanically and high cross-flow velocities can also be used to control fouling. To further improve the packing density of the tubular membranes, they can be fabricated as multi-channel tubes called monoliths, with a surface area to volume ratio up to 782 m^2/m^3, as shown in Table 2.1. In an effort to improve the packing density, hexagonal monoliths were also developed by Pall Corporation (Pall® Membralox®) (Figure 2.3(a)). Monolith membranes offer the same advantages as singular tubular membranes. However, when running in the inside-out configuration, the pressure drop of the permeate flow across the monolith could be high as a result of the long and tortuous path it has to travel to reach the outer surface of the monolith, which limits the size of the outer diameter that can be used. The patented CeraMem® from Veolia Water Ltd (Tundrasolutions) solves this problem by adding multiple conduits across the monolith through which permeate will flow through and then be collected at the end of the module (Figure 2.3(c)).

Ceramic hollow-fibre membranes have diameters of 2.0–4.0 mm (Han et al., 2011; Kingsbury & Li, 2009; Liu, Li, & Hughes 2003; Tan, Liu, & Li, 2001) (Figure 2.4), which means that compact modules with highly effective membrane surface areas can

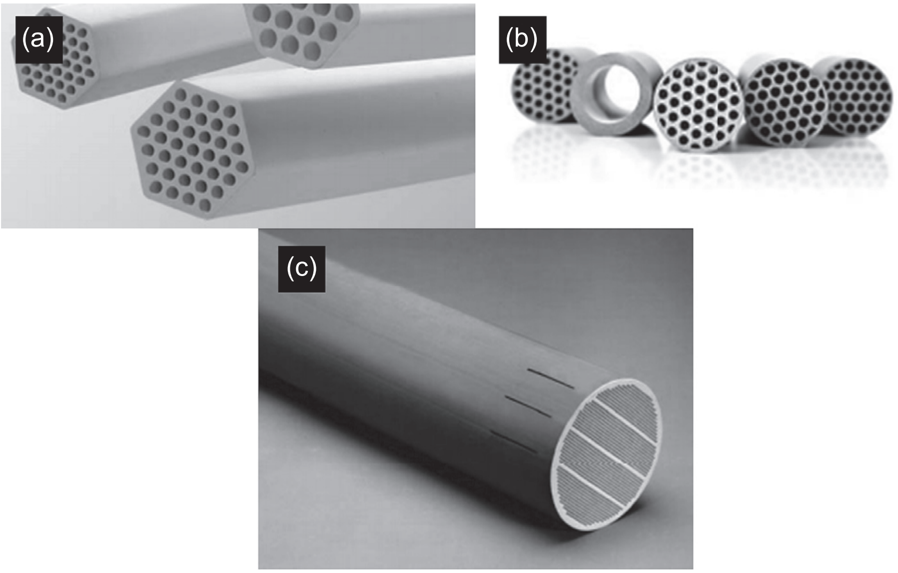

Figure 2.3 Product photograph of (a) Pall Corporation Membralox® multi-channelled alumina membranes (Pall® Membralox®) (Image courtesy of Pall Corporation), (b) LiqTech International, Inc's SiC SteriMem® products (LiqTech SiC SteriMem®) (Reproduced by permission of LiqTech International A/S) and (c) Veolia Water, Ltd CeraMem® element (Tundrasolutions) (Reproduced by permission of Veolia Water Technologies).

Figure 2.4 Product photograph of hollow-fibre alumina membranes from Hyflux, Ltd (InoCep®) (Reproduced by permission from Hyflux Ltd).

be achieved. Furthermore, Fraunhofer IGB, Ltd stated that ceramic hollow fibres with an outer diameter as low as 0.5 mm have been fabricated via combined phase inversion and sintering (Ceramic capillary membranes), potentially increasing the packing density that can be further achieved. In addition, they require lower trans-membrane pressures to drive permeate flow because of the thinner membrane and can be cleaned easily, using methods such as backwashing and forward flushing.

2.2.4 Fabrication techniques

Fabrication of composite ceramic membranes is generally a multi-step process. It can generally be broken down into three different stages: preparation of the ceramic powder paste or suspension; shaping of the ceramic powder into the desired geometry; and heat treatment, which includes calcination and sintering (Li, 2007). After these main steps, additional layer deposition followed by further heat treatment steps can tailor membrane selectivity as well as other membrane properties. The choice of method for each step depends on the desired membrane configuration, quality, morphology, mechanical and chemical stability and selectivity of the final membranes. However, the fabrication method should also be economical and easy to replicate without compromising the quality of the final membrane.

2.2.4.1 Ceramic powder paste and suspension preparation

The ceramic powder preparation stage processes the raw inorganic material into the shape and size distribution desired for membrane fabrication. This can be in the form of milling or chemical particle preparation. Often the ceramic powder is made into a paste or suspension so that shape formation is possible. During this step additives can also be introduced to the ceramic material. The choice of suspension medium, additives and powder is important and affects the membrane's microstructure and quality. Deflocculants or dispersants, often in the form of various fatty acids and esters, can be added to stabilize the ceramic particles in suspension to achieve high particle loadings and continuously high-quality ceramic membranes (Calvert et al., 1986; Li, 2007; Sushumna, Gupta, & Ruckenstein, 1992; Zürcher & Graule, 2005). Magnesium oxide has been used as a sintering additive to lower the sintering temperature required to form alumina hollow-fibre membranes via a combined phase-inversion and sintering method (Choi et al, 2006). Other additives such as the polymer binder are used to maintain the shape of the ceramic membrane precursor, and plasticizers can be used to increase flexibility and ease of handling of the suspensions for tape casting or extrusion methods (Burggraaf & Cot, 1996).

2.2.4.2 Shaping

The shaping step is the physical process whereby the ceramic material is transformed from a suspension or powder paste form into the membrane geometry. Methods that can create ceramic membranes and substrates include pressing, tape casting, slip casting, extrusion, phase inversion, foam techniques and leaching techniques.

Pressing is a simple and quick method for producing flat ceramic membranes (Silva et al., 2012; Wang et al., 2008a; Xin et al., 2007). A force is applied over an area of ceramic powder (varying from 10 to 100 MPa (Drioli & Giorno, 2010)) until the particles are consolidated. This method produces membranes of a symmetric structure owing to the uniform force applied across the area of ceramic material, and are commonly used to make disc membranes. Meanwhile, this method is not flexible in fine-tuning microstructures and there is a limitation on the thickness to diameter ratio of the membrane that can be achieved. In addition, it is a batch fabrication process and has been used primarily to make membranes for use in laboratories rather than commercially.

The tape casting method is used to form flat-sheet ceramic membranes (Das & Maiti, 2009; Das et al., 1996; Lindqvist & Lidén, 1997). A tape cast suspension is first prepared with the ceramic material, a liquid-dispersing medium and organic additives to provide the suspension with pseudo-plastic behaviour. Then the suspension is transferred into a reservoir controlled by a blade that can be height adjusted over a mobile carrier film. Subsequently, the suspension film is dried in a controlled environment. Tape casting is a more flexible method that can make flat-sheet membranes as well as coat layers onto membrane supports.

Slip casting uses a porous mould to form the shape of the ceramic membrane (Falamaki & Beyhaghi, 2009; Lin & Tsai, 1997). When the ceramic suspension is poured into the mould the solvent is extracted into the pores of the mould as a result of the capillary force, leaving ceramic particles on the surface of the mould. Slip casting is commonly used to form tubular membranes with high surface quality, density and uniformity. Important factors that affect the final quality of the membranes created via this method include slip density and viscosity.

Extrusion is a method popular for fabricating tubular, monolith and hollow-fibre/capillary membranes (Castillon & Laveniere, 1995; Feenstra, Terpstra, & Van Eijk, 1998; Smid et al., 1996; Terpstra, Bonekamp, & Veringa, 1988; Wang et al., 1998). It is a process in which an inorganic stiff paste is forced through an orifice of a designed shape and compacted by applying high pressure. The paste must have plastic properties to form and maintain the shape of the membrane precursors; hence, additives are added to the ceramic powder. The paste is then forced through a die at high pressure (around 20 MPa) to produce hollow tubes.

Combined phase-inversion/sintering (Kingsbury & Li, 2009; Liu et al., 2003; Tan et al., 2001) is a relatively new method for fabricating microstructured ceramic hollow-fibre membranes. Solvent—non-solvent exchange-induced precipitation of the polymeric binder and viscous fingering phenomenon occur during membrane fabrication, which distinguishes this method from conventional ram extrusion, and will be further introduced in Section 2.5.

2.2.4.3 Heat treatment

After the forming step the ceramic membrane precursors are produced. They are then dried and treated with heat. This heat treatment step consists of three main steps (Li, 2007): pre-sintering, thermolysis and final sintering with the purpose of removing components other than the ceramic material, to strengthen the membrane and consolidate the microstructure and dimensions of the final membrane.

Presintering occurs at around 200 °C. Presintering is used to remove water from the membrane precursors, which may be in the form of water chemically bonded to the ceramic particle surfaces or as crystallized water within the inorganic phases. Thermolysis, or the calcination step, is the process by which all organic components in the membrane precursor are removed. The sintering stage is where the major changes to the porosity and pore size occur, the final shape of the ceramic membrane is consolidated and mechanical strength is improved. In general, the higher the sintering temperature, the higher the mechanical strength but the porosity of the final membrane is lowered.

Important parameters that affect thermal stability of ceramic membranes are sintering activity and phase transformation of the membrane material and the support (Mallada & Menéndez, 2008). During sintering, the ceramic material is kept at a certain temperature long enough for the material to approach its equilibrium structure. The membrane structure can be maintained for temperatures up to 100—150 °C below the sintering temperature, which is normally extremely high (over 1000 °C) (Burggraaf & Cot, 1996).

2.2.4.4 Layer deposition for composite membranes

Additional layer deposition can be used to alter or enhance the ceramic membrane properties: for example, by changing the membrane selectivity, porosity, hydrophilicity, conductivity, permeability, biocompatibility, etc.

To form composite membranes, layer deposition methods are required to add layers onto a symmetric substrate. Each layer normally consists of ceramic particles of different sizes to achieve a gradient pore structure across the membrane cross-section. Multiple layers are normally required to reach the desired selectivity at the end.

Dip or spin coating is the most commonly used method for layer deposition onto a support (Babaluo et al., 2004; Gu & Meng, 1999; Lindqvist & Lidén, 1997). Dip coating is when a support is dipped into and then withdrawn from a ceramic powder suspension. Upon withdrawal from the suspension the liquid will be sucked into the support pores because of capillary forces along with the ceramic particles if they are small enough in size. Spin coating rotates the substrate while the suspension is deposited over the substrate surface.

Sol-gel method can be used to fabricate membranes with high selectivity with pores from 100 nm down to a few nanometres and is commonly used to form ceramic UF membranes (Agoudjil, Kermadi, & Larbot, 2008; Das & Maiti, 2009; Hao et al., 2004; Kim & Lin, 1998; Larbot et al., 1988; Wu & Cheng, 2000). A colloidal (consists of alkoxide) or polymeric solution is first deposited over a membrane substrate by means of dip coating, whilst it is converted into a gel form by hydrolysis and condensation or polymerization. Afterward, it is heat treated to form a thin and uniform skin over the membrane.

There are many other coating techniques such as chemical vapour deposition, neutron sputtering and plasma; details about these can be found elsewhere (Burggraaf & Cot, 1996; Hsieh, 1996; Li, 2007).

2.2.5 Combined phase-inversion and sintering fabrication technique

As described in the previous section, the traditional and common method for producing hollow-fibre membranes is to use extrusion followed by sintering. However, this would give rise to symmetric membranes, and additional layer deposition and heat treatment steps are required to produce the required selectivity with a gradient pore size along the membrane cross-section, as shown in Figure 2.1(b). An alternative and innovative method for producing ceramic hollow-fibre membranes is the combined phase-inversion and sintering technique (Choi et al., 2006; Kingsbury & Li, 2009; Kingsbury, Wu, & Li, 2010; Koonaphapdeelert & Li, 2007; Liu et al., 2003; Tan et al., 2001; Wang et al., 2008b; Wang et al., 2009; Wei et al., 2008). It is a flexible technique that can produce both symmetric ceramic membranes and a wide range of asymmetric ones in a single step for both flat-sheet and hollow-fibre geometries, as shown in Figure 2.1(a) and (c). Because of the presence of large finger-like structures, they can reduce mass transfer resistance for permeation fluxes competitive to the membranes formed via conventional methods.

A suspension consisting of ceramic particles and polymer binder in a solvent is first prepared, and then through solvent—non-solvent exchange induced phase inversion of the polymer binder the ceramic particles are immobilized in their desired geometry by casting (flat membrane) or spinning (hollow-fibre membrane). This method can easily tailor and form membrane precursors with various specific morphologies. Then, similar to all other ceramic fabrication methods, the membrane precursors undergo a heat treatment session (Section 2.4.3) to remove all organics as well as consolidate the final membrane structure and mechanical strength.

Preparation of the ceramic—solvent—polymer suspension solution is a step that has a major impact on the properties of the final membrane. The particle size and particle size distribution of the ceramic components can affect the pore size and selectivity of the membrane as well as the suspension rheology. Porous alumina hollow-fibre membranes developed using this method have selectivity in the MF range when 1-μm particles are used (Kingsbury & Li, 2009) and in the UF range when mixtures of 0.01- and 1-μm particles are used (Tan et al., 2001). Yttria-stabilized zirconia (YSZ) porous membranes have pore sizes in the UF range when polydispersed YSZ particles (0.1 and 0.02 μm) are used (Wei et al., 2008). Other factors such as the ceramic to polymer binder ratio can affect the mechanical strength and quality of the sintered membrane, and a ratio of up to 10 has been suggested (Kingsbury & Li, 2009; Tan et al., 2001).

Although the process of spinning ceramic hollow-fibre membranes is similar to spinning polymeric ones, the rules and optimization of the polymeric spinning system cannot be applied directly to the ceramic spinning process because of the significantly different composition of the spinning suspension. The presence of a large amount of ceramic particles also changes the mechanisms behind the formation of the different membrane sub-structures. Two basic sub-structures have been achieved within the membrane cross-section: sponge-like denser structures and finger-liker structures that can be isolated or micro-channels, as shown from Figure 2.5. The positioning and dimensions of these different sub-structures can be tailored mainly by changing the parameters during spinning.

Improved understanding of spinning parameters such as the air gap, bore fluid choice, and bore fluid flow rate on the alumina membrane morphology was achieved by Kingsbury and Li (Kingsbury & Li, 2009; Kingsbury et al., 2010). The designing and engineering of the two types of sub-structures led to distinctively different membrane morphologies (Figure 2.5) and generated a string of potential applications. These applications include hollow-fibre membrane micro-reactors, membrane contactors, solid-oxide fuel cells, gas separation, etc. (Kanawka et al., 2011; Kingsbury et al., 2010; Koonaphapdeelert, Wu, & Li, 2009; Othman et al., 2012; Rahman et al., 2011). In particular, the morphology consisting of one sponge-like skin layer on top of a layer of finger-like micro-channels (Figure 2.5(d)) is expected to dramatically reduce the trans-membrane resistance to permeate flow. The single thin separation layer provides the membrane with its selectivity and the finger-like micro-channels can reduce the mass transfer resistance significantly. This morphology is expected to excel in aqueous MF/UF applications compared with conventional composite asymmetric ceramic membranes.

Current research has made significant progress in understanding the effects of different process parameters on membrane morphology and properties but the scientific mechanisms behind the formation of different sub-structures need further research effort. In recent years, the common viscous fingering phenomenon has been applied to explain formation of the finger-like structures in the ceramic—polymer—solvent and non-solvent systems (Kingsbury & Li, 2009; Kingsbury et al., 2010; Wang & Lai, 2012). Viscous fingering is a hydrodynamic phenomenon in which a less viscous fluid displaces a more viscous fluid, forming finger-like patterns. Important factors that

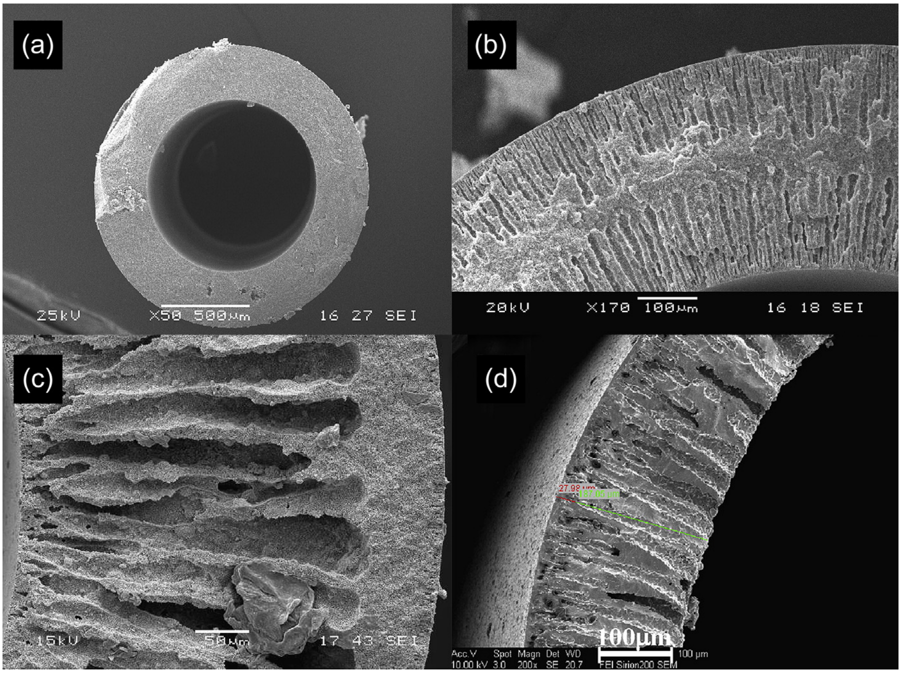

Figure 2.5 Scanning electron micrograph of (a) cross-section morphology of a symmetric alumina hollow fibre and (b—d) different asymmetric alumina hollow fibres formed by combined phase-inversion and sintering (Reprinted from Kingsbury & Li (2009), with permission from Elsevier; Reprinted from Kingsbury et al. (2010), with permission from Elsevier; Reprinted from Tan et al. (2011), with permission from Elsevier).

affect the initiation, propagation and termination of these finger-like structures include viscosity difference, density difference, moving interface velocity and polymer precipitation rate. Finger-shielding, coalescing and spitting of the finger-like structures have also been observed (Wang & Lai, 2012). A clearer understanding of the mechanisms behind the formation of the unique sub-structures would allow easier and more advanced designing of the different morphologies and engineering of the production process.

The combined phase-inversion and sintering technique has been successfully applied to a wide range of ceramics as well as metals with a range of different pore sizes (Liu et al., 2003; Luiten-Olieman et al., 2011, 2012; Yang, Tan, & Ma, 2008; Zhang et al., 2009b, 2012). However, a compromise always has to be made between the porosity and mechanical strength when a high sintering temperature is involved. A study suggested the use of a controlled sintering process by using PESf as not just a polymer binder but also a pore structure 'stabilizer' (Wu et al., 2013). By thermally treating the membrane precursors, the PESf is not completely removed during the first stage of heat treatment. Instead, some of the PESf is converted to carbon at 1450 °C in an environment devoid of oxygen, which allows mechanical strengthening of the alumina membranes without losing significant porosity.

As a result, the combined phase-inversion and sintering method can potentially create the opportunity to use ceramic membranes in large-scale water and wastewater treatments by offering a hugely reduced fabrication process cost and great flexibilities in microstructure design. However, further improvements are required before this method can be fully commercialized, for example, to improve surface porosity and pure water permeation without sacrificing its mechanical strength, and to have a better fundamental understanding of the microstructure formation mechanisms to enable reliable and reproducible fabrication process on a large scale.

2.3 Development in membrane modules and units

The design of the membrane module is important for achieving the highest packing density possible for the particular membrane element whilst offering effective filtration. The different membrane elements are packed in a unit called a module and these modules are often arranged and connected in a specific way to form a unit, offering great efficiency. The unit(s) is then integrated with other components such as pumps, pipes, control systems, etc., to form a membrane system and part of the water or wastewater treatment plant. The following section describes the ceramic MF/UF modules and units available commercially.

2.3.1 Module and unit designs

Many different module designs are available for the different ceramic membranes and their choice depends largely on the application, the demand of the process and any spatial limitations and economical factors. The arrangement and packing of the membrane elements can be divided into two main types, i.e. flat membranes and cylindrical membranes.

The membrane elements may be contained in pressure vessels or immersed in a fluid medium at atmospheric pressure. For the contained modules the ceramic membranes are packed and fitted inside a pressure vessel and trans-membrane pressure is applied at one end of the vessel with the feed. The immersed unit allows easier replacement of the membrane elements or modules and is also more flexible to tailor to specific needs and demands. Furthermore, it enables air sparging in the unit to improve permeation and reduce fouling by promoting turbulence. Both flat-sheet and cylindrical membranes can be packed in this way and this type of system requires less energy to operate than contained units.

2.3.1.1 Flat membranes

Ceramic flat membranes can come in the form of flat sheets or flat discs, as described in Section 2.3.1 and can both be packed into plate-and-frame modules. The contained plate-and-frame configuration consists of stacking the flat membranes on top of one another with porous spacers in between. The size of the spacing depends on the amount and size of suspended solids in the feed. The feed enters the module from one end and is

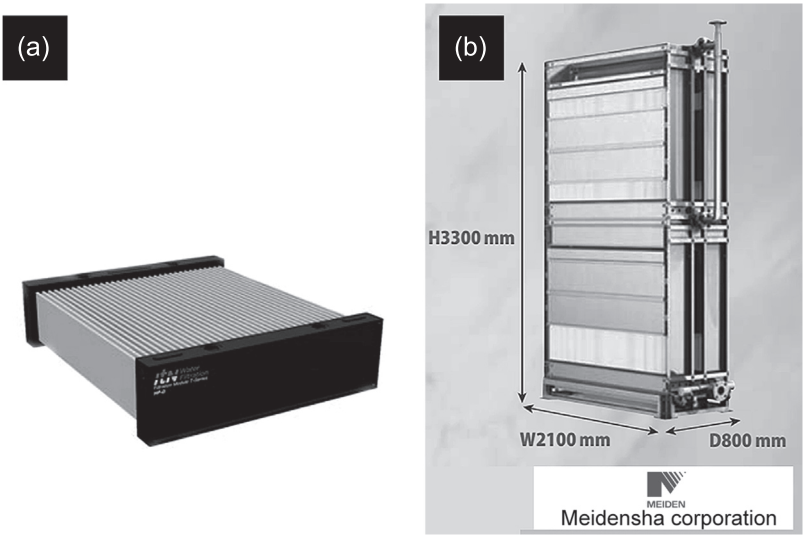

Figure 2.6 Product photograph of (a) a ceramic flat-sheet module from ItN Nanovation AG (Itn-nanovation) (Reproduced by permission of ItN Nanovation AG) and (b) a ceramic flat sheet system from Meidensha Corporation (Ceramic membrane unit, 2013) (Reproduced by permission of Meidensha Corporation).

collected at the membrane support plates. Such a module is easy to operate and membrane defects can be detected and replaced simply. However, their packing density is low and so most of the time they are limited to use for small-scale applications.

Flat-sheet membranes with multiple channels can be stacked next to each other and form an immersed module, as shown in Figure 2.6. These flat-sheet membranes are connected at the two ends to permeate collector(s) and then packed together and supported by a metal framework that is then immersed into the feed medium. Permeate enters from the membrane's outer surface into the channels inside the flat sheets and is then collected at the end(s) of the membrane. These modules can then be further stacked together to easily increase productivity. The energy consumption of the immersed module is lower than that of the contained module because of the lower pressure–driving force requirements. The membranes can also be replaced easily because they are produced and sealed sheet by sheet. In addition, their ability to handle feeds with a high content of suspended solids means that they are commonly used in MBRs to treat wastewater. Packing densities of about 91.8 m^2/m^3 are reached using the CFM Systems® from ItN Nanovation AG by stacking units on top of each other (Table 2.1). However, this is still significantly lower than the packing densities offered by polymeric flat-sheet membranes that are spiral wound (700–1000 m^2/m^3) (Crittenden et al., 2012).

2.3.1.2 Cylindrical membranes

Tubular membranes are often packed as a bundle inside a casing, which could be a contained vessel (Figure 2.7) or an open vessel. The feed solution may be fed though the

Figure 2.7 Product photograph of a contained module from Pall Corporation (Pall® Membralox® IC) (Image courtesy of Pall Corporation).

centre of the tubular or monolith membranes and permeate is collected outside the tube in the module casing. This operating mode requires high operating flow rates and the pressure drop can be large; hence, energy consumption is highest compared with other module designs. However, because of the relatively large channel diameters of tubular and monolith membranes, they are suitable for feed streams with larger particles, and cleaning these membranes is also more facile. The tubular or monolith membranes can also be packed and supported by a partly open housing support and operated by immersion into the feed solution, similar to the immersed flat-sheet modules, offering similar advantages and disadvantages. The immersed tubular modules are commonly used in MBRs for larger-scale applications and also to treat harsh feed streams.

Hollow-fibre membranes can also be packed in a similar way in their modules, as shown in Figure 2.4. Ceramic hollow-fibre membranes are generally packed together and immobilized at both ends and then placed in a cylindrical housing. The fully contained module is more suited to small-scale applications such as domestic-scale drinking water treatment. Hollow-fibre modules can potentially offer a much higher packing density and form more compact systems, saving space and improving productivity. As shown in Table 2.1, the packing density offered by commercial ceramic hollow-fibre modules is not as competitive (502 m^2/m^3 offered by Media and Process Technology, Inc.) as some of the multi-channel tubular module designs (up to 782 m^2/m^3 offered by Ceramem® module from Veolia Water, Ltd). This is mainly because of the relatively large ceramic hollow-fibre outer diameters from most of the suppliers (3–4 mm from Table 2.1). Furthermore, their intrinsic brittleness makes it more difficult to pack them into bundles and it limits their length. Hence, cassette-style modules for ceramic hollow-fibre membranes are not available in which the hollow fibres are supported at the top and bottom only and are immersed fully into the feed solution with no housing. In addition, the lack of open vessel designs for hollow-fibre membrane elements means that their application in immersed MBR is limited.

2.3.2 Housing, sealing and operation

Membrane modules consist of the housing, sealing materials and membrane. The type of housing used for the membrane varies depending on the membrane and module type and operating configuration. For contained cylindrical membranes the membrane is packed and enclosed in a vessel, shown in Figure 2.8. For outside-in feed configuration or immersed cylindrical membranes, the housing may have openings that expose certain areas of the membrane element. Flat-sheet ceramic membranes are normally sealed at the top and bottom to a permeate collector. They are then stacked together and supported by a stainless-steel frame into modules such as the Meidensha Corporation's ceramic membrane unit (Ceramic membrane unit, 2013) and ItN Nanovation AG's CFM System® (Itn-nanovation) (Figure 2.6).

Typical module housing materials include stainless steel, titanium and plastic. Stainless steel is most commonly used because of its good chemical and thermal stability as well as great robustness. Although plastic housing is a cheaper option, it often limits the conditions within which the membranes can operate.

The type of seal used on the membranes varies depending on the membrane and module type. They are important because they prevent contaminant leakage into the permeate stream. Mostly O-rings and gaskets are used to cover the perimeter of the membrane ends where both the feed and permeates are exposed. The material used to seal the membranes depends on the required operating conditions of the MF/UF, which will change depending on the application. Typical sealing material includes rubber, silicon, polytetrafluoroethylene and poly(vinyl chloride).

There are many different module designs for flat-sheet and tubular (single and multi-channel) ceramic membranes. However, because of the much larger dimensions of the flat-sheet and tubular elements, their packing density is lower than the polymeric membrane modules offered, which makes them less competitive for large-scale applications or when space is limited in a treatment plant. Hollow-fibre membrane modules have the potential to improve the packing density significantly, but most of the ones offered on the market have relatively large outer diameters, leading to lower packing

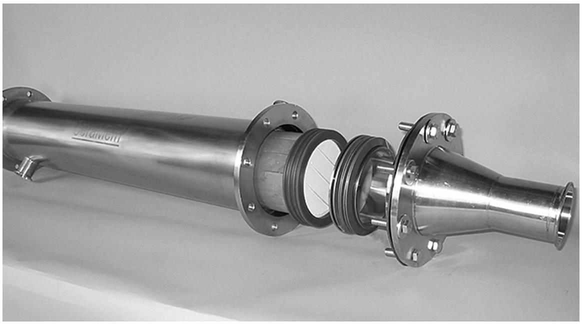

Figure 2.8 Product photograph of the CeraMem® contained module and housing from Veolia Water, Ltd.

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densities. Commercially available hollow-fibre modules are limited; for example, there are limited open-vessel modules and no cassette-style ceramic hollow-fibre modules for large-scale immersion applications, which is a problem for their application to small-scale MF/UF applications.

2.4 Ceramic membranes for water treatment

Because of the high chemical and thermal stability and robustness of ceramic membranes, they have been commonly applied in applications for which polymeric membranes cannot be used because of their lower stability. For example, ceramics can be used in harsh environments such as at high temperatures and in aggressive chemicals (solvents, highly acidic or caustic solutions) and oily water. Unlike polymeric membranes, ceramic membranes do not swell in solvent and can be treated with strong cleaning agents and sterilized at high temperatures, and can withstand high pressures for backwashing. All of these advantages have made long-term flux stability possible for ceramic membranes to be used on a commercial scale (Mallada & Menéndez, 2008). Recently, ceramic membranes have garnered increasing attention for applications in milder operating conditions in which polymeric membranes dominate, because of the increase in the packing density of the membrane modules and reductions in capital costs.

2.4.1 Drinking water production

MF and UF membranes are used extensively in producing drinking water, and can handle both small- and large-scale capacities (Staff, 2011). Small-scale MF/UF applications include portable membrane systems and in large-scale applications MF/UF membranes can be used as stand-alone or hybrid systems in a water treatment process train. This market has been and is still currently dominated by polymeric membranes but recently the incorporation of ceramic membranes to produce drinking water has been increasing (Bottino et al., 2001; Li et al., 2011; Mahesh Kumar, Madhu, & Roy, 2007; Muhammad et al., 2009). Water sources used to produce drinking water can vary considerably from groundwater, lakes and rivers to municipal wastewater and seawater. The final water that is safe to drink must fulfil standards set by the World Health Organisation or by the European Union, and be free of suspended solids, microorganisms and harmful chemicals.

Small-scale ceramic membrane MF/UF systems can serve several purposes, such as to improve the quality of tap water, reduce the volume or recycle household wastewater, provide safe drinking water in remote areas with limited resources such as during camping or hiking, and provide safe drinking water in developing nations or during humanitarian crises.

To produce drinking water from surface water for a large community — in other words, for municipal use — large systems are required. The water purification process will consist of a process train of different steps. Because the design of the process depends on the feed quality and the final water quality, preparing drinking water from surface water is much more expensive because it requires more purification steps. A typical process train for purifying surface water consists of a pre-filtration unit, addition of chemicals, natural filtration, disinfection, fine filtration and preservation and storage. Ceramic MF/UF membrane units may be used to replace conventional particle removal units such as coagulation and sedimentation, as well as disinfection unit(s). Furthermore, the ability to reject microorganisms, bacteria and viruses can reduce the amount of chemicals required to be added to drinking water, saving considerable space overall. For the production of drinking water from seawater, ceramic MF/UF units may be used to provide pre-treatment to reverse osmosis.

Studies in literature have shown that ceramic MF/UF membranes alone can provide permeate turbidity low enough for drinking standards and are effective in removing microorganisms, organic matter and disinfection byproduct (DBP) precursors (Bottino et al., 2001; Harman et al., 2010; Muhammad et al., 2009). Because of the hydrophilic and inorganic characters of the ceramic membranes, they are less affected by organic fouling compared with polymeric membranes (Hofs et al., 2011). However, high-turbidity water (up to 80 NTU) can lead to membrane fouling and significant permeate flux declination, which can be recovered via chemical cleaning. The membrane pore size also appears to affect the rate of flux decline, because Harman et al. suggested that the smaller 4-nm pore-size membrane fouls mainly by forming a cake layer whereas pore clogging may dominate in the larger 10-nm pore-size membrane (Harman et al., 2010).

To minimize the effect of fouling, much research has been carried out to analyse the performance of hybrid ceramic membrane systems such as the combination of ceramic membrane MF/UF with activated carbon for natural organic matter (NOM) removal (Karnik et al., 2005b; Konieczny & Klomfas, 2002; Lee, Park, & Yoon, 2009; Stoquart et al., 2012), coagulation for reducing organics and viruses (Fiksdal & Leiknes, 2006; Konieczny, Bodzek, & Rajca, 2006; Lerch et al., 2005; Matsushita et al., 2005), photocatalytic reactions (Alem, Sarpoolaky, & Keshmiri, 2009; Chin et al., 2007; Mozia, 2010) and ozonation to remove NOM (Karnik et al., 2005a; Kim et al., 2008) and subsequent formation of DBPs (Karnik et al., 2005b). The use of the coagulation and MF/UF hybrid system is preferred from an economic point of view.

2.4.2 Municipal wastewater/sewage treatment

Treatment and recycling of municipal wastewater is common and a highly important part of today's water management. Municipal wastewater consists of household, commercial and institutional wastewater. A typical sewage treatment plant consists of the following steps: pre-treatment to remove large and heavy debris, followed by primary treatment used to remove the suspended inorganic and some organic particles, and then secondary treatment for the biological conversion of dissolved and colloidal organics into biomass, and finally tertiary treatment for the further removal of suspended solids or nutrients and disinfection.

MF/UF can be incorporated in the treatment train as stand-alone processes or combined with the activated sludge process to form hybrid systems such as the MBR.

This can reduce the steps in secondary and tertiary treatment, for example, eliminating the need for sedimentation and secondary disinfection, saving space as well as reducing waste such as DBPs that need to be treated and disposed of. Ceramic membranes can be used to replace the traditional polymeric membranes for sewage treatment because the quick fouling of polymeric membranes limits them to short operating lifetimes. They can be cleaned under harsher cleaning conditions and therefore offer longer and more reliable operation as well as less servicing and maintenance, reducing long-term operating costs. Flat-sheet and cylindrical membrane elements are suitable for being combined with MBRs and the modules can be operated in the immersed mode or as a separate external unit. The immersed mode consists of the membrane module immersed in the aeration basin, and permeate is extracted via suctioning. The external configuration consists of pumping the mixed liquor at high pressure through the membrane from one surface. Because of the higher trans-membrane pressure required for the external configuration, their permeate flux is also generally higher (Marrot et al., 2004). However, the energy and space consumption of the immersed configuration tends to be lower, which makes them more suited to large-scale wastewater treatment.

Many studies have been carried out to analyse the effectiveness of ceramic MBR systems to treat municipal wastewater (Waeger, Delhaye, & Fuchs, 2010; Xing et al., 2000; Xu et al., 2003; Zhang et al., 2009a). Xing et al (2000) looked at using external cross-flow ceramic UF MBRs for urban wastewater reclamation. The system provided high removal efficiency, removing carbon oxygen demand (COD) of an average of 97%, and the reclaimed water could be reused directly for municipal or industrial purposes after additional treatment (Xing et al., 2000). The lab-scale immersed ceramic MBR offered COD removal of more than 92% during the course of a prolonged sludge retention time (142 days) to treat simulated high-strength wastewater (consisting of glucose and protein) (Sun, Zeng, & Tay, 2003). Using longer sludge retention times can reduce the amount of sludge produced and cut down on the cost of sludge treatment.

Fouling was mainly affected by the membrane's microstructure, surface roughness and pore sizes in immersed ceramic bioreactor systems (Jin, Ong, & Ng, 2010). The ceramic membrane with the roughest surface and largest pore size (0.3 μm) has the highest fouling potential, whereas the membrane with the smoothest surface and smallest pore size (0.08 μm) fouls the least. Air sparging has been found to be an effective, simple and economical method to improve permeate flux and reduce concentration polarization and fouling in external-loop air-lift ceramic MBRs and the immersed ceramic MBR (Fan et al., 2006; Sun et al., 2003; Zhang et al., 2009a). Anaerobic MBRs may have lower energy consumption (Liao, Kraemer, & Bagley, 2006). However, inorganic fouling in anaerobic MBRs by struvite has been observed in ceramic membranes (Kang, Yoon, & Lee, 2002) and requires periodic alkaline backflushing to recover permeate flux.

2.4.3 Industrial wastewater treatment

The composition of industrial wastewater varies dramatically across the industries, and the choice of membrane technology will vary according to the contaminants. Because of increasingly stringent regulations on waste discharge and the increasing cost of clean water, industries are more motivated to treat and recycle wastewater, which can potentially save significant operating costs.

Typical contaminants in industrial wastewater are suspended solids, particulates, colloids, bacteria and viruses; dissolved inorganics such as heavy metals, salts, nuclear wastes, acids or alkalis; volatile organics such as aromatics, aliphatics, alcohols and halogenated hydrocarbons; and non-volatile organics such as phenolics, polyaromatic compounds, pesticides, insecticides, surfactants and dyes. Similar to sewage treatment, MBRs are a popular treatment unit in the treatment train. Upstream and downstream treatment units will vary depending on the desired quality of the final effluent (ultra-pure water, process water, etc.). Ceramic MBRs are commonly used for small-scale treatment of high-strength industrial wastewater because they are robust, stable and reliable.

2.4.4 Produced water

Produced water is the largest waste stream generated from oil and gas operations. MF/UF is a promising technology for use to treat produced water because it is a low-energy consumption process and can cut down on the amount of harsh and expensive chemicals required to treat the wastewater. Polymeric membranes have been commonly used to remove organic contaminants as well as suspended particles before desalination so that the water can be reused. However, because the feed has a high composition of organic contaminants, oil and grease, the polymeric membranes can be degraded and fouled easily, requiring regular replacement. Ceramic membranes offer higher stability in such conditions and may prolong the lifetime of the membrane, and can also be cleaned more easily.

Many studies have been carried out to investigate the performance of ceramic membranes in oil—water treatment in the laboratory or on a pilot scale (Ashaghi, Ebrahimi, & Czermak, 2007; Chen et al., 1991; Ebrahimi et al., 2010; Li & Lee, 2009). Studies showed that using MF/UF ceramic membranes gives permeate streams of very high quality, with less than 6 ppm total hydrocarbons, and perform better than polymeric membranes. However, an important limitation is permeate flux decline as a result of fouling by waxes and asphaltenes. Backwashing is a useful cleaning method to prevent permeate flux decline (Abadi et al., 2011).

2.4.5 Food and beverage industries

MF and UF are important processes in the food and beverage industries. They can be used to achieve clarification, sterilization, concentration and purification of the final product in place of multiple traditional process units. For the dairy industry MF can be used to clarify cheese whey (Skrzypek & Burger, 2010) and to concentrate and defat milk and sterilize it by rejecting microorganisms (Fernández García, Álvarez Blanco, & Riera Rodríguez, 2013). In the sugar-refining and beverages industry, MF and UF membranes are used to clarify products such as maple syrup, wine, beer, juice and vinegar (Ceramic membranes, 2000; Fukumoto, Delaquis, & Girard, 1998; Gan et al., 1999; Hinkova et al., 2002; van der Horst & Hanemaaijer, 1990; Li et al., 2010). Wastewater generated in these industries can also be recycled with the help of MF/UF membranes to save operating costs. Ceramic porous MF/UF membranes have demonstrated success in the food and beverage industries, offering superior long-term performance in these applications over polymeric membranes.

2.4.6 Commercial ceramic applications

Ceramic membranes have been implemented commercially in the industries mentioned in Sections 4.1—4.5 to treat aqueous feeds. In terms of producing drinking water, there are far fewer portable ceramic membrane drinking production systems than polymeric ones, mainly owing to their high capital costs. However, Veolia Water Ltd developed a mobile ceramic UF system for providing emergency drinking water (Veoliawaterst; Berkefeld). The system consists of a treatment train in the order of coagulation, adsorption, pre-filtration and UF using ceramic monolith elements and ultraviolet and chlorination disinfection, providing up to 360 m^3/day permeate flow fit for drinking purposes.

For large-scale drinking water production the cost of ceramic membranes can be recuperated by their reliable performance and long operating lifetimes; for example, a ceramic MF system by Metawater Co., Ltd has been operating for 15 years (Metawater). Metawater Co., Ltd's systems typically consist of coagulation, dead-end MF using ceramic monolith elements, followed by disinfection with chlorine, and have the treatment capacity of 1000—1,00,000 m^3/day for the treatment of clear raw water.

Because of the superior stability and operating lifetimes of ceramic MF/UF membranes, they can also be used as a pre-treatment step before reverse osmosis for desalination. A drinking water plant in Qassim replaced polymeric UF pre-treatment membranes with ceramic flat-sheet ones, which reduced the membrane replacement frequency dramatically and has a treatment capacity of 42,000 m^3/day (Itn-nanovation Ground water).

For the treatment of municipal wastewater or sewage, the performance of ceramic MBRs is highly competitive compared with polymeric systems. Similar to drinking water production plants, implementation of ceramic membranes is limited mainly by their high cost. There are examples of commercial ceramic MBR systems being implemented in small-scale wastewater treatments, such as in a school and an airport by Likuid Nanotek (Likuid-CBR®). They use an external cross-flow configuration to treat domestic wastewater with capacities ranging from 38 to 50 m^3/day and permeate flux is recovered solely by periodic chemical cleaning. For larger-scale wastewater treatment, the ceramic immersed MBR is more commonly used; for example, ItN Nanovation AG installed immersed ceramic flat-sheet membrane modules with a capacity to treat 150 and 1300 m^3/day of sewage feed in two different sewage treatment plants (Itn nanovation MBR; Itn nanovation MBCR). No membrane servicing or maintenance has been required since operation began in 2011 for one of the plants, and chemical cleaning is used once a year (oxidant and chelating agent) to maintain permeation flux.

Ceramic membranes have found more frequent use in the treatment of industrial wastewater, because they are normally more challenging to treat. An example of a ceramic MBR includes an external MBR using ceramic tubular membranes from Likuid Nanotech to treat industrial waste of 3–300 m^3/day, which has been commercially used in olive oil, wine and narcotics production plants. For all of their ceramic MBRs the quality of the final effluent is clean enough to be directly discharged (Likuid-CBR®). Another application includes the ceramic MBR installed for treatment and recycling of up to 1400 m^3/day of highly pigmented wastewater by Pall Corporation (Membralox® pall). Complete retention of insoluble pigments is achieved using monolith ceramic membranes running in external configuration, and up to 50% of wastewater can be recycled. A larger-scale ceramic MBR has been scheduled for installation in a demonstration plant by Meidensha Corporation to treat and recycle up to 4550 m^3/day of industrial wastewater by combining up-flow anaerobic sludge blanket technology with the 0.1-μm alumina flat-sheet MBR system (Singapore collaborate on ceramic membrane MBR demonstration plant, 2012).

The commercial operation of ceramic membranes in produced water treatment is much more limited compared with other application areas such as in the food and beverage industry and industrial wastewater treatment. To treat produced water, the ceramic membranes typically run in cross-flow configuration (Elshorbagy, 2013). An example is the full-scale facility in Colorado, which uses ceramic membranes as one of the units to treat oily wastewater (Aqwatec). The process train consists of dissolved air floatation, pre-filtration, ceramic MF and activated carbon adsorption, and then the water is supplied to a reverse osmosis plant, providing municipal drinking water. In addition, Veolia Water, Ltd has developed a system consisting of ceramic monolith membranes to treat produced water, which so far has been installed at 60 locations (Veoliawaterst CeraMem®). Their typical performance includes removal of 98.7% turbidity and effluent has less than 1 ppm oil and grease (Veoliawaterstna). Furthermore, a ceramic (SiC) membrane module will be installed for commercial use in Columbia and Venezuela, after the trial period offered consistent reductions of oil concentration from 20–100 ppm to less than 5 ppm (Success for LiqTech ceramic membranes in oil & gas trial, 2012).

Ceramic membranes are most commonly used in the food and beverage industry (Fernández García et al., 2013). One commercial system for the removal of bacteria and spores from milk using MF is the Tetra Alcross® Bactocatch. The raw milk is first separated into skim milk and cream, and then the former undergoes MF, leaving the concentration of bacteria in permeate to be less than 0.5% of the original value (Peinemann, Nunes, & Giorno, 2011). Ceramic membranes were also chosen and installed by Atech Innovations GmbH over polymeric membranes in a commercial citrus fruit juice production plant because of their high performance as well as resistance to essential oils from the fruit skins. Another example of commercialization includes the use of tubular ceramic monolith membranes in a high-velocity cross-flow configuration in a glucose production plant to minimize gel layer formation, which is able to produce 180 m^3/day of glucose (Bolduan & Latz, 2005).

Ceramic MF/UF membranes have been used across a wide range of different applications involving water and wastewater treatment. They are most commonly used in the food and beverage industry and in the small-scale treatment of industrial wastewater. Laboratory, pilot and some commercial case studies have shown potential and advantages of using ceramic membranes for large-scale municipal wastewater treatment and the provision of safe drinking water. As a result of the many benefits offered by ceramic membranes, their global incorporation into more drinking water treatment plants is anticipated. Promising developments include the installation of ceramic flat-sheet membranes from ItN Nanovation AG in Saudi Arabia to pre-treat seawater in 2013 (Itn nanovation receives significant orders from Saudi Arabia, 2013). In addition, three pilot plants using ceramic membrane hybrid systems with suspended ion exchange and ozone for drinking water treatment plants will be installed in the United Kingdom, Australia and Singapore by PWN Technologies (Pwntechnologies). The incorporation of ceramic membranes in MBRs also clearly offers many advantages including ease of maintenance and long-term reliability. High capital membrane costs along with energy consumption from continuous aeration contribute to a large proportion of the MBR's operating costs, and both deter the growth of ceramic MBRs for large-scale sewage treatment. Therefore, further research and optimization of the immersed MBR is anticipated to widen the use of ceramic membranes. The main overriding limitation to the commercial implementation of ceramic membranes for most large-scale water treatments is their high capital cost, despite their overall longer lifetime and ease of maintenance.

2.5 Ceramic membrane cleaning

Over time, permeate flux of the ceramic membrane will inevitably decrease, which is same as for their polymeric counterparts. To recover as much as the initial flux as possible, many different cleaning methods are available. The choice of the cleaning method(s) depends on the reversibility of the fouling, the foulant(s) characteristics, the membrane material and the membrane element and module design.

2.5.1 Physical cleaning methods

Physical cleaning methods remove reversible foulants from the membrane surface via mechanical forces. Examples of physical cleaning include forward and reverse flushing, back-pulsing/backwashing, use of turbulence promoters, air flushing, rinsing and sponge ball cleaning.

Forward flushing is achieved by using high cross-flow velocities at the feed side to loosen and then remove foulants from the membrane surface. The direction of the flush is often reversed for a few seconds to improve the effectiveness of the cleaning, which is called reverse flushing. Rinsing the membrane can also be used to dislodge and remove fouling layers. One study found that rinsing with water alone for 15 min could recover 90% of the original membrane flux of multi-channel tubular membranes fouled by whey proteins (Cabero, Riera, & Álvarez, 1999).

Backwashing is when a larger pressure is applied on the permeate side, causing the reverse flow of permeate into the feed side, and can help flush membrane pores as well (Laitinen et al., 2001; Mugnier, Howell, & Ruf, 2000). For MF tubular ceramic membranes fouled during treatment of oily wastewater, over 95% recovery of the original flux or prevention of flux decline was achieved by periodic backwashing (Abadi et al., 2011). However, once permeate flux has dropped to 40−50% of the original value, chemical cleaning is required.

Air flushing/sparging can be used during MF/UF to reduce the rate and extent of fouling, or it can be used periodically to clean the membrane surfaces (Cui, Bellara, & Homewood, 1997; Matis et al., 2004; Mercier-Bonin, Lagane, & Fonade, 2000). It can also increase permeate flux when used during filtration because the air bubbles on the feed side can increase turbulence in the stream but increase energy consumption for the entire process. Sponge ball cleaning scrubs foulants from the membrane surfaces and is suitable for use in cleaning large-diameter tubular membranes fouled by high-turbidity feed streams such as industrial wastewater (Psoch & Schiewer, 2006).

Forward flushing, backwashing and air sparging can be combined because backwashing can loosen the fouling cake layer and forward flushing and air sparging can sweep the foulants away.

2.5.2 Chemical cleaning methods

Chemical cleaning methods are required to remove physically irreversible fouling by dissolving foulants without damaging the membrane. A wide range of chemicals can be used to clean the membranes; their choice depends mainly on the type of foulant as well as the membrane material. For example, acids may be used to treat inorganic fouling (Yoon, Kang, & Lee, 1999), and alkalis are commonly used to remove organic fouling (for membranes fouled by organic contaminants in surface water (Zondervan & Roffel, 2007) and whey protein (Bartlett, Bird, & Howell, 1995)). Ozone and oxidants have also been used to improve the removal of organic fouling (Chang et al., 1994). The chemical cleaning cycle normally consists of several steps and factors such as cleaning temperature, chemical concentration, pH, pressure and flow rates and time, all of which can affect the cleaning efficiency (Bartlett et al., 1995; Bird & Bartlett, 2002). The cleaning agent can be introduced into the membrane channels or the membranes can be immersed into cleaning agents.

Often, physical cleaning and chemical cleaning methods are combined for better fouling control and shorter membrane cleaning time. Using mechanical rinsing or backflushing with caustic soda (NaOH) and oxidation (H_2O_2) leads to fast and effective cleaning in which 87% of permeate flux is recovered within 8 min for ceramic membrane fouled during beer filtration (Gan et al., 1999).

2.5.3 Unconventional physical cleaning methods

The use of chemical cleaning methods generates undesired additional waste streams and conventional physical cleaning removes only reversible fouling. Unconventional or developing techniques targeted for efficient and more environmentally friendly means to remove fouling material include the use of ultrasonic, electric or magnetic fields.

Ultrasonic fields can be used to aid in cleaning membranes. Cavitation caused by ultrasound can prevent the membranes from clogging when applied during operation and has the potential to improve permeation flux (Kyllönen et al., 2006). They work by first loosening particles of the cake layer and then transporting them away by acoustic streaming (Lamminen, Walker, & Weavers, 2004). The same research found that frequencies between 70 and 620 kHz could be used without damaging the alumina membranes. However, damage to the membrane has been observed when it is placed within the cavitation region of the system (Chen, Weavers, & Walker, 2006). Furthermore, this may be an expensive method because the cost of energy to implement this may be high and can potentially be used to remove foulants periodically instead.

Electric fields can be used to clean membranes or enhance MF/UF processes because they can provide an additional driving force to the filtration system. Charged solids or species on the membrane can be moved as a result of the electric field applied to the membrane surface, thus reducing the effects of concentration polarization as well (Jagannadh & Muralidhara, 1996). When electric fields are applied to the membrane, fouling that is irreversible and resistant to physical cleaning methods can become physically reversible, especially for membranes that are fouled by proteins. Magnetic fields can also potentially be applied to remove or reduce the extent of inorganic membrane fouling (Baker, Judd, & Parsons, 1997). This is because magnetic fields change the calcium carbonate scale from its calcite form to the less soluble form aragonite, and hence enhance the crystallization of $CaCO_3$, preventing its formation on membrane surfaces (Zaidi et al., 2013).

There is a lot of freedom in choosing the cleaning method for ceramic membranes owing to their high thermal, chemical and mechanical stabilities. Fouling can be removed effectively via a combination of physical and chemical cleaning methods, but the use of chemicals to clean introduces new potentially hazardous wastes that may then need further treatment. Unconventional methods such as using ultrasonic, electric and magnetic fields can potentially be useful in aiding membrane cleaning and reducing the need for chemical cleaning agents. However, the available literature regarding the performance and mechanisms of these methods in realistic situations is limited and does not provide adequate evidences to prove their feasibility in improving membrane lifetime.

2.6 Prospects and challenges

From a technical viewpoint, the outstanding robustness and integrity of ceramic membranes have secured their positions in dealing with wastewater systems where at least an aggressive environment is involved, and contribute to sustainable and strong growth toward wider applications. Technical innovations in promoting separation performance and engineering designs keep driving the development of ceramic membrane products toward an application-oriented pattern. In particular, new membrane fabrication techniques such as the combined phase-inversion and sintering methods are expected to see wider applications in membrane production facilities. They offer a much simpler fabrication cycle and can make highly microstructurally varied membrane morphologies that can be tailored according to the application. In terms of membrane design, the presence of hollow-fibre membranes is expected to grow in the ceramic membrane market, to offer much greater treatment capacities for larger-scale applications. The potential of a wider range of ceramic materials other than the commonly used alumina membranes and membrane substrates is also expected. In terms of applications, there is a trend toward the increasing use of ceramic membranes for larger-scale wastewater treatments, especially in MBRs, because the cost of ceramic membranes is reduced. Anticipated cheaper ceramic membrane prices combined with higher packing densities of hollow-fibre configuration will increase applications in municipalities, and more space-efficient module designs, especially for hollow-fibre membranes, are expected to penetrate the market to meet the higher demands.

The widespread use of ceramic MF/UF membranes in water treatment is limited by many problems. A key challenge is to reduce the capital cost of ceramic membranes, which can be met by reducing the steps in the fabrication process and lowering the sintering temperature. The emergence of cheaper fabrication processes such as the combined phase-inversion and sintering method can potentially reduce the fabrication costs of ceramic membranes. However, further research and development are required to reduce the sintering temperature and maintain a continuously high-quality membrane. The performance of the porous membranes formed by this method needs to be improved so that both good mechanical strength and high porosity can be achieved. Improved fundamental understanding of the formation mechanisms of ceramic membrane microstructures can help improve the reliability and reproducibility of the fabrication process, which is particularly useful when producing membranes from different ceramic materials and when production is scaled up. Furthermore, challenges regarding the up-scaling of the combined phase-inversion and sintering process include developing a continuous fabrication and sintering process. To meet the demands for large-scale treatment capacities, more space-effective module and unit designs would also be required, to cut down the costs of housing material as well as improve productivity. Hollow-fibre membrane elements may offer much higher packing densities but improvements in element and module designs will be required, such as creating smaller-diameter hollow fibres and improving their mechanical strength. In terms of fouling, the mechanism varies from case to case depending on the application. Although a combination of physical and chemical cleaning of ceramic membranes can be easily achieved, this leads to additional waste products that require treatment and disposal; hence, more environmentally friendly approaches to membrane cleaning are desired. This means that challenges arising in this area include better understanding of fouling mechanisms in ceramic membranes, particularly the interactions between ceramic membranes and the different foulants, to ensure that the right choice of cleaning methods is made for reliable long-term operation.

Abbreviations

COD	Carbon oxygen demand
DBP	Disinfectant byproduct
MBR	Membrane bioreactor
MF	Microfiltration
NOM	Natural organic matter
UF	Ultrafiltration

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Advances in water treatment by microfiltration, ultrafiltration, and nanofiltration

3

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3.1 Introduction

In 2012, access to safe drinking water became the first millennium development goal to be met by the international community (Url-1). The original aim set in 2000 was to halve by 2015 the proportion of the population without sustainable access to safe drinking water and basic sanitation (UN, 2010, pp. 58−60). This encouraging achievement should underscore the progress that can be made through the development of often simple and cheap technologies in low-income economies. At the same time, it can be expected that challenges related to water systems will continue to increase, requiring further investment and technological innovation to meet global needs. Access to clean water is a simple human need and an important driver of social and economic development (UN Water, 2006). Predictable and consistent access to clean drinking water is globally seen as a core function of states because it is crucial to a society's public health, economic vitality, and national security (Elimelech & Phillip, 2011).

3.1.1 Global membrane market

The global membrane market for microfiltration (MF) products used in liquid separations was estimated to be $1.6 billion in 2013. It was projected to rise at a compound annual growth rate (CAGR) of 10.0% during the next 5 years, to reach $2.6 billion in 2018 (Url-2).

The U.S. market for ultrafiltration (UF) technologies was worth $882 million in 2009 and reached $932 million at the end of 2010. By 2015, the market is estimated to be valued at $1.2 billion, a CAGR of 5.7% (Url-3).

The global market for nanofiltration (NF) membranes increased from $172.8 million in 2012 to 190.2 million in 2013, at the end of 2014 and 2019, it is estimated to reach $215.6 million and 445.1 million, respectively. CAGR will be 15.6% during 2014−2019 (Url-4).

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3.1.2 Membrane filtration technology for water treatment

Membrane technology has become a significant separation technology over the past 2 decades. Continuing advances in regulatory constraints and aesthetic criteria for consumer water quality have driven the water community to seek new technologies. Membrane technology is one of those new technologies. In this technology, membranes are used as filters in separation processes in various applications. They provide effective alternatives to related technologies such as adsorption, ion exchangers, and sand filters. Major uses of this technology are water filtration (including desalination) and purification (including groundwater and wastewater) as well as industries such as food and beverages and biotechnology (Kurt, Koseoglu, Dizge, Chellam, & Koyuncu, 2012; Ozgun et al., 2012). It also has medical uses such as in dialysis.

3.1.3 Membrane processes

A membrane is defined as a selective barrier between two homogenous phases. In principle, membranes can carry out most of the separation processes and can complement or form an alternative for chemical processes such as distillation, extraction, fractionation, and adsorption. Some advantages of membrane filtration are low energy consumption, the possibility of continuous separation, and simple up-scaling (Baker, 2004).

The membrane process is not suitable for every fluid stream because of the content of feed and product requirements as well as the nature of the membrane process and the membrane designed for that process. There are four developed industrial membrane processes for water treatment. The main difference in these processes is the pore size of the membranes. Membrane processes are:

1. Microfiltration
2. Ultrafiltration
3. Nanofiltration
4. Reverse osmosis (RO)

RO is beyond the scope of this chapter but the other processes will be covered here. The schematic separation spectrum given for membrane processes is shown in Figure 3.1 (Baker, 2004).

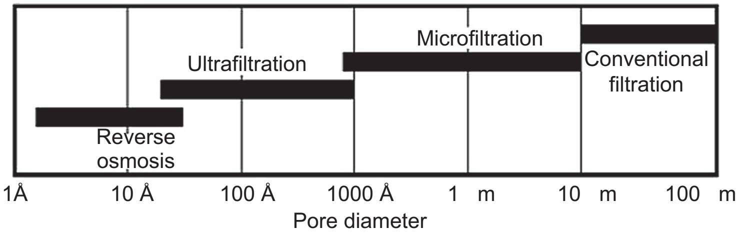

Figure 3.1 Schematic spectrum for membrane processes and conventional filtration. Reprinted from Baker (2004), Overview of membrane science and technology, p. 7.

Membrane processes can be used for various applications. There are various guidelines for selecting the proper membrane process. For example, if particles $>0.2\ \mu m$ are removed, the process becomes MF; if dissolved contaminants can be precipitated or coagulated, the proper process may be MF or UF. In the NF process, it is possible to remove both organic and inorganic ions; however, if monovalent ions exist or total dissolved solids removal of 3000 mg/L is achieved, the RO process is required (AWWA, 2007).

General comparisons between MF, UF, and NF membranes can be found in Table 3.1.

3.2 Water treatment by MF, UF, and NF

3.2.1 Microfiltration process

The MF and UF processes are commonly used for water treatment systems. After a sand filter or cartridge filter, MF can be applied to groundwater and surface waters. In RO systems, generally MF is in the pretreatment section of the treatment plant.

The pore size of MF typically varies from 0.1 to 10 μm. However, the separation mechanism is not simple because particles of sizes are smaller than the pore size flow freely through the pore while the larger particles are rejected.

Volume flow through MF membranes can be described by Darcy's law, where flux J through the membrane is directly proportional to the applied pressure (ΔP):

$$J = A \cdot \Delta P$$

where permeability constant A contains structural factors such as the porosity and pore size distribution (Mulder, 1996).

MF is used in a wide variety of industrial applications where particles of a size $>0.1\ \mu m$ have to be retained from a suspension. The most important applications are still based on dead-end filtration using cartridges. However, for larger-scale applications, dead-end filtration will slowly be replaced by cross-flow filtration. One of the main industrial applications is the sterilization and clarification of all kinds of beverages and pharmaceuticals industries. Other applications are summarized below (Eykamp, 1995; Mir, Micheals, Goel, & Kaiser, 1992; Mulder, 1996):

- Ultrapure water in the semiconductor
- Drinking water treatment
- Clarification of fruit juice, wine, and beer
- Wastewater treatment
- Pretreatment.

3.2.2 Ultrafiltration process

For UF, pore sizes generally range from 0.01 to 0.05 μm (nominally 0.01 μm) or less. UF membranes have the ability to retain larger organic macromolecules;

Table 3.1 Characteristic features of MF and UF membranes

	Microfiltration (MF)	Ultrafiltration (UF)	Nanofiltration (NF)
Operation mode	Cross-flow and dead-end operation	Cross-flow and dead-end operation	Cross-flow operation
Operating pressure	0.1–3 bar (Transmembrane)	0.5–10 bar (Transmembrane)	2–40 bar (Transmembrane)
Separating mechanism	Separation based on particle size	Separation based on based particle size	Separation based on differences in solubility and diffusivity
Molecular separation size	Solids: >0.1 μm Separation of particles	Colloids: 20,000–200,000 Da Solids: >0.5 μm Separation of macromolecules	Dissolved matter: 200–20,000 Da, solids >0.001 μm Separation of low-MW solutes (salt, glucose, lactose, micro-pollutants).
Membrane types	Predominantly symmetric polymer or ceramic membranes	Asymmetric polymer composite or ceramic membrane	Asymmetric polymer or composite membrane
Module types	Spiral-wound, hollow-fiber, and tube modules, plate or cushion modules	Spiral-wound, hollow-fiber, and tube modules, plate or cushion modules	Spiral-wound, tube, and cushion modules
Osmotic pressure negligible	Osmotic pressure negligible	Osmotic pressure negligible	Osmotic pressure high (1–25 bar)
Thickness of separating layer	Symmetric = 10–150 μm Asymmetric = 1 μm	0.1–1.0 μm	0.1–1.0 μm

Source: Adapted from Pinnekamp and Friedrich (2006), volume 2, 2nd edition.

they have been historically characterized by a molecular weight cutoff (MWCO) rather than by a particular pore size (Membrane Filtration Guidance Manual, 2005). Both UF and MF membranes can be considered porous membranes in which rejection is determined mainly by the size and shape of the solutes relative to the pore size in the membrane. In fact, MF and UF involve similar membrane processes with the same separation principle. However, an important difference is that UF membranes have an asymmetric structure with a much denser top layer (smaller pore size and lower surface porosity) and consequently much higher hydrodynamic resistance (Mulder, 1996).

There are two different operation modes for MF and UF systems. Figure 3.2 shows the cross-flow configuration in which the feed water is pumped tangential to the membrane. Clean water passes through the membrane while the water that is rejected is recirculated as concentrate and combined with additional feed water. In dead-end or direct filtration, all of the feed water passes through the membrane. Therefore, recovery is almost 100% and a small fraction is periodically used for backwash in the system (2−15%) (Jacangelo et al., 1997).

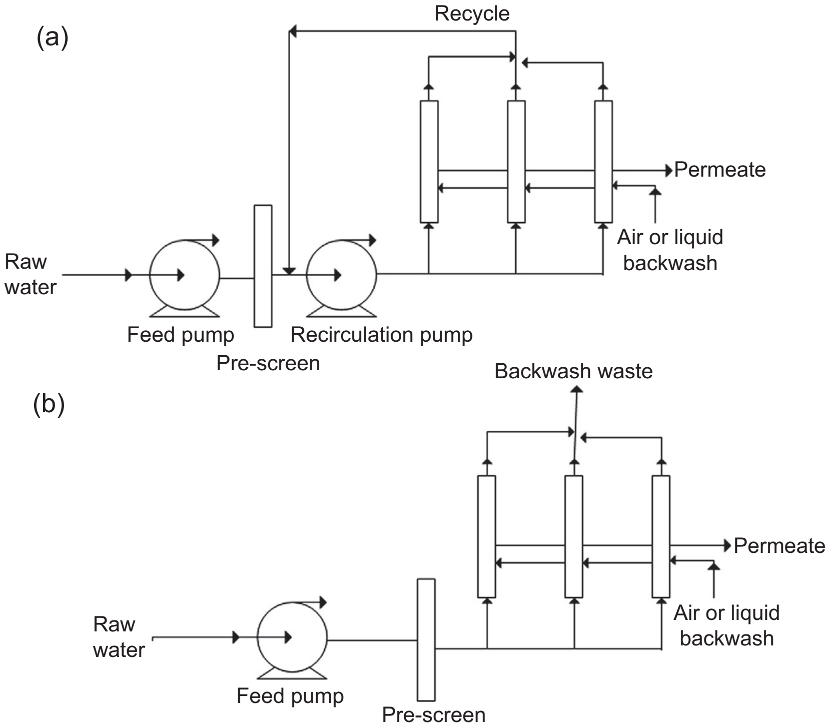

Figure 3.2 (a) Cross-flow configuration MF and (b) dead-end filtration for microfiltration (MF). Reprinted from Jacangelo, Trussell, and Watson (1997), with permission from Elsevier.

Nowadays, most MF/UF plants operate in dead-end filtration mode, because the energy required is lower compared with cross-flow systems, as the high cross-flow velocity required to prevent fouling results in increased head loss and energy consumption.

3.2.3 Nanofiltration process

NF membranes have applications in several areas (Koyuncu & Cakmakci, 2010). The main applications of NF are in water treatment for drinking water production as well as wastewater treatment and also reuse (Debik, Kaykioglu, Coban, & Koyuncu, 2010). NF can be used to treat all kinds of water including groundwater, surface water, and wastewater or as a pretreatment for desalination (Cakmakci, Baspinar, Balaban, Koyuncu, & Kinaci, 2009; Koyuncu, Arikan, Weisner Mark, & Rice, 2008; Uyak, Koyuncu, Oktem, Cakmakci, & Toröz, 2008). The introduction of NF as a pretreatment is considered a breakthrough in the desalination process. NF membranes have ability to remove turbidity, microorganisms, and hardness, as well as a fraction of the dissolved salts. This results in a significantly lower operating pressure and provides a much more energy-efficient process compared with RO (Hilal, Al-Zoubi, Darwish, Mohammad, & Abu Arabi, 2004).

These membranes, which fall into a transition region between pure RO membranes and pure UF membranes, are called loose RO, low-pressure RO, or more commonly, NF membranes. Typically, NF membranes have sodium chloride rejections between 20% and 80% and MWCOs for dissolved organic solutes of 200−1000 Da. These properties are intermediate between RO membranes with a salt rejection of more than 90% and MWCO of less than 50 and UF membranes with a salt rejection of less than 5%. The neutral NF membrane rejects various salts in proportion to their molecular size, so the order of rejection is simply $Na_2SO_4 > CaCl_2 > NaCl$ (Baker, 2004).

Many researchers have studies the softening of groundwater using NF. Scheap et al. (1998) used different NF membranes and their experimental results showed that 60−70% of multivalent ions can be removed by NF membranes. Sombekke, Voorhoeve, and Hiemstrap (1997) compared NF membranes with activated carbon adsorption. According to the results, both processes had good performance. However, NF membranes had some advantages in terms of investment costs (Hilal et al., 2004; Schaep et al., 1998; Sombekke et al., 1997).

NF membranes are used for their ion selectivity. The retention of a dissolved salt is determined by the valence of the anions. Therefore, most salts with monovalent anions (e.g., Cl^-) can pass through the membrane, whereas multivalent anions (e.g., SO^{2-}) are retained. The separation spectrum for NF membranes is given in Figure 3.3.

Some parameters are crucial for the operation of an NF unit: solvent permeability/flux through the membrane, rejection of solutes, and yield/recovery. Similar to other pressure-driven membrane processes, the flux, J, or the permeability (flux per unit of applied pressure) of a membrane is a crucial parameter. Most NF membranes are hydrophilic, except some used for solvent applications.

Rejection in NF is mainly determined by molecular size, hydrophobicity, and charge, but the effects of the molecular shape and dipole moment, for example, might have an important role as well. The pore/void dimensions are statistically distributed

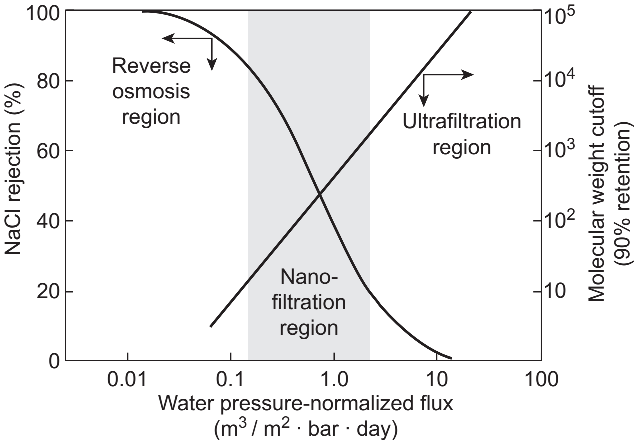

Figure 3.3 Separation permeability spectrum of nanofiltration and other processes. Reprinted from Baker (2004), Membrane transport theory, p. 83.

and can be described by a log-normal distribution (Bowen & Welfoot, 2005). This explains the smooth transition from no rejection to complete rejection in a typical S-shaped curve when molecular size is varied. The MWCO value is often used to indicate the lower limit of molecules that are (almost completely) retained, similar to UF membranes. For NF membranes with MWCO values between 150 and 1000 (but often in the range 150–300), this concept should be used with care: Hydrophobic molecules larger than the MWCO, for example, often have a low rejection. The pH of the solution might change the membrane's surface charge as well as the charge of the solute, so the rejection of this solute can be higher or lower than expected.

Another parameter is the recovery or yield, which is generally used for the design of an industrial application rather than a membrane characteristic. The recovery is the ratio of the permeate stream to the feed stream; values range from 40% to 90%.

3.2.3.1 Applications of NF membranes

NF membranes can reduce the ionic strength of the solution. Moreover, hardness, organics, and particulate contaminants can be removed by NF membranes. Many researchers have used NF to achieve those objectives.

Some researchers have investigated the softening of groundwater using NF systems. All of the results gave good data. Retentions higher than 90% were found for multivalent ions, whereas monovalent ions were about 60–70% (Hilal et al., 2004; Scheap et al., 1998). NF membranes with pellet softening and granular activated carbon for softening water were compared. Although all methods had good results, NF membranes had several advantages from the point of health and lower investment costs. The advantage of NF softening is that a smaller stream of water can be softened because NF membranes remove essentially all hardness cations. In municipal water treatment works, it is not necessary to reduce hardness to very low values, and therefore the use of NF membranes allows for side-stream treatment. This involves sending only a portion of the flow to be softened to the membranes, and permeate is then blended with the bulk flow stream to obtain a target blended value. In contrast, precipitated lime softening cannot reduce hardness to below approximately 50 mg/L $CaCO_3$, and therefore side-stream treatment is generally not practical.

A typical NF membrane system consists of three separate subsystems: pretreatment, membrane processes, and posttreatment.

The primary application of NF membranes is desalting of saline, surface, or groundwater. Surface waters often have unsettled chemistry or composition owing to seasonal changes or after dilution with rain. NF is a reliable option for surface water treatment, although the focus is on removing organics rather than on softening (Hilal et al., 2004; Van der Bruggen & Vandecasteele, 2003).

Disinfection by-products (DBPs) are a significant regulatory concern. NF membranes are increasingly applied to remove DBP precursors such as natural organic matter (NOM), which can react with various disinfectants used in the water treatment process to form potential carcinogens. NOM removal is an important water treatment target for many utilities. NF as a standalone process has been shown in many cases to reduce total organic carbon (TOC) to less than 0.5 mg/L (AWWA, 2007).

NF is also more effective than RO for lime softening, removing naturally occurring color and DBP precursors both consist primarily of organic carbon.

Semipermeable NF membranes are not porous; they have the ability to screen microorganisms and particulate matter in the feed water. This ability has been verified in a number of studies, such as one that demonstrated that NF membranes provide between 4 and 5 log removal of viruses.

3.2.4 Integrated membrane systems

For acquiring regulation standards for drinking water, NF and low pressure RO processes are considered however they are too sensitive to fouling and advanced pretreatment processes like UF and MF are used to increase the productivity of systems. These integrated systems are called as integrated membrane system (IMS) and their purpose is to reduce and control fouling.

3.3 Pretreatment requirements

Pretreatment is typically applied to the feed water before entering the membrane system to minimize membrane fouling. However, in some cases it may be used to address other water quality concerns or treatment objectives. Pretreatment is most often used to remove foulants, optimize recovery and system productivity, and extend membrane life. Pretreatment may also be used to prevent physical damage to the membranes.

Different types of pretreatment can be used in conjunction with any given membrane type. Pilot testing can be used to compare various pretreatment options, optimize pretreatment, and/or demonstrate pretreatment performance (Membrane

Filtration Guidance Manual, 2005). The feed water may contain various concentrations of dissolved matter and suspended solids depending on the source. Suspended solids may include inorganic particles, colloids, and biological debris such as microorganisms and algae. Dissolved matter may consist of highly soluble matters such as chlorides, soluble salts, and sparingly soluble salts, such as carbonate and sulfates.

Depending on the raw water quality, the pretreatment process may follow steps such as:

- Removal of large particles using a coarse strainer
- Water disinfection with chlorine
- Clarification with or without flocculation
- Clarification and hardness reduction using lime treatment
- Media filtration
- Reduction of alkalinity by pH adjustment
- Addition of scale inhibitor
- Reduction of free chlorine using sodium bisulfite or activated carbon filters
- Water sterilization using ultraviolet (UV) radiation
- Final removal of suspended particles using cartridge filters (Membrane Fouling Considerations, 2001).

3.3.1 General pretreatment methods

Membranes can be fouled by organic or inorganic substances. Therefore, pretreatment of the feed stream is required to control colloidal, organic, and biological fouling, as well as scaling. For low-pressure membranes, a number of pretreatment methods are currently used (Abdelrasoul, Doan, & Lohi, 2013).

UF can sufficiently produce disinfected water directly from surface water for different applications. MF can also be used for disinfection, although not all viruses are removed. Because direct membrane filtration is limited by fouling, it leads to a continuous increase in transmembrane pressure during constant flux filtration (Kennedy et al., 2008).

3.3.1.1 Prefiltration

Prefiltration, involving screening or coarse filtration, is a common means of pretreatment for membrane filtration systems that is designed to remove large particles and debris. Prefiltration can be applied to the membrane filtration system as a whole and to each membrane unit separately. The particular pore size associated with the prefiltration process varies depending on the type of membrane filtration system and the feed water quality. Generally, hollow-fiber MF and UF systems are designed specifically to remove suspended solids, large particulate matter that can damage or clog the membranes fibers. Use of these types of filtration system depend on the influent water quality and manufacturer specifications; the pore size/micron rating of a chosen prefiltration process may range from as small as 100 μm to 3000 μm or higher. Because of this, hollow-fiber MF/UF membrane systems that operated in an inside-out mode are more suitable to fiber clogging and thus may require prefiltration (Membrane Filtration Guidance Manual, 2005).

NF and RO are nonporous membranes that cannot be backwashed and are most commonly designed in a spiral-wound configuration for municipal water treatment applications. NF and RO systems must use finer prefiltration to minimize membrane exposure of particulates of any size. At this point, spiral-wound membrane modules are highly sensitive to particulate fouling that can reduce system productivity and reduce membrane life (Membrane Filtration Guidance Manual, 2005). Table 3.2 lists required prefiltration systems for NF/RO according to the silt density index (SDI) value.

In cartridge filtration technology applications, prefiltration is not required in high-quality source water treatment.

Typical prefiltration requirements associated with various types of membrane filtration are presented in Table 3.3.

In some cases, one type of membrane filtration may be used as prefiltration for another. This type of treatment scheme is known as an IMS. Generally, this involves MF/UF use as pretreatment for NF/RO applications that require the removal of particulates and microorganisms as well as some dissolved contaminants such as hardness, iron, and manganese, or DBP precursors. The most significant advantages of an

Table 3.2 **Required prefiltration systems for NF/RO according to SDI value**

Feed water SDI value	Proposed prefiltration	Rating ranges
≤5	Cartridge filters	5–20 μm
>5	MF/UF	0.1–0.01 μm

Source: Membrane Filtration Guidance Manual (2005).

Table 3.3 **Typical membrane system prefiltration requirements**

Membrane system		Prefiltration requirements	
Classification	**Configuration**	**Size (μm)**	**Type(s)**
Membrane cartridge filtration[a]	Cartridge	300–3000	Strainers; bag filters
MF/UF	Hollow-fiber, inside-out	100–300	Strainers; bag filters
	Hollow-fiber, outside-in	300–3000	Strainers; bag filters
NF/RO	Spiral-wound	5–20	Cartridge filters

[a] Prefiltration is not necessarily required for membrane cartridge filtration systems.

Source: Membrane Filtration Guidance Manual (2005).

IMS treatment scheme is that MF/UF filtrate is of consistently high quality with respect to particulate matter and maintains stable operation by reducing the rate of membrane fouling (Membrane Filtration Guidance Manual, 2005).

3.3.1.2 Coagulation and filtration

Coagulation as a pretreatment process can substantially reduce the concentration of biodegradable organic matter found in raw water; thus, it can decrease the potential for fouling and enhance membrane rejection. However, this method can be a problem because coagulant residuals and increased solids loading can reduce membrane fluxes and increase cleaning requirements. Generally, coagulation is required for MF processes in water treatment. Some research suggested that flocs need to reach a certain critical floc size before MF; on the contrary, pores of MF membranes are irreversibly fouled by small particles (Judd & Hillis, 2001).

3.3.1.3 In-line coagulation

In-line coagulation (IC) involves the use of coagulants without the removal of coagulated solids. After that, coagulated water is given to MF or UF. Conventional coagulation and IC are different from each other in terms of initial membrane flux decline. IC has better results than conventional coagulation for initial membrane flux (Escobar, project report).

The IC (without settling)/UF process improves membrane performance and water quality for surface water treatment. Employing coagulation before UF increased permeate quality to the extent that dissolved organic matter removal is controlled by the coagulation step (Guigui, Rouch, Durand-Bourlier, Bonnelye, & Aptel, 2002).

Antelmi, Cabane, Meireles, and Aimar (2001) reported that aggregates produced under sweep floc conditions are more compressible than for charge neutralization conditions, resulting in compaction when the membrane filtration system is pressurized. They thought that cake resistance is lower than the resistance resulting from the unsettled flocs and the noncoagulated organics.

3.3.1.4 Coagulation–sedimentation process

In coagulation and sedimentation processes, a coagulant is applied to form flocs that are settled out by sedimentation. After sedimentation, the supernatant is fed to the membranes. If coagulation and sedimentation are applied before UF, UF membranes are less fouled. Experimental studies showed that membrane life can be increased as a result of coagulation–sedimentation processes (Kruithof, Nederlof, Hoffman, & Taylor, 2004; Minegishi, Jang, Watanabe, Hirata, & Ozawa, 2001).

3.3.1.5 Coagulation–adsorption process

Some research showed that membrane fouling can be minimized by pretreatment. NOM in feed water can be caused trihalomethane (THM) formation in the disinfection step. Although coagulation and MF are a good flowchart for water treatment, THM precursors cannot be removed by the MF process. When pre-adsorption is used for NOM, the removal of THM precursors or NOM is improved (Bérube, Mavinic, Hall, Kenway, & Roett, 2002; Carroll, King, Gray, Bolto, & Booker, 2000; Maartens, Swarta, & Jacobs, 1999).

3.3.1.6 Flocculation and filtration

Colloids can be removed by co-precipitation with Al(III), Fe(III), or Si(IV) hydroxides. The negatively charged colloids are surrounded by the metal cations and thus form a nucleus for their precipitation. The same thing happens when lime is used for softening. When polymer is added for coagulation, the long chains can act as bridges linking colloidal particles and aiding in floc formation.

Flocculation and filtration processes are used to achieve three objectives: eliminating the penetration of colloidal particles into the membrane pores, increasing the critical flux, and modifying the characteristics of the deposits (Abdelrasoul et al., 2013; Kennedy et al., 2008).

3.3.1.7 Ion exchange

Some dissolved salts or divalent cations in feed water can cause scaling on the membrane surface. To overcome this problem, softening of feed water is required. Ion exchange process can be used for this purpose.

The softening approach uses cationic resins to replace the calcium ions (or other divalent cations) with sodium ions, which do not form insoluble salts with carbonate ion. Ion exchange is well-suited for incorporation into an RO system. Depending on the salinity and pH, the RO concentrate may be used as a regenerate solution. Cation exchange resins can be adequately regenerated at lower concentrations than 10% with lower flow rates and longer regeneration cycles (Wilbert, Leitz, Abert, Boegli, & Linton, 1998).

3.3.1.8 Chemical conditioning

Chemical conditioning is used for various pretreatment purposes such as pH adjustment, disinfection, biofouling control, scale inhibition, and coagulation. Some type of chemical conditioning is almost always used with NF/RO systems, most often the addition of an acid or proprietary scale inhibitor recommended by the membrane manufacturer to prevent the precipitation of sparingly soluble salts such as calcium carbonate ($CaCO_3$), barium sulfate ($BaSO_4$), strontium sulfate ($SrSO_4$), or silica species (e.g., SiO_2) (Membrane Filtration Guidance Manual, 2005).

A number of different chemicals can be added to MF or UF systems as a pretreatment related to treatment objectives. However, as with NF and RO membranes, applied pretreatment chemicals must be compatible with the particular membrane material used. An MF/UF system may be able to operate efficiently with the in-line addition of lime or coagulants. On the other hand, presettling in association with these pretreatment processes can enhance membrane flux and increase system efficiency (Membrane Filtration Guidance Manual, 2005).

3.3.2 Pretreatment requirements for membrane bioreactors

The first generation of membrane bioreactors (MBR) in the 1970 and 1980s were built with large-diameter tubular membranes and were primarily used for small-scale industrial effluents containing little waste. Pretreatment to MBR first became an issue when hollow fibers and plate-immersed membranes were introduced in the 1990s for application to municipal wastewater.

Today, municipal MBR systems capacities are up to 50,000 m^3/d and much larger systems are under construction or in the planning stages. Current research goals are to reduce the cost of technology and increase the packing density. These improvements make it significantly important to install adequate pretreatment to protect the membranes at the core of an MBR. Possible negative effects of poor pretreatment on the membranes themselves include.

- Buildup of trash, hair, lint, and other fibrous materials
- Increased risk of sludge accumulation
- Eventually damage to the membrane (Côté, Brink, & Adnan, 2006).

3.4 Advances in membrane materials for water treatment by MF, UF, and NF

Membrane technology is used to improve water quality, treat wastewater, and reuse processes for years. The surge of interest in membrane separations increased owing to two developments: high-flux, defect-free membranes and high-surface-area, economical modules. Membranes range from porous structures to nonporous ones and can be asymmetric or symmetric. They are used for removal from macropollutants up to ions. Because pressure-driven membranes consist of selective barriers, pore characteristics are important. Macrofiltration, UF, and NF processes are classified by their pore structure (pore size, pore size distribution, and porosity). Hydrophilicity, surface charge, roughness, etc., should also be considered. The membrane material has great significance. An appropriate membrane material should resist chemical and thermal attack and should be robust, thin, defect-free, and cheap (Baker, 2004; Fane, Tang, & Wang, 2011).

For membrane materials, polymers are generally preferred because they are inexpensive and easily form pore structures. In addition, metallic, ceramic, and composite materials are used. These materials are now thought of as conventional. Recently, membrane materials have improved. Some novel membrane materials exist, such as nanostructured, reactive, bioinspired membranes (Ng, Mohammad, Leo, & Hilal, 2010; Pendergast & Hoek, 2011).

3.4.1 Conventional membrane materials

Conventional membranes include polymeric, ceramic, and thin-film composite (TFC) membranes in general.

Polymers are by far the most popular membrane material used for membrane fabrication. A good polymer material should resist thermal and chemical attack and have good mechanical strength and the ability to form flat-sheet or hollow-fiber configurations easily. Mostly polymeric membranes are fabricated with the phase inversion technique. Commonly used polymeric membrane materials are cellulose acetate (Chou & Yang, 2005; Saljoughi, Amirilargani, & Mohammadi, 2010), polyvinylidene fluoride (PVDF) (Han, Xu, Yu, Wei, & Cao, 2010; Li, Liu, Xiao, Ma, & Zhao, 2012), polyacrylonitrile (PAN), polypropylene (PP), polyethersulfone (PES) (Chen, Li, Han, Xu, & Yu, 2010; Loh, Wang, Shi, & Fane, 2011; Xu, Lü, Zhen, Ku, & Yi, 2008), and polysulfone (PS) (Ohya, Shiki, & Kawakami, 2009; Rugbani, 2009). Polymeric membranes have varying process uses; they can be applied from MF to RO. Commercial UF/MF membranes can be fabricated from both hydrophilic and hydrophobic polymers. Both polymers have some pros and cons because hydrophilic membranes lower the attachment of bacteria owing to adsorption but they are less robust than hydrophobic polymers. Table 3.4 shows commonly used polymeric materials and their properties.

Cellulose acetate membranes have good permeability and rejection characteristics, are susceptible to hydrolysis, have limited pH resistance and low chlorine tolerance, and are resistant to fouling. On the other hand, PES, PVDF, PS, and PAN can be modified as a blend to improve their limited abilities. They show good permeability, flexibility, and high strength. PP polymer has limited blending capacity and is prone to oxidation (Fane et al., 2011).

Ceramic membranes are better than polymeric membranes because of their narrow pore size distribution, higher porosity, separation characteristics, mechanical and chemical stability, and lower fouling. Typical ceramic membranes are fabricated using the sol-gel process and are asymmetric in structure. Generally, materials used for ceramic membranes are zirconia, silica, alumina, mullite, oxide mixtures, and sintered metals (Harman, Koseoglu, Yigit, Beyhan, & Kitis, 2010; Hofs, Ogier, Vries, Beerendonk, & Cornelissen, 2011; Mohammadi & Maghsoodloorad, 2013; Pendergast & Hoek, 2011). They are well-suited for water treatment because they have higher stabilities. Flux decrease can be easily recovered after fouling because they can resist destructive cleaning conditions, so their lifetime is extended. However, they are expensive in industry and owing to their inexpensiveness, polymeric membranes are preferred.

TFC membranes are asymmetric in structure; therefore, support and selective layers can be independently selected for optimization; they are generally fabricated through interfacial polymerization or coating and then cross-linking. By changing the properties of cross-linking, thin-film structure stability, selectivity, and permeability can be changed. Generally used TFC membranes are polyurea, polyamide, and polyurea-amide (Lau, Ismail, Misdan, & Kassim, 2012; Pendergast & Hoek, 2011). The support part of the membrane can be fabricated from PES, PS, PAN, etc. The film structure is important for TFC membranes. By changing monomers, surfactants, and additives within the film composition, different types of structure can be obtained (Lau et al., 2012). TFC membranes are used to obtain high flux and high selectivity in desalination. Also, these kinds of membranes are used to desalt brackish water and for water reclamation, water softening, and removing dissolved organics.

Table 3.4 Commonly used polymeric materials and their properties

Polymer material	Specifications
Cellulose acetate	Cellulose acetate and its blends are widely used for MF and UF membranes. Cellulose acetate is susceptible to hydrolysis and microbial attacks and has a stable pH between 4 and 6.5.
Polysulfone	Polysulfone is an amorphous polymer. It has excellent chemical and thermal stability. It is mainly used for UF and MF membranes and as a support layer for NF and RO membranes. Polysulfone membranes have a wide range of pore sizes and their modules can be capillary, flat-sheet, and hollow-fiber.
Polyethersulfone	Polyethersulfone membranes have high chemical and thermal stability. They are mainly used for UF and MF. Flat-sheet or hollow-fiber module configurations exist.
Polyacrylonitrile	Polyacrylonitrile possesses superior resistance to hydrolysis and oxidation. It is mainly used to prepare UF membranes and porous supports of composite membranes
Polyamide	Polyamide has good thermal and mechanical stability. It is resistant to organic solvent attacks. However, it is susceptible to chlorine attacks. It is used as a thin layer for RO and NF.
Polyimide	Polyamides exhibit excellent thermal and chemical stability because of their high glass transition temperature. They are used to make NF membranes.
Polycarbonate	Polycarbonate is a transparent thermoplastic with high-performance properties. It has good mechanical strength and can be used to make UF and MF membranes by the phase inversion process.
Polyvinylidene fluoride	Polyvinylidene fluoride is semicrystalline with a low glass transition temperature. It is resistant to chemical and thermal attacks as well as to most inorganic and organic solvents. It can tolerate a wide range of pH.

Source: Adapted from Fane et al. (2011) and Gupta (2013).

3.4.2 Novel membrane materials

Novel membrane materials can be defined as nanotechnology based membranes. These materials can be zeolite-coated ceramic membranes; reactive/catalytic membranes; nanocomposite membranes, which can be either mixed matrix or TFC; and biologically inspired membranes that are aquaporin, vertically aligned carbon nanotube, or block copolymer membranes (Pendergast & Hoek, 2011).

Zeolites are naturally occurring alumina silicate minerals that have high uniformity and nanometer-scale crystallinity. People prefer zeolite-coated ceramic membranes because by using them, one can obtain permeability in the range of UF membranes and also selectivity in the range of NF or higher. Typical zeolite membranes are fabricated by hydrothermal, layer-by-layer crystallization, etc., synthesis methods with amorphous silicate, aluminosilicate, which is inert and has good thermal and chemical stability. Zeolite crystals are tetrahedral frameworks that consist of cross-linked (Si/Al) O_4 (Figure 3.4) (Georgiev, Bogdanov, Angelova, Markovska, & Hristov, 2009). Water permeability and ion selectivity are primarily affected by the ore and framework density of zeolite particles. On the other hand, the Si:Al ratio is the most important factor for obtaining chemical stability and hydrophilic properties. They can be applied to both polymers and ceramic membranes (Pendergast & Hoek, 2011). Dahe, Teotia, and Bellare (2012) fabricated nanozeolitepolysulfone composite membranes for UF purposes. They found that the addition of nanozeolite increased water permeability up to 22 L/m^2 h bar and also increased the MWCO value from 9500 to 54,000 Da.

Other novel membranes are reactive catalytic ones. Reactive catalytic membranes activate semiconductor-based membranes by sunlight or UV to degrade organic contaminants. Semiconductors are characterized by a filled valence band and an empty conduction band. When photon energy (hν) exceeds band gap energy, an electron leaps from the valence band to the conduction band (Figure 3.5). This excited state of bands can recombine or dissipate input energy as heat and can get trapped in metastable surface states or react with electro-donors and acceptors that are adsorbed on the surface of semiconductors or within the electrical double layer of charged particles. If there is a surface defect, this defect can trap an electron or hole so that the band cannot recombine; subsequently, a redox reaction may occur. Valence bands are good oxidants, whereas conduction bands are good reductants. For interactions in bulk semiconductors, an electron or hole is available;

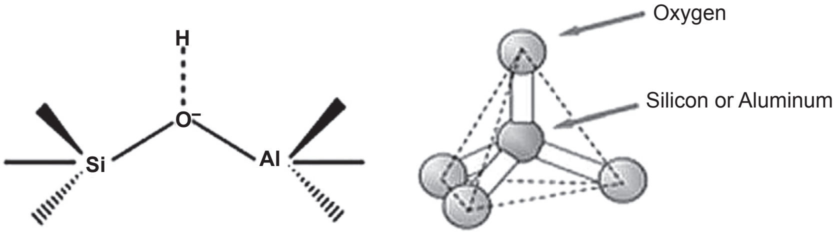

Figure 3.4 (Left) Chemical structure of zeolite. (Right) Building unit of a zeolite structure. Reprinted from Georgiev, Bogdanov, Angelova, Markovska, and Hristov (2009).

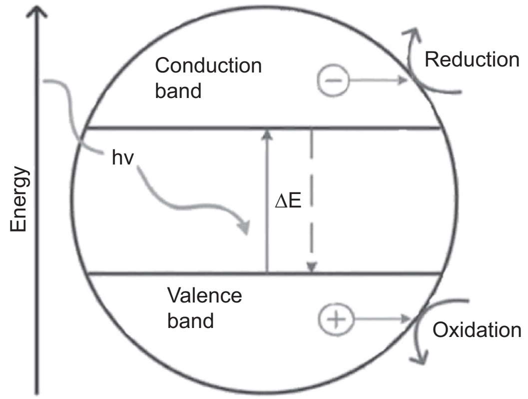

Figure 3.5 Schematic of photocatalysis.
Reprinted from Pendergast and Hoek (2011), with permission from Royal Society of Chemistry.

nanomaterials allow highly efficient interactions owing to their surfaces. Organic photo-degradation requires oxidizing and reducing species. This degradation could be by indirect or direct oxidation. With semiconductors contaminants such as alkanes, phenols, polychlorinated biphenyls, alkenes, alkanes, surfactants, and pesticides as well as heavy metals such as chromium(VI) can be removed (Hoffmann, Martin, Choi, & Bahnemannt, 1995).

Titanium, zinc oxide, and ferric oxide are the most commonly used semi-conductor-based membranes (Chong, Jin, Chow, & Saint, 2010). The performance of this kind of membrane for degrading contaminants and inactivating complex, dense cell wall structures is limited. Also, these types of membranes have a high cost and low packing density (Pendergast & Hoek, 2011). Crock, Rogensues, Shan, and Tarabara (2013) fabricated exfoliated graphite nano-platelets decorated with Au nanoparticles (Figure 3.6). The resulting membrane was catalytic with UF properties. When nano-platelets and the amount of Au were changed, different catalytic activities were obtained. Ma, Zhang, Quan, Fan, and Zhao (2010) fabricated photocatalytic MF membranes with Ag-TiO_2/hydroxyapatite/Al_2O_3 to treat surface water. According to their results, humic acid removal synergistically affected filtration and photocatalysis. The antifouling ability of the membrane comes mainly from photocatalytic activity. Zhu et al. (2011) fabricated MF ceramic membranes combined with titanium oxide and alumina with ozonation for water treatment. They obtained a fluxes of 79 L/m^2 h and 90 L/m^2 h with alumina and titanium oxide, respectively.

Nanocomposite membranes are advantageous because of their low cost, easy fabrication, and high mechanical stability and because they show both polymeric and inorganic material properties. Typically used nanoparticles are silver-, magnesium-, iron-, aluminum-, silica-, zirconium-, and titanium-based as well as carbon nanotubes and graphenes. Nanoparticles can be formed by sol-gel processes, ion sputtering, spray pyrolysis, pulsed laser ablation, laser pyrolysis, mechanical alloying/milling, electrodeposition, and so forth (Buonomenna, 2013; Goh, Ismail, & Ng, 2013; Mishra & Ramaprabhu, 2011; Ng et al., 2010; Pendergast & Hoek, 2011).

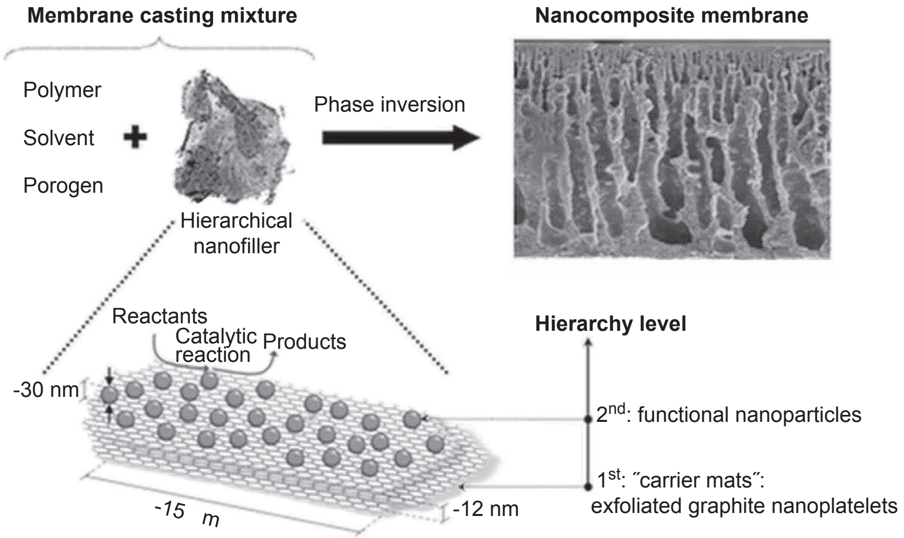

Figure 3.6 Catalytic nanocomposite membrane fabricated with exfoliated graphite nanoplatelets and Au nanoparticles.
Reprinted from Crock et al. (2013), with permission from Elsevier.

Many applications exist for these kinds of membranes in water treatment applications. Nanoparticles used within these types of membranes enhanced membrane selectivity and pore connectivity, inhibit macro void formation, and increase surface to volume ratios. Attention is given to nanoparticles because of their ability to disinfect, adsorb, and degrade organics (Akar, Asar, Dizge, & Koyuncu, 2013; Koseoglu, Kose, Altinbas, & Koyuncu, 2013). In this manner, for example, silver nanoparticles can be used to decrease fouling and increase antibacterial properties. Razmjou, Resosudarmo, Holmes, and Li (2012) studied the effects of TiO_2 nanoparticles on PES hollow fiber (HF) membranes. They used both mechanically modified and chemically and mechanically modified TiO_2. Higher thermal resistance, permeability, hydrophilicity, porosity, and pore size and lower elasticity and tensile strength were found for chemically and mechanically modified TiO_2. Han et al. (2010) spun hollow-fiber membranes by adding aluminum, silica, and titanium oxide nanoparticles at the same dope solution with different concentrations. They observed high flux values and high tensile strength values. Bovine serum albumin (BSA) rejection changed discordantly. Morphology changed from a macroporous to an asymmetric structure. Denser top layers were obtained and the most obvious effect on membrane morphology was on the inner surface. Liang, Xiao, Mo, and Huang (2012) fabricated a novel ZnO nanoparticle-blended PVDF membrane for anti-irreversible fouling. The addition of ZnO nanoparticle increased the hydrophilicity of the membranes and 100% water flux recovery was observed. Permeability values were doubled compared with pristine membranes. In addition, they found that adding ZnO increased the mechanical stability of the membranes. Sengur (2013) fabricated PES hollow-fiber membranes with UF properties with both hydroxylated and carboxylated multi-walled carbon nanotube (MWCNT). The effects of different MWCNTs were different. Fabricated carboxylated MWCNT membranes had antifouling ratios and better water recovery ratios whereas hydroxylated MWCNT membranes had higher permeabilities. Turken (2013) fabricated PES/Ag-nanocomposite UF hollow-fiber membranes. According to their results, the membranes showed improved antibacterial properties, antifouling, and mechanical stability.

Thin-film nanocomposite (TFN) membranes are fabricated through interfacial polymerization by incorporating nanomaterials into the active layer of TFC membranes via doping into casting solutions or by surface modification; their advantages are enhanced separation, reduced fouling, antimicrobial activity, and some other novel properties. For TFN membranes, the particles most used are zeolites, carbon nanotubes, TiO_2, silica, and silver (Buonomenna, 2013; Kim, Hwang, El-Din, & Liu, 2012; Pendergast & Hoek, 2011; Qu, Alvarez, & Li, 2013). Tiraferri, Vecitis, and Elimelech (2011) used covalently bonded single-walled carbon nanotubes (SWCNT) to a TFC membrane. With that method, they used a tiny amount of nanomaterials. The resulting membrane had improved antibacterial properties and potentially decreased fouling. In the literature, TFN membranes are generally used for RO, so there is little literature containing NF, UF, or MF applications.

On the other hand, biologically inspired membranes offer huge potential and improved membrane properties. However, they are far from commercialization because there are some difficulties in scaling. Aquaporin-based membranes, one of the biologically inspired membranes, are highly productive and selective but not cost-effective. Aquaporins are protein channels that have the ability to control water flux within membranes. Their ability to transport to water is higher than any kind of commercial RO membrane. Their water permeability is in the order of glucose, glycerol, salt, and urea (Pendergast & Hoek, 2011; Qu et al., 2013; Tang, Zhao, Wang, Hélix-Nielsen, & Fane, 2013; Zhong, Chung, Jeyaseelan, & Armugam, 2012). Generally, they are applied in desalination and water reuse. Table 3.5 shows studies from the literature.

Another kind of biologically inspired membrane is vertically aligned carbon nanotubes (CNTs) (Figure 3.7). Water transport within CNTs is as high as aquaporins. Selectivity of the vertically aligned CNT membranes is described in Corry (2008). CNT—based membranes also have excellent mechanical properties. Aligned CNTs are generally fabricated by chemical vapor deposition (CVD) such as microwave plasma-enhanced CVD, catalytic CVD, spray pyrolysis, and self-assembly (Pendergast & Hoek, 2011). Vertically aligned CNT membranes can be used to remove microbial contaminants from drinking water. They are superior to conventional membranes because they can be cleaned by ultrasonication or autoclaving, whereas conventional membranes should be disposed of at the end of their limited life, which is affected by fouling (Pendergast & Hoek, 2011).

The last type is block copolymer membranes. These are macromolecules that have the ability to self-assemble into highly ordered structures when added into the proper solvent. Their densely packed cylindrical pores are ideal for water separation. In the literature there are many studies using block copolymers to fabricate UF membranes. Wandera, Himstedt, Marroquin, Wickramasingh, and

Table 3.5 **Examples of biomimetic membranes designed for water reuse and desalination. Performance data are presented as water permeability (WP) (l/m^2 h bar), NaCl rejection (R_{NaCl}) (%), membrane area (A) (cm^2), and maximal external pressure applied (P_{max}) (bar) when operated in RO. CA: cellulose acetate, PC: polycarbonate**

Approach	WP (l/m^2 h bar)	R_{NaCl} (%)	Area (cm^2)	P_{max} (bar)	Upscaling issues	Remarks
Charged lipid mixture vesicles depositions onto NF membranes	0.83	n.d.[a]	3.5	10	Difficult to produce large defect-free membranes	No aquaporin included
Vesicle fusion facilitated by hydraulic pressure on hydrophilic NF membranes coated with positively charged lipids	3.6 ± 0.2	35 ± 8	12.6	1	Difficult to produce large defect-free membranes	Low R_{NaCl}. Only suitable for NF
Membranes across multiple micron-scale apertures as freestanding lipid or polymer membranes	n.d.[a]	n.d.[a]	4	n.d.[a]	Nanofabrication required. Low robustness	WP/R_{NaCl} not tested. Not suitable for RO
Membranes across multiple micron-scale apertures and stabilized by hydrogel encapsulation	12–40	n.d.[a]	3.5	2	Nanofabrication required. High robustness	Characterization with gramicidin channels. No aquaporin included

Aquaporin containing polymersomes on methacrylate functionalized CA membranes	34.2 ± 6.9	32.9 ± 9.1	0.07	5	Medium robustness	Small area. High WP but low R_{NaCl}. Only suitable for NF
Detergent-stabilized His-tagged aquaporin added to monolayers with nickel-chelating lipids	n.d.[a]	n.d.[a]	n.d.[a]	n.d.[a]	Complex fabrication. Low robustness	WP/R_{NaCl} not tested. May be not suitable for desalination
Proteopolymersome deposition onto gold-functionalized PC track-etched substrates	n.d.[a]	n.d.[a]	0.096	n.d.[a]	Complex fabrication. Low robustness	Small area. Relatively high WP in FO. No RO data
Interfacial polymerization method with embedded proteoliposomes	4 ± 0.4	96.3 ± 1.3	>200	14	Simple fabrication. High robustness	Combined high WP and R_{NaCl}. Suitable for RO

[a] n.d., not defined.

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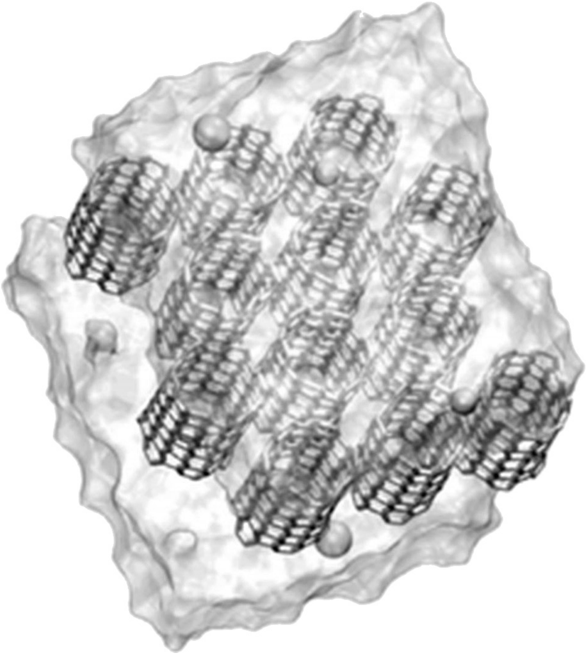

Figure 3.7 Carbon nanotube membrane simulation.
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Husson (2012) modified low-MWCO cellulose UF membranes with block copolymer nanolayers. They used poly(*N*-isopropylacrylamide)-block-poly([polyethylene glycol] methacrylate) (PNIPAAm-b-PPEGMA) nanolayers and investigated the role of polymer on the performance of the membrane. According to their results, the nanolayer structure affected fouling. Optimization resulted in high, stable flux. The coating chemistry and structural properties of coating affected antifouling properties. Fabricated Ps-b-PMMA films showed unique porous morphology (Figure 3.8) (Kim, Yang, Lee, & Kim, 2010). Nanopores were observed only at the bottom and top membrane surfaces. The structure had high resistance to all organic solvents and showed great dimensional stability after filtration tests. In another study (Zhao, Su, Chen, Peng, & Jiang, 2011), the block-like copolymer poly(butyl methacrylate)-b-poly(methacrylic acid)-b-poly(hexafluorobutyl methacrylate) (PBMA-b-PMAA-b-PHFBM) material, which has hydrophobic, hydrophilic, and fluorine-containing segments, was used. Copolymer was added into the PES membrane matrix. According to the results, the membrane showed excellent pH-responsive permeability and desirable fouling release properties. To increase the hydrophilicity of PS membranes, Roux, Jacobs, van Reenen, Morkel, and Meincken (2006) used branched PEO-block-PS copolymers and incorporated them into the membrane matrix. Flux and rejection data showed that the membrane morphology was changed after it was modified with copolymer. Figure 3.9 compares conventional and novel-based membranes.

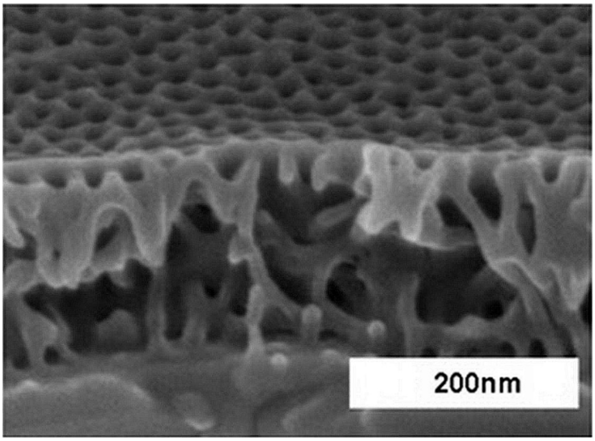

Figure 3.8 Scanning electron microscopy image for block copolymer film with mixed orientation.
Reprinted from Kim, Yang, Lee, and Kim (2010), with permission from Elsevier.

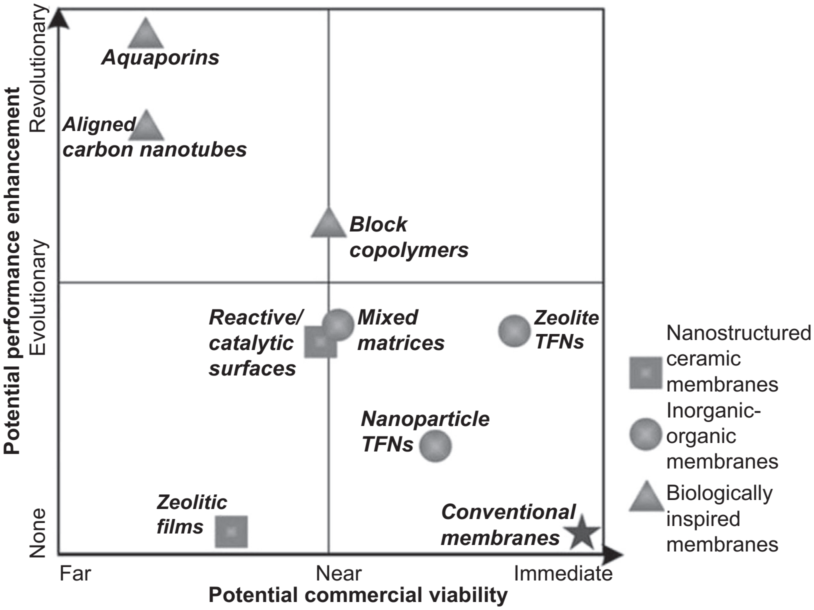

Figure 3.9 Conventional and novel membrane current status.
Reprinted from Pendergast and Hoek (2011), with permission from Royal Society of Chemistry.

3.5 Advances in membrane modules and system configurations for water treatment by MF, UF, and NF

Industrial membrane plants require a large amount of membrane area to perform separation on a useful scale. If membranes are to be used on an industrial scale, efficient packaging methods are required. These packages are called membrane modules. Between 1960 and the 1970s commercial membrane processes had a significant breakthrough with the development of low-cost membrane modules. The earliest designs, which were tubular, plate and frame, hollow-fiber, and spiral wound, were mainly built on basic filtration technology including flat sheet membranes in a type of filter press. Because of this, these systems are called plate-and-frame modules. At the same time 1- to 3-cm-diameter tubes were developed. These designs are still used, but because of their relatively high cost in most applications, two other designs have been largely displaced: the spiral wound and hollow fiber modules. Conventional membrane modules can be seen in Table 3.6.

3.5.1 Recent advances in membrane modules

Liu, Xu, Zhao, and Yang (2010) carried out research using a helical membrane module unit. A terylene filter cloth without modification and with a pore size around 22 nm had been used in the filtration test as a filter membrane. Two pieces of membrane sheets (6 × 18 × 2 cm; total area, 0.022 m^2) were supported on a plastic spacer. The fishbone or broom-like structured spacer is shown in the middle in Figure 3.10(a-1) and (a-3), resembling a deoxyribonucleic acid helix (Figures 3.10(a-4)). The cover membrane forms an empty sleeve outside the spacer once it is sealed around the edge (Figure 3.11). It has a tubing outlet at one end of the membrane to conduct the permeate water. The plastic spacer is flexible for helical rotation and its final total rotation angle, together with the membrane sleeve, can be kept at a certain value by fixing the top and bottom edges. The top end of the membrane can be fixed at a final angle to the bottom end while maintaining a certain helical rotation. Several short pieces of helical membrane or extensions of membrane length can form modules with more helixes (Figure 3.10(a-1)).

Table 3.6 Membrane and module forms

	Tubular	Flat
Conventional membrane modules	Tube module Capillary module Hollow-fiber module	Spiral-wound module Cushion module Plate module Disc-tube module

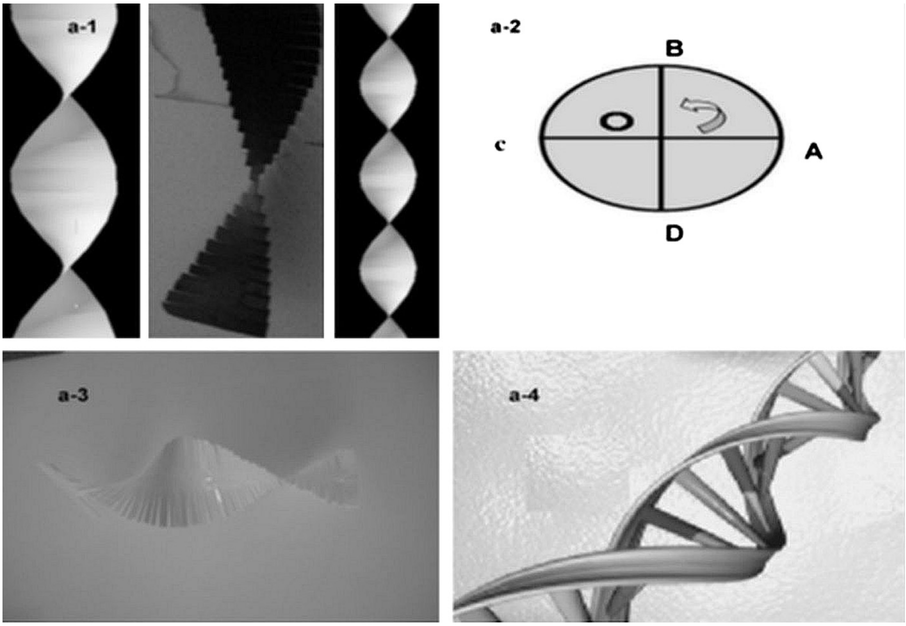

Figure 3.10 Helical membrane module, support spacer, and final helical angles. Reprinted from Liu et al. (2010), with permission from Elsevier.

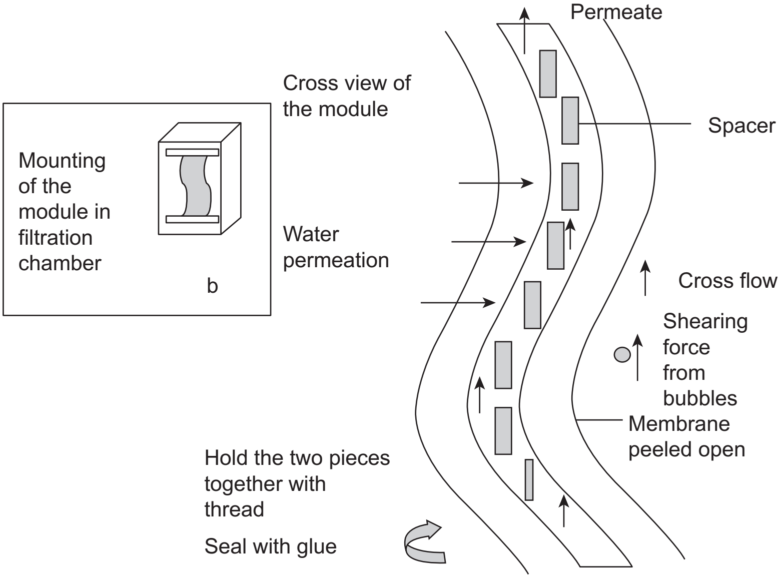

Figure 3.11 Cross-view of helical membrane and its mount in a filtration chamber. Reprinted from Liu et al. (2010), with permission from Elsevier.

The long and rectangular new membrane modules are narrower, thinner, and lighter than conventional wide, flat-sheet membrane modules. The helical membrane may enhance vortex mixing just like a static stirrer in liquid phase. Liu et al. (2010) showed that the higher the cross-flow, the better the mixing.

3.5.1.1 Rotating disk module systems

Rotating disk module systems, including a larger area and capacity module, led to the introduction of multi-disk systems mounted on a single shaft and rotating between fixed circular membranes. This module is used for biotechnological applications and has an area of 2 m^2. Dyno, manufactured by Bokela GmbH (Karlsruhe, Germany), has a similar system design. This system has a diameter of 13.7−85 cm and a total membrane area from 0.13 to 12 m^2. This system is available with both polymeric and ceramic membranes (Figure 3.12).

Another multi-disk system is produced by Spintek (Huntington, CA) with rotating membranes of 2.3 m^2. Initially it was available with organic membranes; currently, it is produced with mineral membranes (Figure 3.13).

In Germany, multi-shaft systems with overlapping rotating membranes per module area are common. For example, the multi-shaft disk (MSD) system has a diameter of 31.2 cm in several ceramic membrane units. All rotating disks turn at the same time; the Hitachi model (Japan) is available at up to a 150- and 100-m^2 membrane area at parallel axes at the same time (Figure 3.14).

3.5.1.2 Vibrating module systems

Vibrating module systems use an original concept called Vibratory Shear Enhanced Processing System (VSEP) including a set of circular organic membranes separated by gaskets and permeate collectors (Figure 3.15). The most important parameter is the maximum azimuthal displacement of the membrane rim (Jaffrin, 2008).

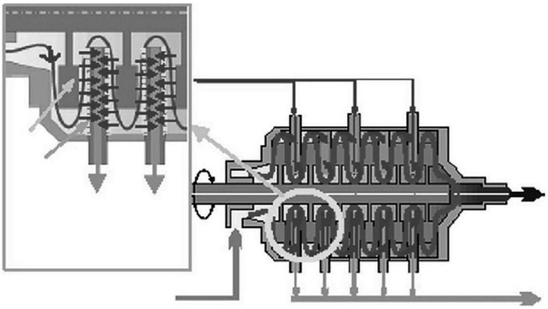

Figure 3.12 Dyno rotating disk module (Bokela, Germany).
Reprinted from Jaffrin (2008), with permission from Elsevier.

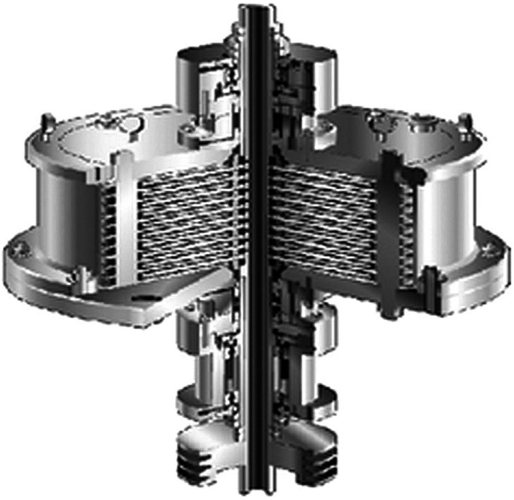

Figure 3.13 Spintek module.
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Figure 3.14 Industrial multi-disk shaft module with eight parallel shafts and 31-cm ceramic disks.
Courtesy of Westfalia Separator. Reprinted from Jaffrin (2008), with permission from Elsevier.

Figure 3.15 Industrial VSEP vibrating modules.
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3.6 Applications of water treatment by MF, UF, and NF

Typically there are four main water sources for drinking and potable water supply: surface water, groundwater, seawater, and rainwater. Different membrane technologies are applicable to these sources because of their chemical and physical characteristics. Figure 3.16 shows a schematic describing water sources and possible membrane steps to safe water. For instance, surface water can be converted into safe water using an MF, UF, MF plus UF plus an auxiliary, or NF membrane. Groundwater has generally high hardness and metal concentrations so MF and UF will not be efficient alone. They need an auxiliary system.

3.6.1 Applications for surface water treatment

Macrofiltration, UF, and NF membranes can be used in surface water treatment alone or with an auxiliary system. They are becoming popular in surface water treatment because of their high efficiency. Macrofiltration and UF process are effective in removing turbidity, particles, bacteria, and cysts. If a high organic content of water exists, MF and UF may not be used to obtain high water quality. On the other hand, the NF process is able to treat many water contaminants such as DBPs and synthetic organic compounds (Glucina, Alvarez, & Laîné, 2000). Table 3.7 lists studies concerning the use of the MF, UF, and NF membrane process to treat surface water.

3.6.2 Membranes for groundwater treatment

Owing to limited rainfall, in some places surface water is scarce. In these types of places, groundwater sources become important. Although they are variable in nature,

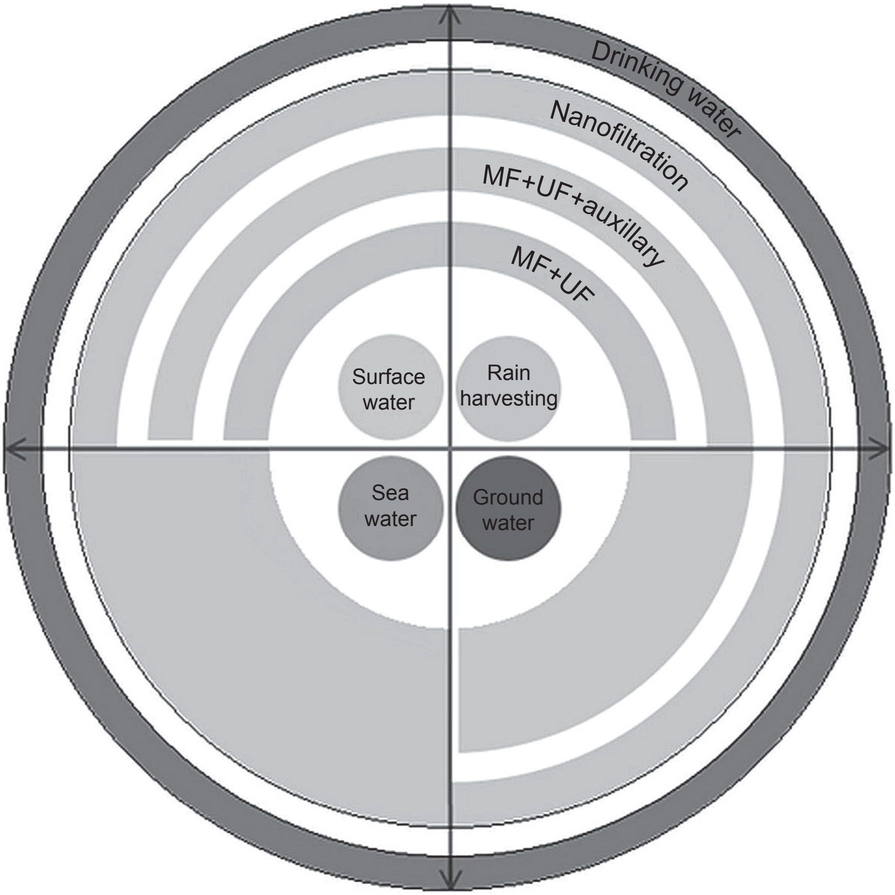

Figure 3.16 Water sources and applicable membrane steps to achieve potable water.

groundwater sources generally contain calcium, magnesium, carbonate/alkalinity, and silica. If these ion concentrations reach high concentrations that exceed mineral solubility limits, precipitation starts. This precipitation forms deposits at the end, and scales. Scale formation can be problematic. To solve this problem, membrane technologies are effective (Kinsela, Jones, Collins, & Waite, 2012). Table 3.8 summarizes studies applying MF, UF, and NF to groundwater treatment.

3.6.3 Nanofiltration for seawater desalination

MWCO values of NF membranes are between 200 and 2000 Da. They reject 98% of divalent ions and 30−85% of monovalent ions. NF membranes have higher permeability than RO membranes, which gives them an advantage in energy consumption. A flow diagram of dual-step NF is given in Figure 3.17. There is disagreement

Table 3.7 **Studies related to microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF) for the treatment of surface waters**

Process used and module type	Approach	Remarks	References
Integrated membrane system was used (UF + RO), spiral-wound and hollow-fiber configuration	Low-salinity water was used to evaluate efficiency of IMS.	UF process found to be effective in controlling RO fouling. UF reduced SDI.	Glucina et al. (2000)
MF and UF, tubular and ceramic membranes	Membrane permeability and fouling properties of ceramic and polymeric membranes were compared.	Increase TMP rate owing to fouling inversely follows the measured pore size. Higher degree of fouling on the polymeric membranes results from the lower volume/area ratio. Aggressive methods are needed to clean non-purgeable organic carbon.	Hofs et al. (2011)
NF, capillary, and flat-sheet membranes	New capillary NF membrane was compared with flat-sheet membranes to find fouling properties and pretreatment requirements.	In capillary membranes, flux decline can be increased by forward flushing and air flushing. Water permeability of capillary membranes was 3–15 times higher than flat-sheet membranes.	Van der Bruggen, Hawrijk, Cornelissen, and Vandecasteele (2003)
UF-MF Capillary membranes	Application of UF polymeric membranes in the disinfection and treatment of surface waters was investigated.	Membranes were able to remove iron, turbidity, bacteria, *Escherichia coli*, organic compounds, and mesophilic bacteria.	Konieczny (1998)
UF, Carbosep M8 tubular inorganic membrane	Different kinds of surface waters were tested for disinfection by UF membranes. Different hardnesses and organic loads were tested.	UF was a reliable method for disinfecting surface waters.	Di Zio, Prisciandaro, and Barba (2005)

PVDF MF, PVDF, and PES UF	Effects of different magnetic ion exchanges (MIEXs) pretreatment on low-pressure membrane filtration were investigated by using different feed water qualities, membrane properties, and MIEX doses.	Decrease in total and irreversible fouling was observed for PVDF MF and PES UF after MIEX treatment. Fouling of PVDF UF membrane was not decreased after MIEX treatment, which showed the importance of membrane properties. MIEX treatment was effective.	Huang, Cho, Schwab, and Jacangelo (2012)
UF, rotating membrane disk module	Irreversible fouling caused by constituents in surface water investigated.	Evolution of irreversible fouling was due to polysaccharide-like organic matter; presumably iron and manganese contributed to some extent.	Kimura, Hane, Watanabe, Amy, and Ohkuma (2004)
MF/UF	Irreversible membrane fouling in an MF membrane was investigated. Feed water containing humic acid or organic matter was coagulated with polyaluminum chloride.	Coagulation conditions (dosage) were effective for irreversible fouling. Acidic conditions enhanced the treated water quality and increased irreversible fouling.	Kimura, Maeda, Yamamura, and Watanabe (2008)
NF, UF, MF; spiral wound	Efficiency of NF modules for the rejection of DBPs from low-turbidity surface waters was investigated.	Dissolved organic carbon (DOC), trihalomethane formation potential (THMFP), haloacetic acid formation potential (HAAFP), and chloral hydrate formation potential (CHFP) rejections were higher than 86% in NF. MF was moderately effective in particle removals. UF did not show significant changes in operational conditions.	Siddiqui, Amy, Ryan, and Odem (2000)

Continued

Table 3.7 Continued

Process used and module type	Approach	Remarks	References
NF, flat-sheet	Study aimed to treat surface water contaminated with pesticides.	NF membranes were able to reduce hardness, COD, and TOC and remove microbial content completely.	Sarkar et al. (2007)
UF, hollow-fiber	Performance of UF membranes was investigated by using raw water from the Bin Xian Reservoir.	Before UF, use of coagulation increased permeate flux and retarded membrane flux decline. UF was able to remove turbidity, coliform bacteria, iron, manganese, and aluminum.	Xia, Nan, Liu, and Li (2004)
UF, hollow-fiber	PVDF UF membranes were tested for the treatment of surface waters.	Permeate quality was stable regardless of different surface waters. TMP should be below 1 bar to decrease irreversible fouling.	Guo, Zhang, Fang, and Su (2009)

Table 3.8 **Microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF) groundwater applications**

Process used and module type	Approach	Remarks	References
Electro-ultrafiltration (EUF)	Effectiveness of EUF system was determined for arsenic removal.	Arsenic removal increased from 1% to 14% to over 79%.	Hsieh, Weng, Huang, and Li (2008)
NF piperazine membrane	Different hardness and salinity values were used.	High hardness retention coefficients (70–76%), satisfactory permeate fluxes, and high mineral fouling resistance but low salinity removal were obtained.	Galanakis, Fountoulis, and Gekas (2012)
NF polyamide membrane	Ozonation, slow sand filtration, and NF processes were combined to remove dissolved organic matter (DOM) from groundwater.	NF was able to remove aromatic, humic acid, and fulvic acid-like substances, and DOM.	Linlin, Xuan, and Meng (2011)
NF flat-sheet membrane module	For fluoride removal from contaminated groundwater, NF module performance was modeled and simulated.	NF membrane was able to remove fluoride and drop the level of pH of groundwater to the desired level.	Chakrabortty, Roy, and Pal (2013)

concerning whether it is possible to desalinate seawater by using dual-step NF at a lower cost than RO. In the dual-step NF process, seawater is fed to the first NF membrane, and then the collected permeate is fed to the second NF membrane. Finally, potable water is obtained. Concentrates are pumped into the NF feed tank optionally. The energy requirement for seawater desalination using dual-stage NF is proportional to the salinity of the permeate. More energy is needed for lower permeate salinity (AlTaee & Sharif, 2011).

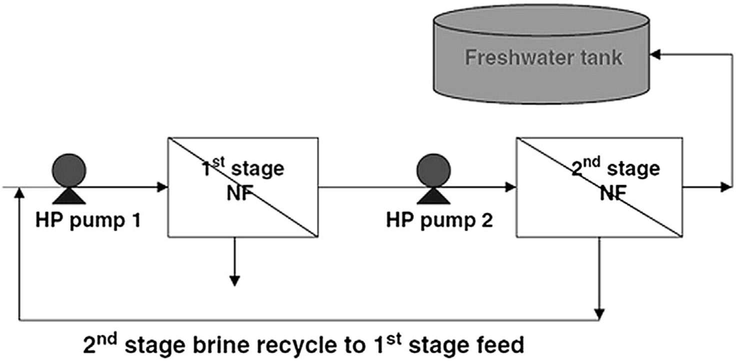

Figure 3.17 Dual-stage desalination process.
Reprinted from AlTaee and Sharif (2011), with permission from Elsevier.

3.6.4 Membranes for harvesting rainwater

Harvested rainwater is preferred for irrigation purposes. On the other hand, there is growing interest in harvesting rainwater for drinking and other indoor uses. Rainwater can be filtered by MF, UF, and NF according to the desired quality. MF treatment is suitable for gray water production. UF and NF treatment can be used for the drinking water supply. Home size water treatment units can be used in drinking water production. UF provides a good option for disinfection to remove viruses and bacteria. A number of companies supply UV, granulated activated carbon, and membrane filtration systems for rainwater purification.

3.6.5 Applications of membranes for specific contaminant removal

Arsenic (As) exists in natural water sources in both organic and inorganic forms. Long-term exposure to arsenic causes cancer. The World Health Organization limits the presence of As in water to less than 0.01 mg/L. Removal of As with membranes is successful and is popular nowadays. There is both pilot and lab-scale research in the literature. Nguyen, Vigneswaran, Ngo, Shon, and Kandasamy (2009) used both MF and NF. NF membranes are more efficient for the removal of As than MF membranes, which have bigger pores. Sato, Kang, Kamei, and Magara (2002) also evaluated As removal efficiency using NF and a rapid sand filtration inter-chlorination system. NF membranes with 99.6% NaCl rejection capacity removed 95% of As(V) and 75% of As(III) with no chemical addition under low pressure. Floch and Hideg (2004) conducted a study with 200–300 μg/L As containing deep well water. Using Zenon ZW 1000 hollow-fiber membranes, they achieved As concentration less than 10 μg/L.

Pesticides are used to control pests such as weeds and insects. They are beneficial in preventing disease and are used for food production. Unfortunately, they have an adverse effect on water quality and may have negative effects on human and aquatic life. Chen, Taylor, Mulford, and Norris (2004) proved that NF membranes can reject pesticides from 46% up to 100%. They found that the rejection rate is directly proportional to the molecular weight (MW) of the pesticide. When the MW increased, the rejection rate also increased. They also revealed rejection could be increased by adjusting the operational flux and recovery. Van der Bruggen, Schaep, Maes, Wilms, and Vandecasteele (1998) researched the removal of pesticides with membrane filtration systems that showed good efficiency of membranes in pesticide removal. They tried NF membranes and obtained approximately 95% rejection of arsenic with an NF-70 membrane.

Disinfection is used in the final step of drinking water treatment to deactivate biological agents. However, NOM in water reacts with disinfectants and causes DBPs to form, such as THMs, halogenated acetic acids (HAAs), haloacetonitriles (HANs), and haloketones (HKs), which are detrimental to human health. Lee and Lee (2007) used NF membranes to remove NOMs from surface water and researched the effect of membrane pretreatment and membrane material. They found that membranes with an MWCO less than 200 Da were better for controlling NOM in surface water. Hydrophobic and positively charged membranes fouled more than hydrophilic and negatively charged membranes. They also revealed that ozone pretreatment was inefficient for preventing NF fouling but powdered activated carbon (PAC) or UF pretreatment was efficient.

Pharmaceuticals have gained attention recently owing to their effects on biological activities. Pharmaceutical emissions to the environment should be controlled. Radjenovic, Petrovic, Ventura, and Barcelo (2008) studied the removal of pharmaceuticals in a full-scale NF and RO drinking water treatment plant using groundwater. An 85% rejection rate was obtained using NF and RO. Boleda, Galceran, and Ventura (2011) studied pharmaceuticals in a full-scale drinking water treatment plant; treatment consisted of dioxychlorination, coagulation/flocculation, and sand filtration units. After sand filtration, the system was split into two parallel lines: conventional (ozonation and carbon) and advanced (UF and RO) treatment. A flow diagram of the plant is shown in Figure 3.18. To remove pharmaceuticals, an advanced system was more effective than a conventional system.

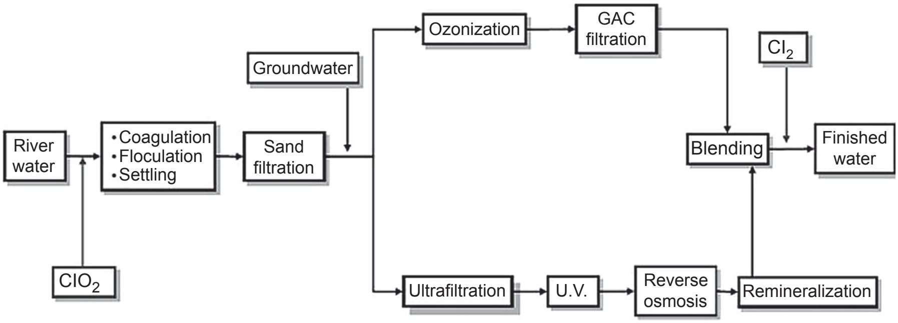

Figure 3.18 Treatment scheme of drinking water treatment plant.
Reprinted from Boleda et al. (2011), with permission from Elsevier.

3.7 Future trends

Water has been a main problem of mankind for years and will continue to be problematic. Membrane technology has a significant role in the water industry. In the future, novel membrane materials, processes, and modules will be used so that we can come closer to obtaining an optimum membrane structure. Membrane technology has some shortcomings, such as higher energy requirements and fouling. Today's technology related to research on this subject consists of fabricating new membrane materials, designing modules, calculating hydrodynamics, and finding new operation modes to decrease energy requirements or application setups to treat water or wastewater more effectively. Future trends will be the reuse of process waters, recovery of valuable compounds, creation of new technologies such as pervaporation and forward osmosis, monitoring of fouling in real time, improvement of new fouling analysis methods, and fabrication of tailored novel membranes and developments of membranes can be used under extreme conditions.

As these aims are realized, cost, capacity, and selectivity should optimized and their environmental impact, such as concentrate handling and minimized chemical consumption, should also be considered.

As novel membrane materials are investigated, the future lies in block copolymers, and biomimetic and patterned membranes such as vertically aligned CNs. These materials show great potential because they have greater permeability rates and higher selectivity; however, commercialization is still a problem. If they are commercialized in near future, we will obtain lower energy consumption, and thus the treatment cost of pollutants will also decrease. The ultimate challenge is extreme conditions such as high temperatures. On this point, developments in ceramic membranes are promising (Abetz et al., 2006; Url-5; Url-6).

Another problem is housing the membranes. Hollow-fiber and spiral wound module geometry are the main membrane housings, as already mentioned in this chapter. Membrane module design focuses on mechanical considerations such as pressure, but also on how to limit concentration polarization. According to studies on membrane surface, there is a valley that causes roughness on membranes surface; because of that, a concentration of rejected species occurs. To resolve these problems, future research will need to resolve them with fluid mechanical and mass transfer approaches. Also, designing new membrane modules can decrease the cost and energy requirements of the membranes. For example, when the transmembrane pressure is low, high fluxes can be obtained. Using novel membrane module technologies such as vibrational modules can decrease the effect of fouling on the membrane surface (Fane et al., 2011; Url-7).

Membrane processes are also significant. With an improvement in membrane processes and materials, it will become easier to use some new applications: for instance, pervaporation, forward osmosis, and new MBR systems. Anaerobic MBRs use anaerobic bacteria to degrade organic substances. In this system, it is possible to use biogas instead of air in the submerged reactor. Anaerobic MBR systems are better than conventional systems because of their lower energy consumption. Anaerobic MBR systems are promising because they can sustain high organic loadings, high biomass concentration can be maintained, energy and organic acid are recovered, and sludge production is low. Another new technology is microbial fuel cells, which are a novel type of MBR. Decentralized treatment systems can be used to lower cost and increase sanitation and reuse in wastewater systems (Abetz et al., 2006; Fane et al., 2011).

In this century, great challenges will need to be overcome, such as energy, water, and a clean environment. Membrane technology and its development have an important role in solving these problems efficiently with new research and development and innovations in process designs.

3.8 Sources of further information and advice

In the future, we will see membranes much more in the water treatment sector. High performance and low fouling membranes are the main targets in all membrane research, developments, and applications. Membrane materials, module configurations, and processes are becoming more important for improving membrane system performance and decreasing membrane fouling. They will have a critical role in the future performance of membranes. Interdisciplinary studies should be increased to improve performance based on materials, configurations, and processes.

3.9 Conclusion

This chapter summarizes MF, UF, and NF membranes for water treatment. New membrane materials have improved membrane technology by enhancing permeability and selectivity. As a result of these improvements in membrane performance, concentration polarization and fouling phenomena have become important factors in determining membrane performance. Membrane modules improve fluid flow so that fouling and concentration polarization problems decrease. In this chapter, novel membrane materials and module design to increase membrane performance were summarized. Applications of MF, UF, and NF membranes were also provided. They may be applied to treat surface water, groundwater, and seawater desalination and to harvest rainwater. Many specific contaminants can be removed efficiently with these membrane processes.

List of acronyms

AMBR	Anaerobic membrane bioreactor
CA	Cellulose acetate
CAGR	Compound annual growth rate
CHFP	Chloral hydrate formation potential
CNT	Carbon nanotube

COD	Chemical oxygen demand
CVD	Chemical vapor deposition
DBP	Disinfection by-products
ED	Electrodialysis
EDR	Electrodialysis reversal
FO	Forward osmosis
GAC	Granulated Activated Carbon
HAA	Halogenated acetic acids
HAAFP	Haloacetic acid formation potential
HAN	Haloacetonitrile
HK	Haloketone
IC	In-line coagulation
IMS	Integrated membrane system
MBR	Membrane bioreactor
MCF	Membrane cartridge filtration
MSD	Multi-shaft disk
MF	Microfiltration
MIEX	Magnetic ion exchange
MWCNT	Multi-walled carbon nanotubes
MWCO	Molecular weight cutoff
NF	Nanofiltration
NOM	Natural organic matter
nZVI	Nano zero valent iron
PAC	Powdered activated carbon
PAN	Polyacrylonitrile
PBMA-B-PMAA-B-PHFBM	Poly(butyl methacrylate)-b-poly(methacrylic acid)-b-poly(hexafluorobutyl methacrylate)
PC	Polycarbonate
PES	Polyethersulfone
PI	Polyimide
PNIPAAm-B-PPEGMA	poly(*N*-isopropylacrylamide)-block-poly([polyethylene glycol] methacrylate)
PP	Polypropylene
PS	Polysulfone
PS-B-PMMA	Polysulfone-b-polymethylmethacrylate
PVDF	Polyvinylidene fluoride
RO	Reverse osmosis
SDI	Silt density index
SWCNT	Single-walled carbon nanotube
TDS	Total dissolved solids
TFC	Thin-film composite
TFN	Thin-film nanocomposite
THM	Trihalomethanes
THMFP	Trihalomethane formation potential
TMP	Transmembrane pressure
TOC	Total organic carbon
UF	Ultrafiltration
UV	Ultraviolet
WP	Water permeability

List of symbols

A	Membrane area
Da	Dalton
E	Band gap energy
hν	Photon energy
J	Membrane flux
ΔP	Applied pressure

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Water treatment by reverse and forward osmosis

4

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4.1 Introduction

Water shortages have plagued many communities, and humans have long searched for a solution to Earth's limited freshwater supplies. Less than 1% of the total water available on the earth is considered freshwater. Almost 96.5% of Earth's water is located in the seas and oceans; 1.7% is present in icebergs and the remaining percentage is made up of brackish water (Gleick, 1996; Greenlee, Lawler, Freeman, Marrot, & Moulin, 2009). The population explosion and the expansion of cities have made the production of potable water undependable and have led to an increase in demand compared with availability. Today, the production of potable water has become a worldwide concern; for many communities, the projected population growth and demand exceed available conventional water resources.

Over the years, purified water standards have become more stringent. Water containing less than 1000 mg/L of salts or total dissolved solids (TDS) is referred as freshwater; above this concentration, properties such as taste, color, corrosion propensity, and odor are adversely affected (Sandia, 2003). Many countries have adopted national drinking water standards for specific contaminants, as well as for TDS, but the standard limits vary from country to country or from region to region within the same country. The World Health Organization and Gulf Drinking Water standards, Australia, recommend a drinking water standard of 1000 mg/L TDS (Fritzmann, Lowenberg, Wintgens, & Melin, 2007). Most desalination facilities are designed to achieve a TDS of 500 mg/L or less (Gaid & Treal, 2007; Xu et al., 2007). Desalinated water used for other purposes, such as crop irrigation, may have a higher TDS concentration. Depending on the salinity of the feed water, it can be divided into two types, such as brackish water (often groundwater sources, 1000−10,000 mg/L TDS) and seawater (30,000−45,000 mg/L TDS) (Mickley, 2001). The type of feed water decides the use of pretreatment method, the design of the treatment plant, the waste disposal method, and the recovery of water.

The expanding global population, increasing water pollution, and increasing standard of living have put relentless pressure on water and energy resources. Low-cost methods of purifying freshwater and desalting seawater are required to contend with this destabilizing trend. Hence, the need for water is increasing rapidly and current

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freshwater resources may not be able to meet all requirements. Desalination of sea (or saline) water has been practiced regularly for over 50 years and is a well-established means to obtain a water supply in many countries. In the 1970s, exploration began into using membranes for water desalination. Proving successful at producing purified water from saltwater, membranes became a viable alternative to evaporation-based technologies in the water treatment market. Over the years, purified water standards have become more stringent. However, membranes have risen to the challenge and continue to perform efficiently and effectively (Rastogi & Nayak, 2011).

4.2 Thermal or membrane desalination

Membrane and distillation processes equally share current desalination production capacity worldwide. However, reverse osmosis (RO) will emerge as the leader in future desalination installations and will be the key to increasing water supplies for drinking water production. RO technology can now produce freshwater (from seawater) at one-half to one-third the cost of distillation (Miller, 2003). Brackish water RO membranes typically have higher permeate flux and lower salt rejection, and require lower operating pressures, whereas seawater RO membranes have higher salt rejection and lower permeate fluxes and membrane permeability and require higher operating pressures to compensate for the higher osmotic pressure of seawater. Brackish water desalination is even less expensive than seawater desalination.

The demand for additional freshwater production can be met by adopting water reuse or desalination (Sauvet-Goichon, 2007). Water reuse can be used for irrigation, power plant cooling, and groundwater recharge (Focazio et al., 2008). Desalination has been identified as a potential source for producing drinking water. Desalination is a general term for the process of separating salt from saline water for the production of freshwater. Thermal and membrane desalination both the processes are being used for the recovery of water (Gleick, 2006).

Middle East countries initiated the use of seawater thermal desalination, and today their share is more than 50% of the world's desalination capacity (Henthorne, 2003; Van der Bruggen & Vandecasteele, 2002). Membrane processes have rapidly developed since the 1960s (D'souza & Mawson, 2005; Loeb & Sourirajan, 1963) and now surpass thermal processes in new plant installations (75% of new production capacity). The advent of such membranes with high retention of low-molecular-weight organic compounds and good physical and chemical stability has enabled RO to be used more widely on a commercial scale. RO membrane technology has been developed for both brackish and seawater applications. RO membranes, however, are able to reject monovalent ions (sodium and chloride). Currently, RO membranes are made so that these can reject more than 99% salts (Brehant, Bonnelye, & Perez, 2003; Reverberi & Gorenflo, 2007).

Membrane and distillation processes equally share current desalination production capacity worldwide, RO has emerged as the leader in future desalination installations. RO will be the key to increasing water supplies for drinking water production throughout the world. Although wealthy Middle Eastern countries have been able to afford distillation processes, RO technology can now produce freshwater (from seawater) at one-half to one-third the cost of distillation (Miller, 2003). Brackish water desalination is even less expensive than seawater desalination.

Membranes have risen to the challenge of supplying desalinated water and continue to perform efficiently and effectively. Another membrane process, forward osmosis (FO), can be used to desalinate saline water sources at a notably reduced cost. It involves the use of a draw solution of aluminum sulfate or ammonium sulfate, which is used to transport water from saline water. These draw solutions on chemical treatment or heating result in freshwater (Chanukya, Patil, & Rastogi, 2013; Frank, 1972). This new athermal membrane process has been developed as a possible alternative to desalination. It employs a semipermeable, dense, hydrophilic membrane that separates two aqueous solutions (feed and osmotic agent solution) with different osmotic pressures. The difference in osmotic pressure acts as a driving force. An osmotic pressure-driven process operates on the principle of osmotic transport of water across a semipermeable hydrophilic membrane from a dilute feed solution into a concentrated osmotic agent or draw solution (Nayak & Rastogi, 2010). Recently, FO concentration is gaining importance for concentrating liquid foods and natural colors (Babu, Rastogi, & Raghavarao, 2006; Bolin & Salunke, 1971; Garcia-Castello, Mccutcheon, & Elimelech, 2009; Gusti & Wrolstad, 1996; Loeb & Bloch, 1973; Martinetti, Childress, & Cath, 2009; Popper et al., 1966; Rodriguez-Saona, Giusti, Durst, & Wrolstad, 2001), generating electricity (Kravath & Davis, 1975), treating wastewater (Holloway, Childress, Dennett, & Cath, 2007), and desalinating seawater (Mccutcheon, Mcginnis, & Elimelech, 2006).

4.3 Difference between osmosis, RO, and FO

Osmosis is the movement of solvent molecules through a selectively permeable membrane into a region of higher solute concentration, with the aim of equalizing the solute concentrations on both sides. The net movement of the solvent from a less concentrated (hypotonic) to a more concentrated (hypertonic) solution tends to reduce the difference in concentrations. When a semipermeable membrane separates two solutions, water always diffuses from the solution with the lower osmotic potential to the one with the higher osmotic potential. This diffusion-driven motion of water through a membrane is termed osmosis. It is the tendency of fluids to pass through a membrane so that equal concentrations are achieved on both sides (Figure 4.1(a)). RO is a pressure-driven membrane process that entails forcing fluids through a membrane. It is a separation technique that can be used to concentrate or purify liquids without a phase change. The RO process uses hydraulic pressure as the driving force for separation, which serves to counteract the osmotic pressure gradient that would otherwise favor water flux from the permeate to the feed (Figure 4.1(b)). FO is an osmotic process that, like RO, uses a semipermeable membrane to effect separation of water from dissolved solutes. The driving force for this separation is an osmotic pressure gradient, such that a draw solution of high concentration (relative to that of the feed solution) is used to induce a net flow of water through the membrane into the draw solution, thus

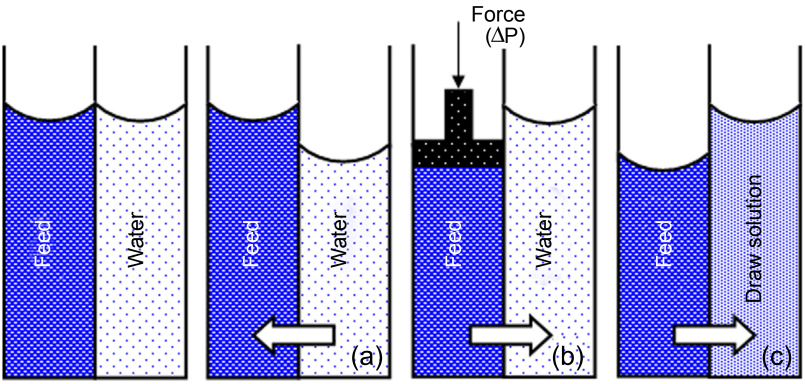

Figure 4.1 Migration of water during (a) osmosis, (b) reverse osmosis, and (c) forward osmosis. The arrows indicate the direction of mass transfer. ΔP is the hydraulic pressure.
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effectively separating the feed water from its solutes. FO uses the osmotic pressure differential ($\Delta\pi$) across the membrane as the driving force for transport of water through the membrane, rather than the hydraulic pressure differential (similar to RO). The FO process results in the concentration of feed solution and the dilution of draw solution (Figure 4.1(c)). (Cath, Childress, & Elimelech, 2006; Rastogi & Nayak, 2011).

4.4 Fundamentals of water treatment by RO

Osmosis is the basis for RO. When a semipermeable membrane separates a dilute solution from a concentrated solution, the solvent (water) crosses from the dilute solution side to the concentrated solution side of the membrane to equalize concentrations on both sides; this process is known as osmosis. The flow of solvent can be prevented by applying an opposing hydrostatic pressure to the concentrated solution. The magnitude of the pressure required to completely impede the flow of water is defined as the osmotic pressure. In the case of RO, a hydrostatic pressure greater than the osmotic pressure is applied for water to move from a high-solute to a low-solute concentration (Figure 4.1(b)). It necessitates high-pressure requirements. The positive difference in pressure creates a chemical potential difference (concentration gradient) across the membrane that drives the liquid through the membrane against the natural direction of osmosis (the movement of water molecules from an area of high concentration to an area of low concentration), while the salts are retained and concentrated on the influent surface of the membrane. Some salt passage through the membrane occurs; salt passage for the same membrane increases with the salt concentration and temperature.

The RO process requires high operating pressures ranging from 2300 to 3500 kPa for seawater and 100 to 300 kPa for brackish water to overcome the osmotic pressure of feed water (Perry & Green, 1997; Sagle & Freeman, 2004).

The dominant mechanism governing transport through RO membranes can be explained as solution-diffusion, which involves preferential dissolution of solvent (water) in the membrane and its transport through diffusion. Water transport across an RO membrane occurs in three separate steps: absorption onto the membrane surface, diffusion through the thickness of the membrane, and desorption from the permeate surface of the membrane. Once a water molecule has absorbed onto the membrane surface, the water concentration gradient (of the water-membrane system) across the membrane causes the water molecules to diffuse down the concentration gradient to the permeate side of the membrane. The water molecule then desorbs from the membrane and becomes part of the bulk permeate (Lonsdale, Merten, & Riley, 1965; Paul, 2004).

The equation that gives the water flux through a membrane as a function of pressure difference during RO can be written in a simple form (Mulder, 1996, p. 298)

$$J_w = A_w(\Delta p - \Delta\pi) \tag{4.1}$$

where A_w is the water permeability coefficient, Δp is the transmembrane pressure, and $\Delta\pi$ is the difference in the osmotic pressures of feed and permeate.

The permeate flux during the course of RO decreases rapidly owing to reversible and irreversible fouling of the membrane that significantly affects the process efficiency (Kwang-Sup, Joo-Heon, Dong-Ho, Seok-Joong, & Soon-Dong, 2004). The permeate fluxes are primarily affected by the phenomena of concentration polarization (i.e., solute buildup) and fouling (e.g., microbial adhesion, gel layer formation, and solute adhesion) at the membrane surface. Fouling is generally caused by the deposition of colloidal particles, inorganic and organic compounds, and microbes on the surface of the membrane (Chien-Hwa, Lung-Chen, Shaik Khaja, Chung-Hsin, & Cheng-Fang, 2010). It is considered a group of physical, chemical, and biological effects leading to irreversible loss of membrane permeability (Chien-Hwa et al., 2010; Sablani, Goosen, AL-Belushi, & Wilf, 2001). Concentration polarization is mainly limited to the buildup of retained solute, i.e., accumulation of matter on the surface of the membrane. It is considered to be reversible and can be controlled in a membrane module by means of velocity adjustment, pulsation (back flush), ultrasound, or an electric field (Vladisavljevic, Vukosavljevic, & Bukvic, 2003).

Considering a situation in which a solution consisting of solvent and solute is subjected to a pressure-driven membrane process such as RO, the solute is preferentially retained on the membrane surface whereas solvent permeates through the membrane. As solvent is removed from the feed, the difference in the osmotic pressure ($\Delta\pi$) increases, which in turn results in a decrease in flux. At the same time, a concentration gradient is developed owing to the rejection of solute with the passage of solvent through the membrane (Figure 4.2). The solvent flux through the membrane increases with an increase in the applied pressure until the concentration of solute on the membrane surface reaches a critical concentration, which is referred to as the gel concentration (C_G). Further increases in pressure do not change the solute concentration at the membrane surface; however, they result in a thicker and compacted gel layer. At equilibrium, the rate of solvent transport through the membrane (flux) can be calculated on the basis of the convective transport of solutes to the membrane surface

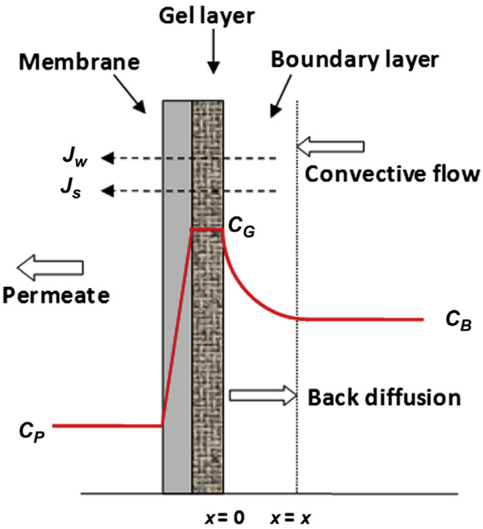

Figure 4.2 Formation of concentration gradient near the surface of the membrane.

$(J_w \cdot C)$ by the solvent, which is equal to the sum of the diffusive back transport of solute $\left[-D \cdot \left(\frac{\mathrm{d}C}{\mathrm{d}x}\right)\right]$ and permeate flow $(J_w \cdot C_p)$, i.e.,

$$J_w \cdot C = \left(-D\frac{\mathrm{d}C}{\mathrm{d}x}\right) + J_w \cdot C_p \tag{4.2}$$

where D is the diffusion coefficient for solute transport through solvent, C is the solute concentration retained on the membrane, C_p is the solute concentration in permeate (in the case of RO, the solute is completely retained by the membrane, i.e., $C_p = 0$), and $\left(\frac{\mathrm{d}C}{\mathrm{d}x}\right)$ is the solute concentration gradient.

The integration of Eqn (4.2) with appropriate boundary conditions ($x = 0$, $C = C_G$; $x = x$, $C = C_B$) results in the following equation:

$$J_w = \frac{D}{\delta} \cdot \ln\left(\frac{C_G}{C_B}\right) = k \cdot \ln\left(\frac{C_G}{C_B}\right) \tag{4.3}$$

where δ is the thickness of the boundary layer, k is mass transfer coefficient, C_B and C_G are the bulk and gel layer solute concentrations, and $\frac{C_G}{C_B}$ is the concentration polarization modulus. Equation (4.3) shows that at this juncture the flux through the membrane is independent of the transmembrane pressure drop or permeability and depends only on the solute characteristics (D and C_G) and boundary layer thickness (δ). Concentration polarization is a reversible fluid dynamic phenomenon. If C_B reaches C_G, solutes will start to precipitate or deposit on the membrane, forming a gel layer, which leads to the permanent loss of flux known as fouling (Echavarria, Torras, Pagan, & Ibarz, 2011).

4.5 Conventional and membrane pretreatment for RO feed water

The primary goal of any RO pretreatment system is to lower the fouling propensity of the water in the RO membrane system. Conventional pretreatment typically consists of chemical additions, including acid, coagulant, and flocculent, that prepare the feed water for granular media filtration (Isaias, 2001; Sauvet-Goichon, 2007). Acid treatment reduces the pH of the feed water (typical pH range, 5−7), which increases the solubility of calcium carbonate, the key potential precipitate in many feed waters (Bonnelye et al., 2004). Coagulants are typically small, positively charged molecules that effectively neutralize like charges (on aqueous particulate and colloidal matter) and allow the suspended solids to group together in flocs (large groups of loosely bound suspended particles). Inorganic coagulants are commonly iron or aluminum salts such as ferric chloride or aluminum sulfate, whereas organic coagulants are typically cationic, low-molecular-weight (<500,000 Da) polymers (i.e., dimethyldiallylammonium chloride or polyamines). Granular media filtration includes materials such as sand, anthracite, pumice, gravel, and garnet (Bonnelye et al., 2004); often, a combination of materials is used in layers in the filtration bed to reduce the feed water silt density index (Morenski, 1992). Cartridge filtration (filter cartridges are usually 1−10 mm) acts as a final polishing step to remove larger particles that passed through media filtration in conventional RO pretreatment (Morenski, 1992; Petry et al., 2007).

Antiscalants are primarily used as pretreatment typically performed after granular media filtration, either before or after cartridge filtration (Sauvet-Goichon, 2007). Disinfection is achieved by adding a strong oxidant such as ozone, chlorine (gas, chlorine dioxide, or sodium hypochlorite), chloramine, or potassium permanganate (Morenski, 1992).

A new trend in pretreatment has been the movement toward using larger pore-size membranes (microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF)) to use RO as a pretreatment to feed water that avoids the passage of colloids and suspended particles contributing to RO membrane fouling (Brehant et al., 2003). The membranes act as a defined barrier between the RO system and any suspended particles. They can reduce silt density index as well as turbidity of the feed water (Pearce, 2007; Vedavyasan, 2007). MF membranes are an appropriate choice for the removal of larger particulate matter, whereas NF membranes are used to remove dissolved contaminants as well as particulate and colloidal material. UF membranes represent the best balance between the removal of contaminants and permeate production of the other three membrane types. Typical final permeate fluxes for a UF-RO system were reported to be in the range of 15−24 L/m^2 h (Kamp, Kruithof, & Folmer, 2000), whereas the permeate flux exiting the UF pretreatment stage was within 60−150 L/m^2 h (Brehant et al., 2003).

Membrane pretreatment reduces the general aging and destruction of RO membranes by feed water components, membrane replacement, and the frequency of chemical (acid or base) cleaning. However, the RO system can be operated at a higher permeate flux. Membrane pretreatment systems are decreasing in capital cost and are becoming more cost-competitive with conventional systems. The risk of membrane fouling prevents general operation at high permeate flux especially for feed waters with impurities such as hydrocarbons (oil) and cellular or extracellular material (from bacteria) (Jian, Kitanaka, Nishijima, Baes, & Okada, 1998; Williams & Edyvean, 1998). Fouling results in membrane damage and flux decline requires membrane replacement every 5—10 years (Pearce, 2007).

4.6 Fundamentals of water treatment by FO

FO can be considered a technique for the recovery of the water from saline water. It employs an asymmetric semipermeable dense hydrophilic membrane that separates two aqueous solutions (feed and draw solution) with different osmotic pressures. The osmotic pressure gradient is the sole driving force for the transport of water. Concentration polarization is a significant problem in pressure-driven membrane processes such as RO. It reduces permeate flow as a result of buildup of the retained molecules, leading to enhanced osmotic pressure at the membrane surface. The FO phenomenon with a dense symmetric membrane can result in the occurrence of concentration polarization on both sides of the membrane. The solute is concentrated and diluted on the feed and permeate sides, leading to concentrative and dilutive external concentration polarization, respectively (Figure 4.3(a)). The standard flux equation for forward equation is given by the following equation:

$$J_w = A(\pi_d - \pi_f) \tag{4.4}$$

where π_d and π_f are the bulk osmotic pressures of draw and feed solutions, respectively; J_w is the water flux; and A is the pure water permeability coefficient.

The asymmetric membrane employed in the case of FO consists of a dense active membrane layer (active layer) and a loosely bound support layer (porous support layer) (Figure 4.3, Nayak & Rastogi, 2010). The membrane can be placed between the feed and the osmotic agent solutions in two different ways such that they feed toward the support layer (normal mode) and toward the active layer (reverse mode), which are referred as modes I (Figure 4.3(b)) and II (Figure 4.3(c)), respectively (Gray, Mccutcheon, & Elimelech, 2006; Nayak & Rastogi, 2010).

4.6.1 Modeling of flux when feed toward support layer (internal concentration polarization concentrative)

When the feed (0.5 M NaCl solution) is placed against a porous support layer and a draw solution is kept on the active layer side (mode I), water is diffused into the porous support layer and traversed to the draw solution side through the active layer of membrane as a result of the osmotic pressure gradient across the membrane. The use of

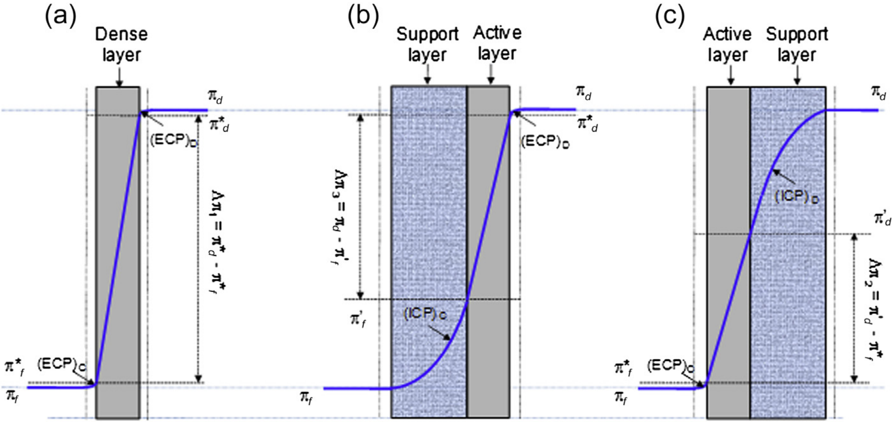

Figure 4.3 Mechanism of forward osmosis indicating water transport (a) with a dense symmetric membrane; and with asymmetric membrane (b) feed toward the support layer (mode I) and (c) feed toward active layer (mode II). π_d and π_f are the bulk osmotic pressures of draw and feed solutions, respectively; π_d^* and π_f^* the osmotic pressures on the membrane surface of draw and feed solutions, respectively; π_f' and π_d' are the osmotic pressures of the feed and draw solutions on the inside of the active layer within the porous support for concentrative internal concentration polarization on the feed side and dilutive internal concentration polarization on the draw side for modes I and II, respectively. $\Delta\pi_1$, $\Delta\pi_2$, and $\Delta\pi_3$ are the corresponding effective driving forces in (a), (b), and (c) situations, respectively. ECP and ICP refer to external and internal concentration polarizations, respectively.
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sodium chloride solution results in buildup of salt within the porous support layer due to the diffusion of water to the draw solution side. Subsequently, it results in a significant internal concentration polarization (concentrative) and negligible external concentration polarization. At the same time, permeation of water to the draw solution side results in external concentration polarization (dilutive). But, internal concentration polarization may not be highly significant. Both the internal (concentrative) and external (dilutive) concentration polarization phenomena are responsible for the reduction in the effective osmotic driving force. The internal concentration polarization occurs within the porous support layer and it cannot be lessened by hydrodynamics such as turbulence (since it is occurring within the pores of the support layer), leading to drastic reduction of effective osmotic driving force (McCutcheon & Elimelech, 2007; Tang & Ng, 2008). The extent of external polarization is much less than the internal concentration polarization during forward osmosis when permeate water fluxes are relatively low (Cath et al., 2006; McCutcheon et al., 2006).

The concentration profile across asymmetric FO membrane for concentrative internal concentration polarization is illustrated in Figure 4.3(b). Assuming negligible external concentration polarization at the outer surfaces of the membrane, the water and salt flux (J_w, J_s) across the membrane is given by

$$J_w = A(\Delta\pi_{\text{eff}}) = A(\pi_d - \pi_f) \tag{4.5}$$

$$-J_S = B(C_2 - C_3) \tag{4.6}$$

where A and B are the water and solute permeation coefficients, respectively; π_d and π_f are the bulk osmotic pressure of draw and feed solutions, respectively, at the membrane surface; and the corresponding solute concentrations are C_2 and C_3. Because π_f is not known, this quantity can be obtained by the following analysis provided by Mehta and Loeb (1978). The diffusion of solute is considered to be in the opposite direction of water flux, and hence it was taken as negative. The salt flow consists of two components acting in opposite directions: a diffusive part caused by diffusion down the salt concentration gradient and a convective part caused by bulk flow of water through the membrane. The salt flux across the porous support layer can thus be written as per the following equation:

$$-J_s = D\varepsilon\frac{\mathrm{d}C}{\mathrm{d}x} - J_w C \tag{4.7}$$

where ε and D are the porosity of the substrate and diffusion coefficient of the salt in the membrane porous substrate, respectively. The distance x is measured from the membrane–solution interface on the porous support layer. Substituting the value of J_s from Eqn (4.2) to Eqn (4.3) results in the following equation:

$$\begin{gathered} B(C_2 - C_3) = D\varepsilon\frac{\mathrm{d}C}{\mathrm{d}x} - J_w C; \\ \text{Boundary conditions } x = 0,\ C = C_4;\ x = \tau t,\ C = C_3 \end{gathered} \tag{4.8}$$

On rearranging:

$$\begin{gathered} Z = \frac{\mathrm{d}C}{\mathrm{d}x} = \frac{J_w C}{D\varepsilon} + \frac{B(C_2 - C_3)}{D\varepsilon}; \quad \text{Boundary conditions} \\ x = 0,\ Z_1 = \frac{J_w C_4}{D\varepsilon} + \frac{B(C_2 - C_3)}{D\varepsilon}; \quad x = \tau t,\ Z_2 = \frac{J_w C_3}{D\varepsilon} + \frac{B(C_2 - C_3)}{D\varepsilon} \end{gathered} \tag{4.9}$$

where t and τ are the thickness and tortuosity of the support layer, respectively.

Solving Eqn (4.7) with the boundary conditions above yields Eqn (4.9).

Differentiating Eqn (4.9) with respect to x results in the following equation:

$$\frac{\mathrm{d}Z}{\mathrm{d}x} = \frac{J_w}{D\varepsilon}\frac{\mathrm{d}C}{\mathrm{d}x} \tag{4.10}$$

Integrating Eqn (4.9) results in the following equation:

$$\frac{D\varepsilon}{J_w}\int_{Z_1}^{Z_2}\frac{1}{Z}\mathrm{d}Z = \int_0^{\tau t}\mathrm{d}x \quad \text{or} \quad \frac{D\varepsilon}{J_w}[\ln Z]_{Z_2}^{Z_1} = \tau t \tag{4.11}$$

$$\text{or} \quad \ln\frac{J_wC_3 + B(C_2 - C_3)}{J_wC_4 + B(C_2 - C_3)} = \frac{\tau t}{D\varepsilon}J_w = K_DJ_w \tag{4.12}$$

where $\frac{\tau t}{D\varepsilon}$ is defined as a membrane (support and active layer) resistivity (K_D) (s/m or d/m).

$$\text{or} \quad \frac{J_wC_3 + B(C_2 - C_3)}{J_wC_4 + B(C_2 - C_3)} = \exp(K_DJ_w) \tag{4.13}$$

On rearranging Eqn (4.13),

$$\frac{C_3}{C_2} = \frac{B\left(e^{K_DJ_w} - 1\right) + J_w\frac{C_4}{C_2}e^{K_DJ_w}}{B(e^{K_DJ_w} - 1) + J_w} \quad \text{or}$$

$$1 - \frac{C_3}{C_2} = \frac{(C_2 - C_3)}{C_2} = \frac{\left(1 + \frac{C_4}{C_2}e^{K_DJ_w}\right)}{\left(1 + \frac{B}{J_w}(e^{K_DJ_w} - 1)\right)} \tag{4.14}$$

$$\frac{\pi_d - \pi_f}{\pi_d} = \frac{\left(1 - \frac{\pi_f^*}{\pi_d}e^{K_DJ_w}\right)}{\left(1 + \frac{B}{J_w}(e^{K_DJ_w} - 1)\right)} \tag{4.15}$$

Substituting the values of $(\pi_2 - \pi_3)$ from Eqn (4.15) to Eqn (4.1),

$$J_w = A\left(\pi_d - \pi_f\right) = \frac{A\pi_2\left(1 - \frac{\pi_f^*}{\pi_d}e^{K_DJ_w}\right)}{\left(1 + \frac{B}{J_w}(e^{K_DJ_w} - 1)\right)} \tag{4.16}$$

The rearrangement of Eqn (4.16) results in the following equation:

$$J_w = \left(\frac{1}{K_D}\right)\ln\frac{(A\pi_d + B - J_w)}{\left(B + A\pi_f^*\right)} \tag{4.17}$$

where π_d and π_f^* are the bulk osmotic pressures at the draw side and osmotic pressures on membrane surface at the feed side, respectively.

For low water flux, π_d and π_f^* can be replaced with bulk osmotic pressures of draw and feed sides (π_d and π_f), respectively. Hence, Eqn (4.17) becomes:

$$J_w = \left(\frac{1}{K_D}\right)\ln\left(\frac{A\pi_d + B - J_w}{B + A\pi_f}\right) \tag{4.18}$$

The value of K_D can be inferred from the plot of J_w versus $\ln\left(\frac{A\pi_d + B - J_w}{B + A\pi_f}\right)$.

4.6.2 Modeling of flux when feed is toward active layer (internal concentration polarization dilutive)

When the feed (0.5-M NaCl solution) is placed against the active layer and the draw solution on the support layer side, the water from the feed is diffused into the active layer, which in turn is diffused to the porous support layer and then to the bulk through the boundary layer, resulting in dilutive internal concentration polarization on the draw solution side (Figure 4.3(c)). The external and internal concentration polarizations toward the feed side are considered negligible. The osmotic solute from the draw solution may penetrate the porous support layer before flux can occur. As water flux crosses the active layer and enters into the porous support layer, it results in dilution of the draw solution owing to convection. The solute diffuses back to the interior surface. A steady state is quickly reached, but the concentration at the interior surface of the active layer is far lower than in the bulk draw solution (Gray et al., 2006). The combined effect of both the diffusion of water through the active layer and the diffusion of the draw solute into the support layer results in dilutive internal concentration polarization. The extent of external concentration polarization is negligible compared with the internal concentration polarization, which has a dominant role in a situation when the draw solution in placed against the support layer (Gray et al., 2006; Tan & Ng, 2008).

Similar to the analysis provided in the above section for concentrative internal concentration polarization, the equation for the dilutive internal concentration polarization can be written as:

$$J_w = \left(\frac{1}{K_C}\right)\ln\left(\frac{B + A\pi_d}{B + A\pi_F + J_w}\right) \tag{4.19}$$

The value of K_C can be inferred from the plot J_w versus $\ln\left(\frac{B+A\pi_d}{B+A\pi_F+J_w}\right)$.

Constants A (0.019 m/atm/day) and B (0.023 m/atm/day) refer to the water and solute permeability coefficients of the active layer of the membrane, respectively (Gray et al., 2006; Loeb, Titelman, Korngold, & Freiman, 1997) and the values were determined as per Eqns (4.5) and (4.6), respectively, based on the data presented for the ammonium bicarbonate draw solution by Achilli et al. (2012).

4.6.3 Quantitative analysis of internal concentration polarization

Studies on the effect of draw solution concentration and temperature on transmembrane flux in the case of modes I and II indicate that transmembrane flux for mode I was higher compared with mode II for all values of the draw solution concentration. At the same time, the transmembrane flux in modes I and II increased with an increase in feed temperature from 30 °C to 45 °C (Figure 4.4(a) and (b)). The increase in transmembrane flux with temperature can be explained using the Wilke–Chang equation (Treybal, 1982), according to which the diffusion coefficient is proportional to the absolute temperature divided by the viscosity of the solvent. The increase in

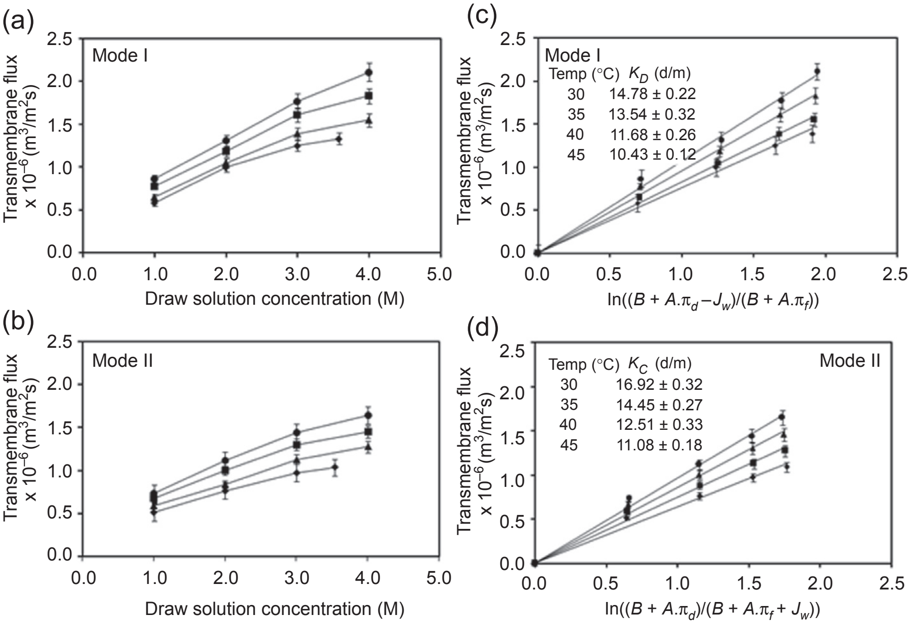

Figure 4.4 (a, b) Effect of the draw solution concentration at different temperatures on transmembrane flux. (c, d) Plot of J_w versus $\ln\left(\frac{B+A\pi_d-J_w}{B+A\pi_F}\right)$ and J_w versus $\ln\left(\frac{B+A\pi_d}{B+A\pi_F+J_w}\right)$ as per Eqns (4.18) and (4.19), respectively. Modes I and II refer to the membrane orientation in which the feed was toward the support layer and active layer, respectively (◆ 30 °C; ▲ 35 °C; ■ 40 °C; • 45 °C).

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temperature reduces the viscosity of solution and increases the diffusion coefficients, which results in an increase in transmembrane flux (Holloway et al., 2007; Mccutcheon & Elimelech, 2006).

The severity of concentration polarizations in modes I and II can be inferred from the resistance to diffusion within the membrane porous layer (K_D and K_C values) (Figure 4.4(c) and (d)). The values of J_w were plotted against $\ln\left(\frac{A\pi_d+B-J_w}{B+A\pi_f}\right)$ and $\ln\left(\frac{B+A\pi_d}{B+A\pi_F+J_w}\right)$ as per Eqns (4.18) and (4.19), respectively, to determine the values of K_D and K_C. The relevant values are reported in Figure 4.4(c) and (d), which indicates that the predicted values are in good agreement with the experimental values ($R^2 > 0.90$). Higher values indicate a higher internal concentration polarization resulting in lower flux.

The low concentration of solute in the feed solution and draw solution results in a higher effective driving force in mode I compared with mode II ($\Delta\pi_{\text{eff},1} > \Delta\pi_{\text{eff},2}$); hence, in this situation mode I is most desirable for desalination to have a higher water flux than mode II. In the case of mode I, external concentration polarization on both the feed and draw solution sides as well as internal concentration polarization on the draw side can be considered insignificant, whereas internal concentration polarization (concentrative) toward the feed side will be the only dominant concentration polarization. Conversely, in the case of mode II, internal concentration polarization (dilutive) toward the draw side will be the most dominant concentration polarization, which will be higher because of the higher concentration of draw solution.

The orientation of the asymmetric membrane had a significant effect on the performance of the membrane. The feed toward the support layer (mode I) was the best option to maximize the flux owing to less concentrative internal concentration polarization compared with higher dilutive internal concentration polarization in the other case when the feed was toward the active layer (mode II). The high agreement between the experimental and predicted values indicated that the proposed model was a good fit and can be used to predict flux at variable conditions.

Nayak and Rastogi (2010) and Nayak, Valluri, and Rastogi (2011) described the mechanism of water transport in FO in a situation in which feed solution was a mixture of low-and high-molecular-weight compounds. When the solution of low-molecular-weight compounds was taken as a feed, mode I was most desirable. However, when the solution of high-molecular-weight compounds was taken as a feed, mode II gave a higher driving force that in turn led to a higher transmembrane flux. Mi and Elimelech (2008, 2010) also indicated that these high-molecular-weight compounds may be deposited within the porous structure of the membrane, leading to cake layer formation owing to the lack of shear force as well as hindered back diffusion in the porous structure. Fouling of the FO membrane as a result of alginate was reported to be almost fully reversible after a simple water rinse with no chemical cleaning reagents. It was attributed to the less compact formation of the fouling layer owing to the lack of hydraulic pressure. Zhao and Zou (2011a, b) and Zhao, Zou, Chuyang, et al. (2012) demonstrated that internal concentration polarization in the support layer strongly depended on the physicochemical properties of the solution facing the support layer. In a situation in which the feed was facing active layer, it resulted in a more stable and higher water flux than that of the situation in which support layer was toward the feed.

4.7 Membranes for FO

Membranes for FO should have high water flux, high solute rejection, minimum porosity, high hydrophilicity, reduced fouling, and high mechanical strength. These membranes are different from standard RO membranes that typically consist of a thin active layer (less than 10 μm) and a thick porous support layer. Any dense, nonporous, selectively permeable material commonly used for RO can also be used as a membrane for FO. However, the presence of a thick support layer results in the occurrence of concentration polarization within the membrane support structure, which may require large osmotic driving forces to sustain adequate water flux (Dova, Petrotos, & Lazarides, 2007a,b; Gray et al., 2006; Mccutcheon, Mcginnis, & Elimelech, 2005; Mcginnis, Mccutcheon, & Elimelech, 2007).

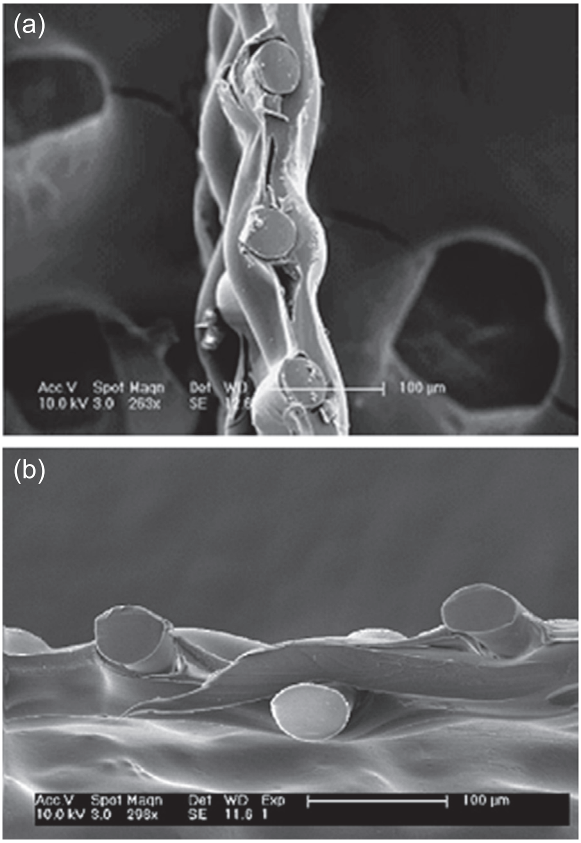

Figure 4.5 Scanning electron microscope images of cross-sections of cellulosic forward osmosis membrane (CA). A polyester mesh is embedded within the polymer material for mechanical support. The membrane thickness is less than 50 µm.
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A special membrane for FO made of cellulose triacetate was developed by M/s. Hydration Technologies, Inc., USA (thickness less than 50 µm) (Figure 4.5(a) and (b)) in which the support layer was embedded in a polyester mesh to provide mechanical support (Mccutcheon et al., 2005). A scanning electron microscope image of the cross-section of the cellulose acetate, polyamide composite, and cellulose triacetate membrane is presented in Figure 4.6 (Ng, Tang, & Wong, 2006).

FO membranes can also be made as hydration bags that can be used to recover water (Figure 4.7). They are double-lined bags. The internal bag is made of a FO membrane and is filled with draw solution (e.g., flavored sucrose) and the external bag is a sealed plastic bag. Upon immersing the bag in an aqueous solution, water diffuses into the bag because of the osmotic pressure difference and slowly dilutes the draw solution. The concept of a hydration bag was developed for military, recreational, and emergency relief situations in which reliable drinking water was scarce or not available. The hydration bag is one of the few commercial applications of FO (Cath et al., 2006).

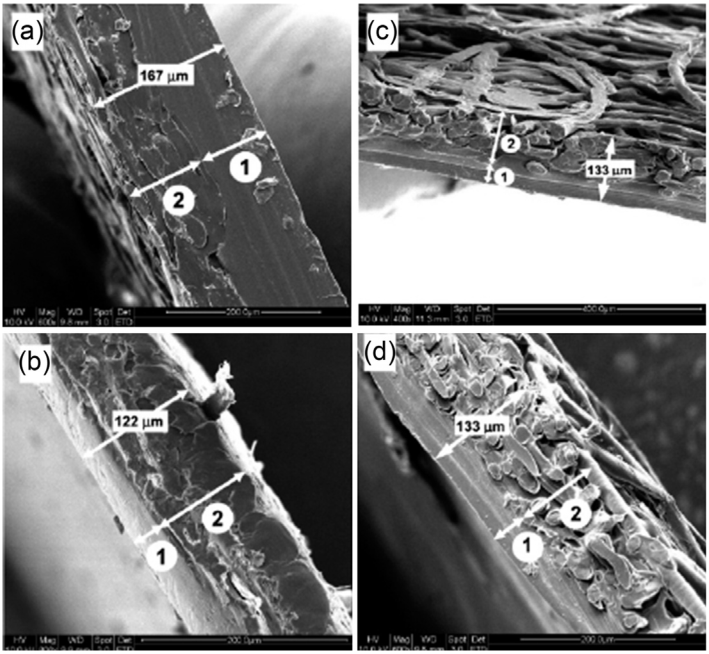

Figure 4.6 Scanning electron microscope images of the cross-section of (a) cellulose acetate (CA) membrane, (b) polyamide composite (AD) membrane, (c) forward osmosis (FO) membrane, and (d) FO membrane at higher resolution where 1 is the dense selective layer and 2 is the support layer.
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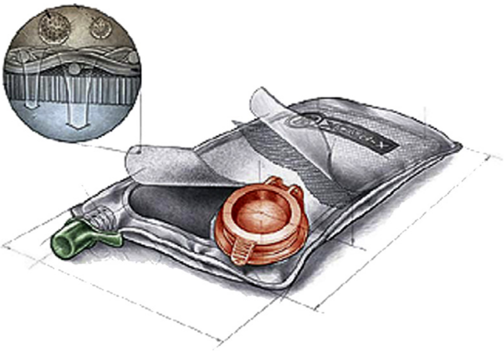

Figure 4.7 Water purification hydration bag.
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With a view to reducing internal concentration polarization, Wang, Ong, et al. (2010) designed a cellulose acetate FO membrane composed of a highly porous sublayer sandwiched between two selective skin layers by using the phase inversion technique. It prevented salt and other solutes in the draw solution from penetrating into the membrane porous support. It also resulted in higher water flux and lower salt transport. Zhang et al. (2010) developed a double dense membrane structure using phase inversion of cellulose acetate that produced low salt leakage and resulted in less internal concentration polarization in the FO process.

A novel dual-layer hollow-fiber NF membrane suitable for FO using co-extrusion technology was developed, consisting of an ultra-thin selective skin (around 10 μm) with a fully open-cell water channels underneath and a micro-porous sponge-like support structure, which could achieve high throughput and high salt rejection (Yang, Wang, & Chung, 2009a,b). Later, Wang et al. (2010) fabricated a polyethersulfone thin-film composite hollow-fiber membrane for FO using a dry-jet wet spinning process with an ultra-thin RO-like skin layer (300−600 nm) on either surface of a porous hollow-fiber substrate by interfacial polymerization. The active layers presented excellent intrinsic separation properties with a hydrophilic rejection layer and good mechanical strength. A high-flux and high-rejection FO membrane for water reuse and seawater desalination was developed by fabricating polybenzimidazole NF hollow-fiber membranes with a thin wall and desired pore size by nonsolvent induced phase inversion, which was chemically modified by cross-linking with *p*-xylylene dichloride (Wang, Yang, Chung, & Rajagopalan, 2009). Cross-linking finely tuned the mean pore size and enhanced the salt selectivity. Furthermore, Su, Yang, Teo, and Chung (2010) developed cellulose acetate NF hollow-fiber membranes suitable for FO processes by subjecting them to a two-step heat treatment (60 °C, 60 min and 95 °C, 20 min), which effectively shrank the membrane pores on the membrane surface with a denser outer skin layer (mean pore radius reduced from 0.63 to 0.30 nm). The resultant fiber has a high rejection to NaCl and $MgCl_2$ and low pure water permeability. Chou et al. (2010) developed a FO hollow-fiber membrane fabricated by the dry-jet wet spinning process. The outer UF skin was made by increasing the air gap in the spinning process and the inner RO skin layer was made by interfacial polymerization using an *m*-phenylenediamine aqueous solution and trimesoyl chloride hexane solution. The developed membrane showed excellent intrinsic separation properties with a water flux of 42.6 $L/m^2/h$. Yip, Tiraferri, Phillip, Schiffman, and Elimelech (2010) made a high-performance thin-film composite membrane consisting of a selective polyamide active layer formed by interfacial polymerization on top of a polysulfone support layer fabricated by phase separation onto a thin (40 μm) polyester nonwoven fabric.

Jia, Li, Wang, Wu, and Hu (2010) demonstrated the suitability of carbon nanotube membranes for seawater desalination using FO. The membrane could achieve the optimal salt rejection property but also the largest water flux, which broke the limit of the tradeoff effect between selectivity and permeability existing in traditional liquid separation membranes. The antifouling ability and good mechanical strength rendered it more suitable for FO. According to a rough estimation, carbon nanotube membranes can achieve a higher water flux far in excess of existing commercial FO membranes.

Qiu, Qi, and Tang (2011) successfully fabricated FO membranes using layer-by-layer assembly of polyallylamine hydrochloride and polysodium 4-styrene-sulfonate on a porous polyacrylonitrile substrate. The chemical cross-linking of layer-by-layer polyelectrolyte layers was performed with glutaraldehyde. The cross-linked and non-cross-linked membranes both had relatively high water permeability. However, the cross-linked membranes showed better $MgCl_2$ rejection, which clearly demonstrated the potential of layer-by-layer membranes for high-flux FO applications. Later, Qiu, Setiawan, Wang, Tang, and Fane (2012) fabricated high-performance flat-sheet FO membranes using polyamide-imide materials via phase inversion followed by polyelectrolyte polyethyleneimine after treatment to form an NF-like rejection layer with positive charges. Polyamide-imide micro-porous substrate was embedded with a woven fabric; the enhanced mechanical strength of the membrane made it possible to reduce the thickness of the substrate to 55 μm and the resultant membranes was able to reach a water flux of 29.65 and 19.2 $L/m^2/h$ when the active layer was facing draw or feed solutions, respectively.

4.8 Desalination by FO

Research has been reported on the desalination of seawater by FO. FO can be used efficiently and effectively to desalinate water. FO using semipermeable polymeric membranes may be a viable alternative to RO as a lower-cost and more environmentally friendly desalination technology.

Frank (1972) described a method of FO using a solution of aluminum sulfate as an osmotic agent, which upon treatment with calcium hydroxide resulted in a precipitate of aluminum hydroxide and calcium sulfate, which was removed by standard methods leaving freshwater. Mccutcheon et al. (2006) reported FO desalination as a lower-cost and more environmentally friendly technology. The driving force was provided by a draw solution composed of highly soluble gases: ammonia and carbon dioxide. Water fluxes ranging from 3.6 to 36.0 $L/m^2/h$ for a wide range of draw and feed solution concentrations were reported. Ammonium bicarbonate was used as a draw solution to extract water from saline feed water by Mccutcheon, Mcginnis, and Elimelech (2009) and Chanukya et al. (2013) in a FO desalination process. High osmotic pressures generated by the highly soluble ammonium bicarbonate draw solute yielded high water fluxes leading to high feed water recoveries. The ammonium bicarbonate solution was used as an osmotic solution (Jung et al., 2011; Mccutcheon et al., 2005) that can be decomposed into ammonia and carbon dioxide gases at about 60 °C. The water transferred from the feed side (seawater) to the osmotic solution can be obtained by distillation methods (Cath et al., 2006; Ng, Tang, & Wong, 2006) and the separated gases can then be recycled to use as a draw solution again (Jung et al., 2011). Mcginnis and Elimelech (2007) presented a schematic diagram of the ammonia carbon dioxide FO desalination process to recover freshwater (Figure 4.8). Similarly, Low (2009) studied the performance of FO with respect to different ammonia–carbon dioxide draw solutions and membranes. The internal concentration polarization resulted in lowering of the flux. The draw solution used

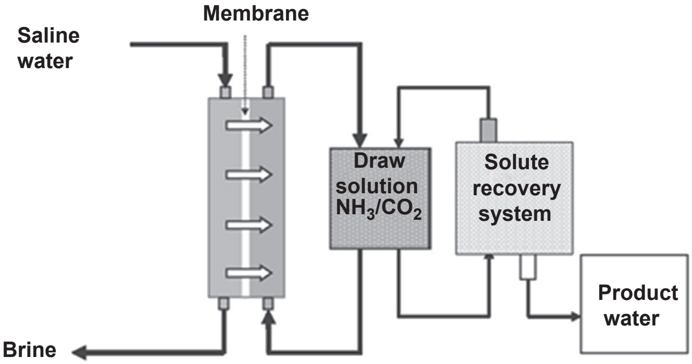

Figure 4.8 Schematic diagram of the ammonia–carbon dioxide forward osmosis desalination process.
Reprinted from Mcginnes and Elimelech (2007), with permission from Elsevier.

for desalination using FO should be highly soluble, highly recoverable, nontoxic, nonreactive with membranes, easily separable from water, and economically feasible.

Kravath and Davis (1975) described a process of seawater desalination by FO across a cellulose acetate membrane using glucose as the draw solute. Upon dilution, salinity was reduced to a level where ingestion would be possible for short-term consumption. The performance of flat-sheet cellulose acetate membranes was reported to be poor in terms of salt rejection. Stache (1989) used a semipermeable membrane bag filled with concentrated fructose solution to desalinate small volumes of seawater while simultaneously creating a nutritious drink. Yaeli (1992) used a concentrated glucose solution as a draw solution and water was extracted from seawater by osmosis. The diluted glucose solution was fed to an RO unit in which a low-pressure RO membrane separated potable water from the glucose draw solution.

An integrated FO process consisting of an RO process to generate potable water was proposed. FO was used to generate significant hydraulic pressure used to driving the RO process in which it could separate salt from seawater to generate potable water from water with a high salt content (Lampi, Beaudry, & Herron, 2007). Bamaga, Yokochi, and Beaudry (2009) designed an integrated desalination unit consisting of a closed FO and RO process in which RO brine was used as the osmotic draw solution and thus the chemical energy stored in the RO brine was recovered and used by the FO membrane process. Also, Choi et al. (2009, 2010) investigated systems combining FO and RO for seawater desalination. Pilot-scale combined systems with FO resulted in higher recovery with higher quality and fluxes than conventional RO-based desalination systems. Similarly, Valladares, Yangali, Li, and Amy (2011) focused on rejecting 13 selected micropollutants employing a clean or fouled FO membrane, using Red Sea water as a draw solution. The resulting effluent was then desalinated at low pressure with an RO membrane to produce a high-quality permeate. Tan and Ng (2010) proposed a hybrid FO–NF process for seawater desalination. The process achieved good-quality product water that met the recommended drinking water total dissolved solids guideline (500 mg/L). Zhao, Zou, and Mulcahy (2012) designed a hybrid

FO—NF system designed for brackish water desalination and compared it with a standalone RO process. Lay et al. (2010) examined possible factors for the slower decline of flux in the FO process. The transmission of draw solutes from the draw solution into the feed had significant effect on performance. Yangali, Li, Valladares, Li, and Amy (2011) indicated that FO coupled with low-pressure RO used for indirect desalination consumed only half of the energy used for high-pressure seawater RO desalination and produced good-quality water extracted from the impaired feed water. A cost analysis revealed that FO is a viable and promising technology.

A comparison of vacuum-enhanced direct contact membrane distillation (VEDCMD) and FO for the desalination of brackish water indicated that water recovery in FO was higher (90%) than with VEDCMD (81%) (Martinetti et al., 2009). Ling and Chung (2011) developed a potentially sustainable integrated FO—UF system for water reuse. During FO, water was transferred from the salt solution to the draw solution (containing super hydrophilic nanoparticles), which was regenerated from the draw solution using UF.

4.9 Conclusion

Membrane processes for water desalination are becoming increasingly interesting. They allow improvements in quality, enhanced process efficiency, and profitability. The expanding capabilities of membrane processes will certainly continue to benefit the industry in future to obtain the required product quality, purity, yield, and throughput along with economic viability. The use of RO and FO on an industrial scale will be even more lucrative in the future if membranes with high selectivity, improved flux, robustness, and greater chemical and mechanical stability are developed.

List of symbols

A **or** A_w	Water permeability coefficient
B	Solute permeation coefficients
C_B	Bulk layer solute concentration
C_G	Gel layer solute concentration
C	Solute concentration retained on membrane
C_p	Solute concentration in permeate
D	Diffusion coefficient for solute transport through solvent
$\left(\frac{dC}{dx}\right)$	Solute concentration gradient
K	Mass transfer coefficient
π_d **and** π_f	Bulk osmotic pressures of draw and feed solutions
J_w **and** J_s	Water and salt fluxes
k_d **and** k_f	Mass transfer coefficients on draw and feed solution sides
$\Delta\pi$	Difference in the osmotic pressures of feed and permeate
Δp	Transmembrane pressure
Δ	Thickness of the boundary layer
ε	Porosity of the substrate

x	Distance measured from membrane–solution interface on porous support layer
t	Thickness of the support layer
τ	Tortuosity of the support layer

Abbreviations

TDS	Total dissolved solids
RO	Reverse osmosis
FO	Forward osmosis
UF	Ultrafiltration
MF	Microfiltration
NF	Nanofiltration

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Membrane bioreactors for water treatment

5

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5.1 Introduction

Water is another synonym of life. According to the World Health Organization, the most dangerous threat to the health of mankind emerging within the next few years is polluted water. In underdeveloped countries, the shortage of clean freshwater will be the most important cause of death for children under 5 years. The low quantities of freshwater for industrial, agricultural, and municipal use have to be well preserved by efficient, sustainable, and cost-effective technologies. Water contaminated from industry and agriculture with heavy metal ions, pesticides, organic compounds, endocrine disruptive compounds, nutrients (phosphates, nitrates, and nitrites) has to be efficiently treated to protect humans from being intoxicated with these compounds or with bacteria. Furthermore, incidental sludge from industrial wastewater treatment facilities is commonly highly contaminated with toxic compounds (BioNexGen, 2013).

Clean water as a basis for health and good living conditions is too far out of reach for most of the world population. Thus, neither sustainable consumption nor reinforcement of governmental regulations is an effective driver to force the industry to adopt sustainability policies. Although polluted water and water shortages demand sustainable water use and recycling of wastewater, the barriers are high for adopt them (BioNexGen, 2013).

Water recycling is widely accepted as a sustainable option to respond to the general increase in water shortages and the demand for freshwater and for environmental protection. Water recycling is commonly seen as one of the main options to provide a remedy for water shortage caused by the increase in the demand for water and draughts as well as a response to some economical and environmental drivers. The main options for wastewater recycling are industrial, irrigation, aquifer recharge, and urban reuse (Pidou, 2006).

Membrane bioreactor (MBR) technology is recognized as a promising technology to provide water with reliable quality for reuse. Today, MBRs are robust, simple to operate, and even more affordable. They take up little space, need modest technical support, and can remove contaminants in one step. This makes it practical to provide safely reusable water for nonpotable use.

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5.2 Fundamentals

MBR technology is a combination of the conventional biological sludge process, a wastewater treatment process characterized by a suspended growth of biomass, and a microfiltration (MF) or ultrafiltration (UF) membrane system (Judd, 2011). The biological unit is responsible for the biodegradation of waste compounds and the membrane module for the physical separation of treated water from the mixed liquor. The pore diametre of the membranes is in the range between 0.01 and 0.1 μm so that particulates and bacteria can be kept out of permeate and the membrane system replaces the traditional gravity sedimentation unit (clarifier) in the biological sludge process. Hence, MBR offers the advantage of higher product water quality and low footprint. Because of its advantages, MBR technology has great potential in wide-ranging applications including municipal and industrial wastewater treatment and process water recycling. By 2006, around 100 municipal full-scale plants (>500 population equivalent) and around 300 industrial large-scale plants (>20 m^3/day) were in operation in Europe (Lesjean & Huisjeslow, 2008). MBR installation capacity grew in 2007 but declined in 2008 and 2009. The market was affected by lower industrial spending because of the economic downturn. However, there was an increase in demand for large plants during the past 2–3 years. Installations of MBR increased significantly in the years of 2010 and early 2011 (GIA, 2013).

The main industrial applications are in the food and beverage, chemical, pharmaceutical and cosmetics, and textile industries as well as in laundries. The technical feasibility of this technology has been demonstrated through a large number of small- and large-scale applications.

5.2.1 MBR configurations

According to MBR configurations, both aerobic and anaerobic MBRs can be divided into two classes as side-stream MBR (sMBR) and submerged or immersed MBR (iMBR) (Figure 5.1).

In side-stream MBRs, the membrane module is placed outside the MBR. The sludge from the MBR is pumped into the membrane module, which creates cross-flow at the membrane surface, and thus permeate is generated. The concentrated sludge rejected by the membrane is recycled to the MBR. This is a pressure-driven membrane filtration process. In the early development of stream MBRs, both the transmembrane pressure (TMP) and cross-flow velocity were generated by the recirculation pump. However, a few modifications were made to reduce the high-energy consumption associated with the side-stream configuration. Therefore, a suction pump was added to the recirculation pump on the permeate side, which increased operation flexibility and decreased the cross-flow rate and energy consumption (Shimizu, Okuno, Uryu, Ohtsubo, & Watanabe, 1996). The latest side-stream MBRs even introduced air flow into the membrane module, which intensified turbulence on the feed side of the membrane and reduced the fouling and operational costs (Jiang, 2007).

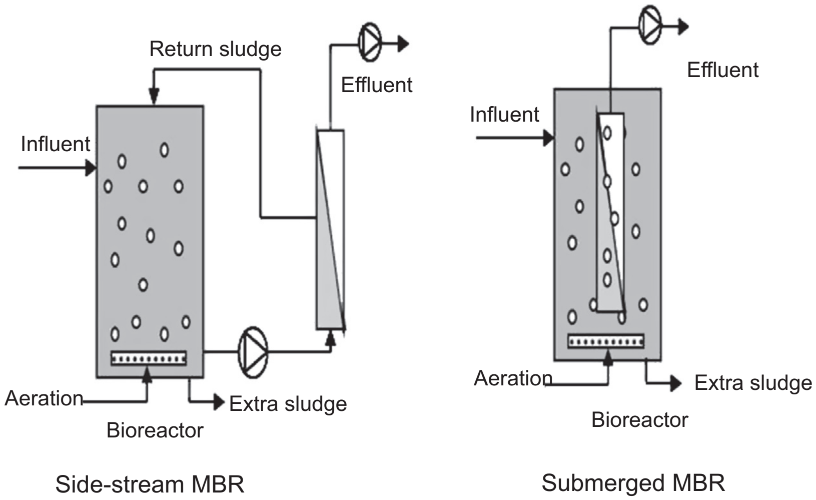

Figure 5.1 Configuration of side-stream and submerged MBRs.
Modified from Jiang (2007).

In submerged MBRs, the membrane module is directly submerged in the reactor. A suction or vacuum pump is needed to create a TMP difference for permeate production. In this case, no circulation pump is needed because cross-flow is created by aeration. This concept was first developed by Yamamoto, Hiasa, Mahmood, and Matsuo (1989) to reduce energy consumption compared with side-stream MBR configuration. In some cases (e.g. MF membrane and very low filtration fluxes), the permeate side is placed in a lower position and gravity itself is the only driving force for the filtration (Ueda & Hata, 1999).

Table 5.1 compares the side-stream and submerged MBRs. The submerged MBR has a simpler configuration because it needs less equipment. The coarse bubble aeration in the membrane tank is multifunctional. In addition to membrane fouling control, it supplies oxygen to the biological process (although the efficiency of oxygen use is low). The biggest advantage of submerged over side-stream configuration is energy savings using coarse bubble aeration instead of the high-rate recirculation pump in side-stream MBRs. The capillary and hollow-fibre membranes used in many submerged MBRs have high packing density and low cost, which make it feasible to use more membranes. However, typical tubular membranes used in side-stream MBRs have low packing density and are more expensive. Gander, Jefferson, and Judd (2000) reviewed four side-stream and four submerged MBR systems and concluded that side-stream MBRs have higher total energy cost by up to two orders of magnitude, mainly owing to the high recycle flow velocity (1—3 m/s) and head loss within the membrane module. In addition, the submerged MBRs experienced fouling and could be cleaned more easily than the side-stream MBRs (Gander et al., 2000).

However, side-stream MBRs have the advantages of more robust physical strength and more flexible cross-flow velocity control and hydraulic loading. They

Table 5.1 **Comparison of side-stream MBRs and submerged MBRs**

Parameters	Side-stream	Submerged
Complexity	Complicated	Simple
Flexibility	Flexible	Less flexible
Robustness	Robust	Less robust
Flux	High (40–100 L/m^2 h)	Low (10–30 L/m^2 h)
Fouling reducing methods	• Cross-flow • Airlift • Backwashing • Chemical cleaning	• Air bubble agitation • Backwashing (not always possible) • Chemical cleaning
Membrane packing density	Low	High
Energy consumption with filtration	High (2–10 kW h/m^3)	Low (0.2–0.4 kW h/m^3)

Source: Jiang (2007, p. 11).

are mostly used in industrial wastewater treatment and small-scale wastewater treatment plants, where influent flow rate and composition have larger variation and operational conditions are tough (e.g. high-temperature conditions) (Jiang, 2007). Furthermore, both MBR systems can be applied as aerobic (in the presence of an aeration system for the module) and anaerobic (in the absence of an aeration system for the module).

5.2.2 Membrane material types and morphology

Membrane materials and pore size are important criteria for MBR application. There are two different types of membrane materials: polymeric and ceramic. Metallic membrane filters exist, but these have specific applications that do not relate to MBR technology. To be made useful, the membrane material must then be formed (or configured) to allow water to pass through it. In MBRs, a dense MF or a loose UF membrane is often applied (average pore size around 0.5–0.05 μm).

A number of different polymeric and ceramic materials are used to form membranes, but they are nearly always composed of a thin surface layer that provides the required permselectivity on top of a more open, thicker porous support that provides mechanical stability. A classical membrane is thus anisotropic in structure, with symmetry only in the plane orthogonal to the membrane surface. Polymeric membranes are also usually fabricated to have high surface porosity, or percent total surface pore cross-sectional area, and narrow pore size distribution so as to provide as high throughput and as selective a degree of rejection as possible. The membrane must also be mechanically strong (i.e. have structural integrity). Finally, the material will normally have some resistance to thermal and chemical attacks (i.e. extremes of temperature, pH, and/or oxidant concentrations that normally arise when the membrane is chemically cleaned) and should ideally offer some resistance fouling (Judd, 2006).

In principle, any polymer can be used to form a membrane; only a limited number of materials are suitable for the duty of membrane separation, the most common of which are:

- Polyvinylidene difluoride (PVDF)
- Polyethylsulphone (PES)
- Polyethylene (PE)
- Polypropylene (PP)
- Polysulphone (PS).

The membrane materials most often used in MBRs are organic polymers, e.g. PE, PP, and PVDF (Judd, 2006). Some are blended with other materials to change their surface charge or hydrophobicity (Mulder, 1996). Ceramic materials have been shown to be suitable for MBR technology because of their thermal, chemical, and mechanical stability.

Through specific manufacturing techniques, all of these polymers can be formed into membrane materials with desirable physical properties, and each has reasonable chemical resistance (Judd, 2011). Based on the common membrane materials, the principle types of membrane are shown in Figure 5.2, which describes the typical morphology of membranes; in MBR technology, isotropic and anisotropic microporous membranes are usually applied. The two other types of membrane represent the morphology of dense membranes applied in reverse osmosis (RO) and nanofiltration (NF).

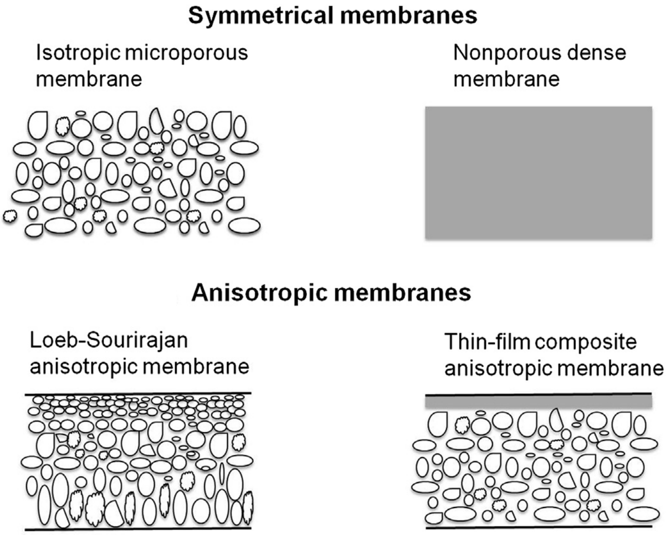

Figure 5.2 Principle types of membranes.
Modified from Baker (2004, p. 4).

5.2.3 Membrane module types

The configuration of the membrane, i.e. its geometry and the way it is mounted and oriented in relation to the flow of water, is crucial in determining overall process performance (Judd, 2011). Large membrane areas are normally required when membranes have to be applied on an industrial scale. The smallest unit into which the membranes are packed is called a module (Mulder, 1996). Three types of membrane modules, such as flat sheet (FS), hollow fibre (HF), and multi-tubular (MT), are available that are suited to MBR technologies (Judd, 2011). Two popular types of modules are shown in Figure 5.3.

Flat-sheet, capillary, and HF membranes are applied in iMBR and typical tubular membranes are used in sMBR (Gander et al., 2000). The geometric structure of a membrane is valuable if it is capable of minimizing fouling during the filtration process and if its module has good specific surface, where for ‘specific surface’ means the filtering surface per unity of occupied volume. Structural simplicity, management flexibility, and modularity are also important when deciding whether a membrane module is valuable. An important parameter often taken into account while considering the membrane filtration process is the molecular weight of the compound that can be retained by the membrane. This is called the molecular weight cutoff; it refers to the molecular weight cutoff the solute at which 90% rejection takes place and is expressed in daltons (Manigas, 2008).

5.3 Aerobic MBR

Aerobic MBR is an MBR configuration associated with aeration systems. In this regard, aeration has two functions: (1) it supplies oxygen to microorganisms in the bioreactor and (2) it scours the membrane surface to create cross-flow, which keeps

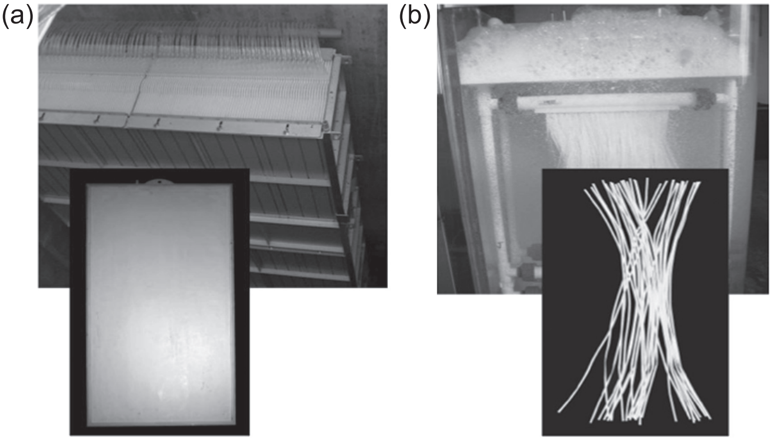

Figure 5.3 Membrane bioreactor (MBR) module types: (a) flat sheet (from Kubota, Japan), (b) hollow fibre (from Motian, China).

the membrane surface comparatively clean. Normally, air is supplied through an air diffusion system. The diffusion rate of oxygen from air to water depends on the air bubble size generated by the diffuser. Coarse air bubbles are preferred for better scouring, whereas fine air bubbles are preferred for higher oxygen mass transfer into the water phase.

5.3.1 Areas of application

Generally, aerobic MBR is applied for low- to intermediate-level strength organic load-oriented wastewater such as municipal wastewater (low organic load), industrial wastewater, and textile wastewater (organic load of intermediate level). Some aerobic MBR applications for treating wastewater are:

- Municipal wastewater
- Textile wastewater
- Agriculture wastewater
- Wastewater from slaughterhouses
- Fisheries
- Food processing industry.

According to Lesjean et al. (2009) and Zheng, Zhou, Chen, Zheng, and Zhou (2010), the growth of MBR applications in the European and Chinese markets is increasing almost exponentially (Figures 5.4 and 5.5). Figures 5.4 and 5.5 indicate that the application of MBRs in European countries is more in the industrial sectors, whereas in China it is more in the municipal field. Globally, there is also a pronounced upward trend in plant size, as well as in the diversity of technology

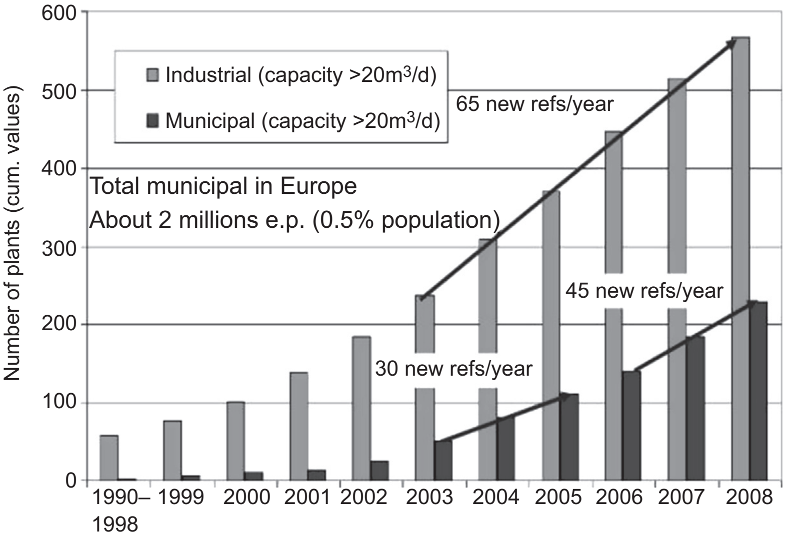

Figure 5.4 Development of industrial and municipal MBR market in Europe (Lesjean et al., 2009).

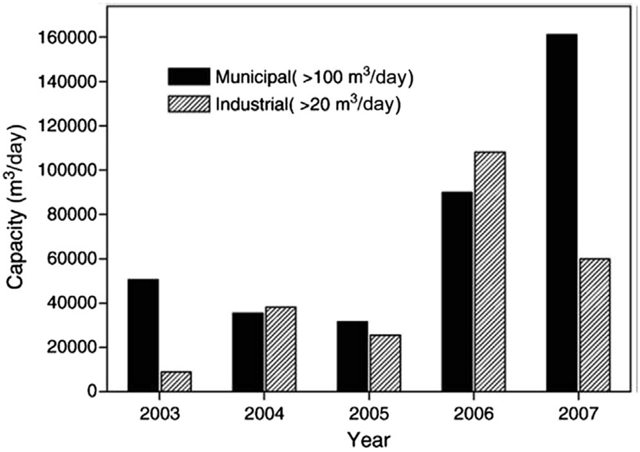

Figure 5.5 Capacity development of industrial and municipal MBR markets in China (Zheng et al., 2010).

providers - although the largest MBRs are predominantly fitted with GE Zenon Technology (Judd, 2011). In 2010, GE Zenon provided more than 40% of the total global installed capacity from MBR treatment (Judd, 2011). In 2014, the United States was the country with the largest number of large-scale MBR plants (over 50 MLD) worldwide (The MBR Site, 2014).

5.3.2 Factors affecting membrane performance

MBRs use a membrane filtration process based on pressure gradient. The process is affected by the following factors:

- Intrinsic resistance of the membrane
- TMP
- Hydrodynamic regime at the interface between the membrane and the solution to be filtered
- Fouling.

Among these factors, hydraulic geometry including microbiological aspects of MBR and fouling of the membranes are the most important.

Microbiological species of MBR are influenced by several common parameters, such as:

- Hydraulic residence time (HRT)
- Mixed liquor suspended solids (MLSS)
- Sludge retention time (SRT)
- Sludge loading (SL) or organic loading rate (OLR).

An overview of these most common influencing parameters is been provided in the following sections.

5.3.2.1 Hydraulic residence time

The HRT indicates the duration in hours that the feed solution remains in the MBR before it is processed as permeate by the membrane. The formula for HRT is

$$\mathrm{HRT\,(h)} = \frac{\text{Hydraulic volume (L)}}{\text{Permeate flow (L/h)}} \tag{5.1}$$

From Eqn (5.1), it is evident that HRT depends on the hydraulic volume of the reactor and the permeate flow. If HRT is high, it is easier for bacterial biocenosis to acclimate to reactor conditions, but low HRT affects conditions inversely.

HRT is an important operating parameter in aerobic MBR operation (Le Clech, Chen, & Faine, 2006; Meng et al., 2009). Lower HRT values result in higher OLR, which result in a reduction of reactor volumes required to achieve a specified removal performance. On the other hand, higher HRTs usually result in better removal performance. Qin, Oo, Tao, and Kekre (2007) reported that for the operation of a submerged MBR for treatment of petrochemical wastewater, the use of HRTs in the range 13−19 h results in effluents that have acceptable qualities. Chang et al. (2006) found a negligible effect of HRT in the range of 12−30 h on the removal performance of MBR used to treat the wastewater of an acrylonitrile−butadiene−styrene unit. Visvanathan, Thu, Jegatheesan, and Anotai (2005) reported similar chemical oxygen demand (COD) and pentachlorophenol removal performance at HRTs in the range of 12−24 h in an MBR used to treat synthetic wastewater. Decreased HRT has also been reported to result in an increase in the rate of membrane fouling in MBRs, although its effect seems to be mostly indirect rather than direct (Chang et al., 2006; Meng, Shi, Yang, & Zhang, 2007; Meng et al., 2009; Qin et al., 2007).

5.3.2.2 Mixed liquor suspended solids

MLSS are the concentration of suspended solids in mixed liquor, usually expressed in grams per litre (Wateronline, 2011). Mixed liquor is a mixture of raw or settled wastewater and activated sludge contained in an aeration basin in the activated sludge process. MLSS are used to control the wastewater treatment plant in the suspended growth process.

According to Lousada-Ferreira et al. (2010), MLSS are a critical operational parameter for aerobic MBR. The possibility of using high solid contents results in a reduced footprint that is considered one of the biggest advantages of MBR technology. However, the influence of MLSS on fouling is not consistent and sometimes is contradictory. MLSS concentrations have a direct impact on viscosity (Hasar, Kinaci, Ünlü, Toğrul, & Ipek, 2004; Rosenberger, Kruger, Witzig, Manz, Szewyk, & Kraume, 2002). According to Hasar et al. (2004), suspensions with higher viscosity require higher cross-flow velocities to create turbulent regimes. If the cross-flow is not enough to scour the solids away from the membrane, it is reasonable that the fouling layer will build up faster on the membrane surface.

Therefore, the theoretical explanation suggests that increasing concentrations of solids result in increasing fouling. However, some authors report no effect of solids on TMP (Harada, Momonoi, Yamazaki, & Takizawa, 1994) or permeate quality (Rosenberger, Kubin, & Kraume, 2002), and demonstrate a decrease in TMP for samples with higher MLSS concentrations (Defrance & Jaffrin, 1999; Le Clech, Jefferson, & Judd, 2003). One explanation for these apparently contradictory results is that the effect of MLSS concentration on filtration resistance varies according to the applied MLSS range in the MBR operation (Lousada-Ferreira et al., 2010).

5.3.2.3 Sludge retention time

SRT indicates how frequently sludge is taken away from the MBR. It also means the age of the sludge. Laeraa, Polliceb, Saturnob, Giordanob, and Sandullia (2009) observed a significant correlation between the SRT and the OLR. That study suggested that the biomass activity is weakly affected by the age of the sludge. Membrane cleaning requirements also appear to depend slightly on the SRT.

According to Ahmed, Cho, Lim, Song, and Ahn (2007), the SRT affects the mixed liquor characteristics and induces changes in the physiological state of microorganisms; thus, variations in membrane fouling substances such as extracellular polymeric substances (EPS) and soluble microbial products (SMP) can occur (Chang & Lee, 1998; Masse, Sperandio, & Cabassud, 2006). However, contradictory reports exist in the literature regarding the effects of SRT on membrane biofouling. Several studies demonstrated that EPS increases as SRT increases (Chang & Lee, 1998; Cho, 2004; Masse et al., 2006); others have shown the opposite trend (Lee, Kang, & Shin, 2003; Ng & Hermanowicz, 2005).

5.3.2.4 Sludge loading or organic loading rate

The SL or ratio of feed to microorganism (F/M) is an important design parameter in the MBR process. Generally, the MBR process can operate at higher F/M ratios compared with an activated sludge plant (Robinsion, 2003). It is defined as kilograms of COD divided by kilograms of MLSS times days. It can also be expressed as kilograms of COD divided by cubic metres times days.

The OLR has an important role in the treatment of wastewater by MBRs. An increased OLR decreases the filterability of the MBR. Kornboonraksa and Lee (2009) reported that an increase in influent COD, biological oxygen demand (BOD), and NH_4—N from 1150 to 2050 mg/L, 683 to 1198 mg/L, and 154 to 248 mg/L, respectively, resulted in a decrease in the removal efficiency of COD, BOD, and NH_4—N. Trussell, Merlo, Hermanowicz, and Jenkins (2006) reported increased membrane fouling with higher OLR. They reported that steady-state membrane fouling rates increased 20-fold over a fourfold increase in F/M. Khoshfetrat, Nikakhtari, Sadeghifar, and Khatibi (2011) found a reduction of COD removal efficiency from 90% to 74%, when OLR increased from 1 to 2.5 kg COD/m^3 day. Shen, Zhou, Mahendran, Bagley, and Liss (2010) reported a higher degradation of organics (glucose) of 98% at OLRs of ≤13 g COD/L day or less compared with an OLR of 30 g COD/L day, which had a degradation of about 70%.

In the biochemical stage of wastewater treatment, organic carbon and nutrients are removed from wastewater by microbes. These microbes live and grow enmeshed in EPS that bind them into discrete micro-colonies forming three-dimensional aggregated microbial structures called flocs. The ability of microorganisms to form flocs is vital for the activated sludge treatment of wastewater. The floc structure enables the adsorption of soluble substrates, but also the adsorption of colloidal matter and macromolecules found in wastewaters (Liwarska-Bizukojć & Bizukojć, 2005; Michael & Fikret, 2002). The diversity of microbial community in activated sludge is large, containing prokaryotes (bacteria), eukaryotes (protozoa, nematodes, and rotifers), and viruses. In this complex microsystem, bacteria dominate the microbial population and have a critical role in the degradation process (Michael & Fikret, 2002).

5.3.2.5 *Fouling*

When treating organic solutions (such as macromolecule solutions), the solute concentration at the membrane surface can attain a high value, and a maximum concentration (the gel concentration) may be reached. The formation of a gel layer on the membrane surface is often seen as fouling, which causes a decrease in the permeate flux or increase in TMP during a membrane process. The gel concentration depends on the size, shape, chemical structure, and degree of solvation but is independent of the bulk concentration.

Generally, membrane fouling can be caused by a variety of constituents, among which are bacteria, suspended solids, and colloids as well as dissolved inorganic and organic compounds (Hilal, Kochkodan, Al-Khatib, & Levadna, 2004). In MBRs, fouling can be attributed to pore blocking (deposition within the pores) or to cake layer formation on the membrane surface (Jiang, Kennedy, van der Meer, Vanrolleghem, & Schippers, 2003) (Figure 5.6). Colloidal and soluble foulants (SMP) can cause pore blocking and irreversible fouling because of their small size.

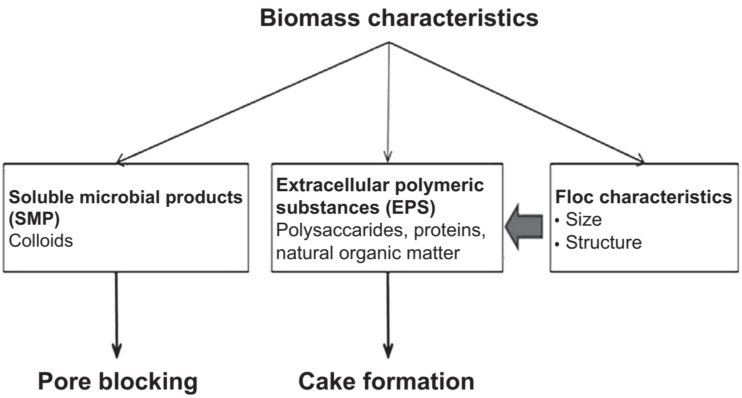

Figure 5.6 Biomass characteristics and biofouling.

5.3.3 *Case study: wastewater reuse by aerobic MBR in a commercial laundry*

In addition to municipal wastewater treatment, aerobic MBR is widely used in industrial wastewater treatment. There are a multitude of industrial sectors, such as laundry, tannery, textile, wheat starch, dairy, beverage, palm oil, and pharmaceutical (Hoinkis et al., 2012; Mutamim, Noor, Hassan, Yuniarto, & Olsson, 2013).

Several operational factors need to be considered, such as HRT, MLSS, SRT, and OLR, to achieve high water quality and high water flux (i.e. to reduce the fouling effect). The hydraulic performance indicates the productivity of the process in terms of water permeability or flux; water quality is usually expressed in terms of COD in permeate. Section 5.3.3.1 presents a typical case study on the treatment and reuse of laundry textile wastewater.

5.3.3.1 *Background*

The process applied in the case study was developed through cooperation between the Karlsruhe University of Applied Sciences and Textile Service Klingelmeyer, Darmstadt, Germany. The wastewater was treated in a two-step process and was recycled in the laundry's washing and rinsing process (Figure 5.7). After coarse screening using a vibrating sieve to retain suspended particles, the wastewater was collected in a storage tank (WW). Subsequently, the wastewater was treated in an MBR as the principal cleaning unit. Air was injected into the reactor to scour the membranes and drive the biological treatment. The MF permeate was stored in an collecting tank (TWW). It was free of turbidity and considerably reduced in microbes. Some of the MF permeate was treated in a second step by a low-pressure RO unit with spiral-wound modules to retain salts as well as organic residues. The MF and RO

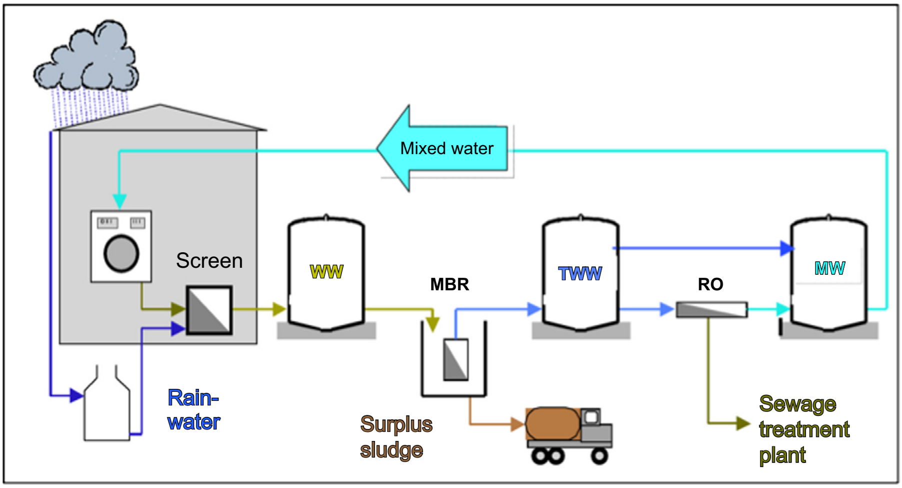

Figure 5.7 Schematic of the water reuse process (WW, wastewater; TWW, treated wastewater; MW, mixed wastewater).

permeates were mixed in a tank (MW) and were used for washing and rinsing. The ratio of mixing (RO permeate to MBR permeate) lies between 2:1 and 1:1 depending on the salt level of the MBR permeate. Before storage, the MBR and RO permeates were treated with a small amount of chlorine dioxide to prevent the growth of germs. Because rainwater did not meet the water quality criteria for the process, it was collected in the wastewater collecting tank. The integrated process generated two kinds of waste that needs to be disposed. The surplus sludge was stored in a separate tank and was collected by commercial waste management enterprises. The concentrate from the RO treatment was drained into the municipal treatment plant (Hoinkis et al., 2012).

5.3.3.2 Plant components

A commercial-scale MBR plant consists of:

- Vibrating sieve (Sweco) with a mesh size of 200 μm
- An MBR
- An RO unit
- Three storage tanks (wastewater, WW; MBR permeate, TWW; mixed MBR plus RO permeate, MW).

The MBR contained a submerged Kubota Type 510 MF plate and frame membranes (single plate: 0.8 m^2) with 0.4-μm pore size, made of chlorinated polyethylene. The MBR tank had a total volume of 126 m^3. It was separated by a barrier into two compartments connected by a spill. One compartment was designed only for biodegradation; the other was for biodegradation and membrane filtration. This gave maximum flexibility for adjusting aeration to the needs of the filtration and biodegradation process. The biomass was circulated between compartments every other day. The filtration compartment contained two double-deck Kubota stacks (System EK300) with 600 plate and frame modules (total membrane area of 480 m^2). The RO unit was fitted with six 8040 spiral-wound modules (Dow LE). The plant was composed of three collecting tanks (wastewater, MBR drain, and MBR plus RO drain), the first with an enamel steel collecting tank of 400 m^3 for wastewater and two 200 m^3 tanks for the MBR and MBR plus RO drains.

5.3.3.3 Results

The results of the case study are shown in Figures 5.8 through 5.10. Average flux was around 15 L/(m^2 h) at a permeability between 300 and 1000 L/(m^2 h bar) (Figure 5.8). After 1 year of operation without chemical cleaning, the flux was lowered to 12 L/(m^2 h) at an average permeability of 150–300 L/(m^2 h bar), as can be seen in Figure 5.9. Figure 5.10 shows the COD values in feed and permeate as well as the elimination rate over more than 2 years of operation. The feed COD started at 600–800 mg/L and increased to more than 1000 mg/L whereas the COD in permeate remained at values below 100 mg/L and the elimination rate was higher than 90%. The aeration rate in the filtration compartment of the MBR tank was 5.2 m^3/min. The biodegradation compartment was intermittently aerated by a fine diffuser at

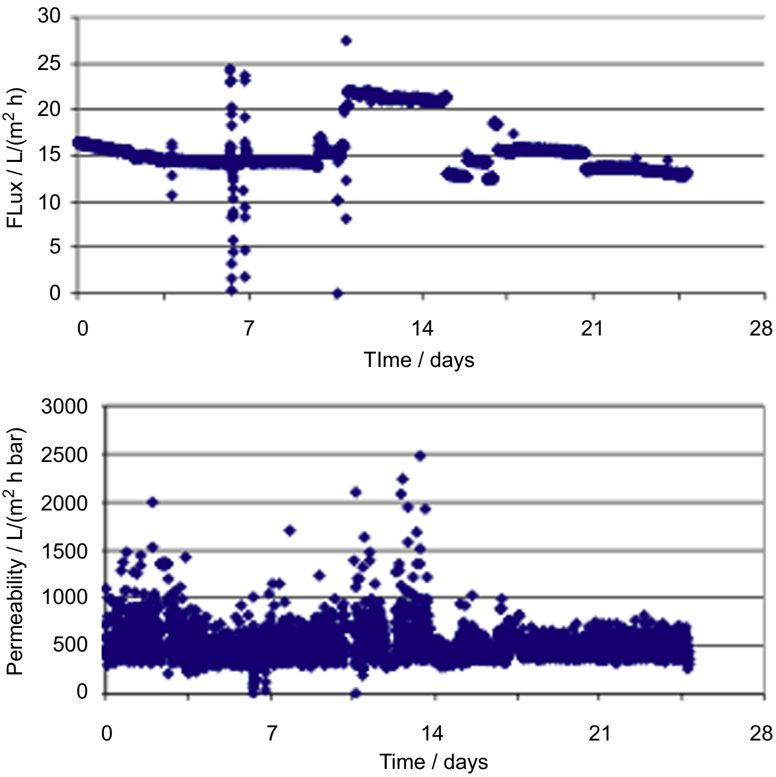

Figure 5.8 Permeate flux and permeability of the MBR treatment plant during a typical operation period of 28 days after start-up.

7.2 m^3/min. The flux rate does not represent full flow capacity; the plant was designed for an eventual flux rate of 12–15 L/m^2 h. The concentration of MLSS in the reactor increased from 3 to 10–15 kg/m^3. The COD sludge loading decreased from 0.14 to 0.04 kg COD/kg MLSS day. The average yield factor for biomass growth was calculated to 0.13 kg MLSS/kg COD degraded. The surplus sludge was collected in a storage tank and delivered to a commercial sludge processing unit.

Typical water quality parameters of the MBR unit are shown in Table 5.2, which demonstrates that the COD removal efficiency was high (94%) and the total N conversion rate was also relatively high (72%)—indications of good permeate quality.

5.4 Anaerobic MBRs

5.4.1 Areas of application

Because anaerobic digestion in wastewater treatment combines pollution reduction and energy production, it is the most interesting process for industrial effluent

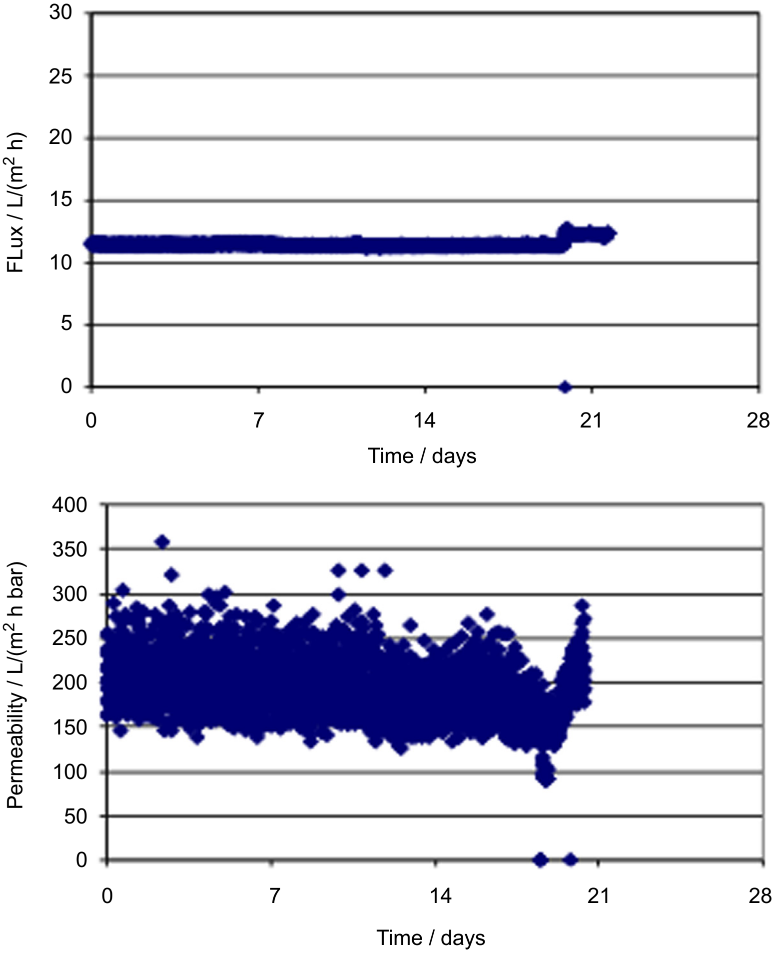

Figure 5.9 Permeate flux and permeability of the MBR treatment plant during a typical operation period of 28 days after 1 year of operation.

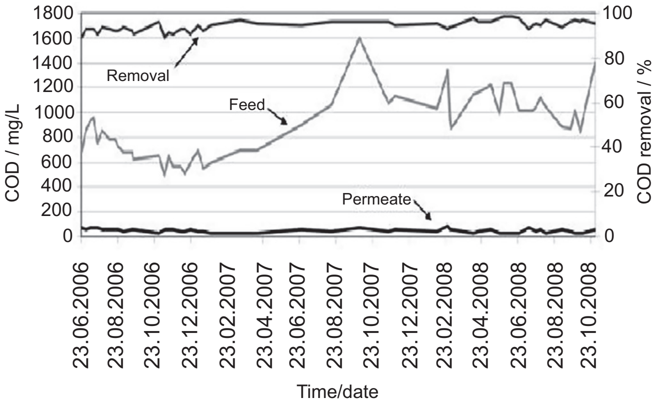

Figure 5.10 COD values in MBR feed, permeate, and COD removal efficiency.

Table 5.2 Typical water quality parameters of the MBR unit

Parameter	Unit	Feed[a] (wastewater)	Permeate[a] (microfiltrate)	Removal rate (%)
BOD_5	mg/L	390	<9	>97
COD	mg/L	1120	67	94
$N-NO_3^-$	mg/L	77	21	73
$N-NH_4^+$	mg/L	1.5	0.1	93
Total N	mg/L	160	45	72
$P-PO_4^{3-}$	mg/L	14	13	7

[a] Typically average values based on several measurements.

treatment. Historically, anaerobic processes have been mainly employed for industrial high strength wastewater and less for municipal wastewater because (1) it is difficult to retain slow-growth anaerobic microorganisms with short HRT for the treatment of low-strength wastewater and (2) anaerobic digestion rarely meets discharge standards (Lin et al., 2013).

Similar to aerobic MBRs (see Section 5.3), AnMBRs combine biodegradation with the MF and UF membrane process, which provides solid—liquid separation. The most salient features of AnMBRs compared with aerobic MBRs are no need of oxygen supply, biogas (methane) production, and lower sludge yield, which significantly lowers the operating costs.

Compared with conventional anaerobic digestion, AnMBR's most important aspect is its ability to offer complete biomass retention owing to membrane filtration. This provides sufficient SRT for the methanogens. Conventional anaerobic biodegradation shows relatively poor settling properties of the biomass and hence results in the loss of biomass into the effluent (Lin et al., 2013). In conventional systems, only the strategy of biofilm or granule formation in modern high-rate anaerobic reactors offers high biomass retention, but at the cost of a long start-up period and complex process conditions (Lin et al., 2013). Many industrial wastewater characterized by high temperature, high fat, oil, and grease content, toxicity, high salinity, or drastic changes in OLR, e.g. have a negative impact on the sludge granulation process and eventually could lead to degranulation (Dereli, Ersahin, et al., 2012). Table 5.3 compares the main features of conventional anaerobic treatment (CAT) and AnMBR treatment, in which AnMBR treatment shows better effluent quality than conventional anaerobic treatment, but also total pretreatment and complete biomass retention. Because of its benefits, such as complete biomass retention, enhanced effluent water quality, and potential net energy production, AnMBR is becoming increasingly interesting for municipal wastewater treatment (Lew, Tarre, Beliavski, Dosoretz, & Green, 2009).

Similar to aerobic MBRs, two configurations are used: side-stream and submerged (see Section 5.2.1). In a side-stream configuration, the membrane filtration module is placed outside the reactor and after filtration the biomass is recirculated into the

Table 5.3 **Comparison of conventional anaerobic treatment (CAT) and anaerobic membrane bioreactor (AnMBR)**

Feature	CAT	AnMBR
Organic removal efficiency	+	+
Effluent quality	o/−	+
Organic loading rate	+	+
Sludge production	−	−
Footprint	+/o	−
Biomass retention	−	Complete
Nutrient requirement	−	−
Alkalinity requirement	+ For certain industrial streams	+/o
Energy requirement	−	−
Temperature sensitivity	−/o	−/o
Start-up time	2−4 months	<2 weeks
Bioenergy recovery	Yes	Yes
Mode of treatment	Primarily pretreatment	Total or pretreatment

++, Excellent; +, high; o, moderate; −, low/poor.
Modified from Lin et al. (2013).

reactor. This offers high fluxes, but at the cost of frequent cleaning and high energy consumption, around 10 kW h/m^3 (Le Clech et al., 2006).

In addition, high cross-flow velocity has a negative impact on biomass activities (Choo & Lee, 1996; Ghyoot & Verstraete, 1997). In submerged MBR, the membranes are placed inside the reactor. Because air cannot be used to provide cross-flow on the membranes, as in aerobic MBR, maintaining high permeability is more difficult in AnMBRs. In many cases, gas sparging with generated biogas is used to scour the membranes (Smith, Stadler, Love, Skerlos, & Raskin, 2012). Most laboratory research or small-scale pilot trials have been conducted with side-stream AnMBRs. However, on a large or full scale, submerged systems are preferred for their lower energy consumption.

Most research work was done at laboratory and on a small pilot scale; only a few studies have been conducted with large-scale AnMBR (Dereli, Ersahin, et al., 2012). Although laboratory-scale studies provide invaluable information on treatability and membrane fouling mechanisms with scientific insight, hydraulics and shear forces acting on a small membrane module will significantly differ from a full-scale membrane module (Dereli, Ersahin, et al., 2012). Table 5.4 shows treatment performance on a large pilot and full scale for various industrial wastewaters. All of these studies used submerged membrane configurations.

Table 5.4 Treatment performance of various industrial wastewaters

	Reactor volume/m^3 temperature/°C	OLR/kg_{COD}/m^3 day	HRT/days	TSS/g/L	COD removal/%	Membrane type: Pore size Flux/L/m^2 h TMP/bar	Reference
Food processing	8700 33	1.2	29	23	99.4	Flat sheet 0.4 μm 2.5–4.2 0.03	Christian et al. (2011)
Potato processing	3.3 35	2–12	3.5–14	40	99	Flat sheet 0.4 μm 0.83–5 0.03–0.04	Singh, Burke, and Grant (2010)
Stillage from tequila production	1.3 37	4.8	12.4	–	95	Flat sheet – –	Grant, Christian, Vite, and Juarez (2010)
Snack factory	0.76 35	5.1	–	7.9–10.4	97	Hollow fibre 0.4 μm 6.5–8 –	Diez, Ramos, and Cabezas (2012)
Ethanol thin stillage	12 37	4.5–7	16	24	98	Flat sheet 0.08 μm 4.3 ± 1.1 0.1–0.2	Dereli, Urban, et al. (2012)

Modified from Dereli, Urban, et al. (2012).

5.4.2 Factors affecting performance

Regarding aerobic MBRs, membrane fouling presents one of the main bottlenecks for AnMBR application (Dereli, Ersahin, et al., 2012). Because of the fouling of organic and inorganic compounds, permeate flux through the membrane can be significantly reduced. Compared with aerobic MBRs, AnMBRs show lower permeate fluxes as a result of less flocculation of the sludge and hence increased concentrations of fine particles and colloidal solids at the membrane surface. Cake layer formation was identified as the most important fouling mechanism in AnMBRs (Dereli, Ersahin, et al., 2012).

5.4.2.1 Temperature

Regarding process temperature, anaerobic digestion basically falls into one of the following categories (Rajeshwari, Balakrishnan, Kansal, Lata, & Kishore, 2000): psychrophilic (0–20 °C), mesophilic (20–42 °C), or thermophilic (ca. 42–75 °C). In AnMBRs, a higher temperature can increase membrane flux owing to reduced viscosity and higher membrane permeability. This is advantageous for lowering energy requirements. With lower sludge viscosity, lower shear rates will be required to obtain the same shear stress (Jeison & van Lier, 2006). Because of higher membrane permeability, the same water flux can be achieved at a lower TMP (Smith et al., 2012). Higher temperatures in thermophilic operations proved to be advantageous only in short-term experiments; in the long-term they were disadvantageous (Jeison & van Lier, 2007).

Jeison and van Lier (2007) showed that permeate water flux in a thermophilic operation was two to three times lower compared with water flux in a mesophilic operation. Hence, it was concluded that in the long-term adverse temperature, effects on the properties and composition of the sludge were more important than the beneficial influence of membrane filtration. These findings are in line with the results of Lin et al. (2009), who investigated the influence of sludge properties on membrane fouling in submerged AnMBRs treating kraft evaporation condensate. The AnMBRs were operated under similar hydrodynamic conditions and MLSS concentrations under both mesophilic and thermophilic conditions. In the long-term, the permeate water flux of the mesophilic system was significantly higher than that for the thermophilic system (7.4 L/(m^2 h) versus 1.8 L/(m^2 h), respectively) (Lin et al., 2009). This was attributed to the increased formation of small particles under thermophilic conditions, which resulted in a more compact and less porous cake layer on the membrane in the case of thermophilic operation. In addition, Lin et al. (2009) found that the concentration of bound EPS and protein in the cake layer was higher under thermophilic conditions, which might be because of the increased decay rate of bacteria at elevated temperatures. Furthermore, the permeate water quality of the mesophilic system was considerably better than that of the thermophilic reactor.

5.4.2.2 Organic loading rate

In theory, a high OLR and short HRT can be employed in AnMBRs. However, OLR should always be evaluated together with SRT and sludge activity (Dereli, Ersahin, et al., 2012). A variety of experimental studies carried out up to very high OLR still showed high COD removal efficiency. Treatment of simulated wastewater from the petrochemical industry demonstrated high COD removal efficiency at OLR up to 25 kg COD/m^3/day (van Zyl, Wenzel, Ekama, & Riedel, 2008). Similar high treatment efficiency has been shown for slaughterhouse and palm oil wastewater as well at ORL up to 13.3 and 11 kg COD/m^3/day, respectively (Abdurraham, Rosli, & Azhari, 2011; Saddoud & Sayadi, 2007).

5.4.2.3 Hydraulic residence time and SRT

The performance of AnMBR and membrane fouling is affected by HRT and SRT. Generally speaking, a low HRT is preferred because it reduces tank volume, and hence the overall footprint of the system. A high SRT is required to achieve better treatment performance, especially at lower temperatures (ÓFlaherty, Collins, & Mahony, 2006). However, increasing the SRT causes higher SMP and EPS production and results in a higher propensity for membrane fouling. Moreover, increasing the SRT under constant HRT increases the biomass concentration, resulting in lower permeate flux (Smith et al., 2012). A variety of publications are concerned with the study of treatment performance on HRT. An insignificant decrease in COD removal efficiency (ca. 5%) was observed by Hu and Stuckey when they studied the treatment of simulated domestic wastewater at mesophilic temperatures (35 °C), lowering HRT from 48 h down to 3 h (Hu & Stuckey, 2006). Even at an HRT of 3 h, COD removal efficiency was higher than 90%. Several other studies similarly concluded that HRT had little effect on AnMBR permeate quality (Smith et al., 2012). Those studies suggested that adequate AnMBR performance may be obtained at relatively short HRTs even at lower temperatures, but that a lower limit on HRT may exist primarily owing to concerns regarding membrane fouling (Smith et al., 2012). For AnMBR, SRT is an easily controllable operational parameter because membrane separation allows complete retention of biomass. Huang et al. studied low-strength domestic wastewater and observed better treatment performance at a longer SRT, but at the cost of increased membrane fouling as a result of higher biomass concentrations and SMP production (Huang, Ong, & Ng, 2011). Despite this, many publications observed that EPS is a major contributor to direct fouling. However, the role of EPS quantity and characteristics in membrane fouling as a function of SRT is not well understood in AnMBRs (Smith et al., 2012).

5.4.2.4 Membrane properties

Fouling in AnMBRs is very much affected by membrane properties such as materials, pore size, and surface characteristics. Although hydrophobic membrane materials are more durable under harsh chemical and thermal conditions, hydrophilic membranes are typically favoured because they are less prone to fouling (Dereli, Urban, et al., 2012). Membrane materials used for AnMBRs can be classified into three major categories: ceramic, metallic, and polymeric. In early experimental studies, ceramic was the most widely used material for AnMBRs. (Lin et al., 2013). In AnMBRs, metallic membranes have also been applied because of their better hydraulic performance, better fouling recovery, and better tolerance to oxidation and high temperature (Kim & Jung, 2007; Zhang et al., 2005). However, because of economic constraints in commercial applications, cheaper polymeric materials have gained more interest. Typically, materials such as PVDF, PES, PE, and PP are applied with pore sizes in the MF or UF range (0.03−1 μm) and in hollow fibre, flat sheet, or tubular configurations. In general, preferred polymeric membrane materials for MBRs are PVDF and PES, which account for around 75% of total products on the market including 9 of the 11 commercially most important products (Santos & Judd, 2010). Because of the high fouling propensity, modification of the hydrophobic membrane surface by hydrophilic coating is a main goal in reducing fouling propensity. Choo et al. (2000) modified the surface of an organic membrane by grafting with 2-hydroxyethyl methacrylate (HEMA), which resulted in 35% flux increase. A 13.5% flux increase was reported by Sainbayar, Kim, Jung, Lee, and Lee (2001), who modified the surface of a PP membrane material by 70% grafting with HEMA. Kochan, Wintgens, Melin, and Wong (2009) studied surface coating via the adsorption of surfactants in which different UF flat-sheet membranes were coated with branched poly(ethyleneimine), poly(diallyldimethyl ammonium chloride), and poly(allylamine chloride) and filtered with sludge supernatant. The experiments showed lower fouling, but also low physical tolerance and chemical stability under MBR conditions. To overcome this drawback, Asatekin et al. (2006) developed a self-assembling technique by coating commercial PVDF UF membranes with the amphophilic graft copolymer PVDF−graft-polyoxyethylene methacrylate.

5.4.3 Case study: treatment of high-strength industrial wastewater using a full-scale AnMBR

Most AnMBR research has been carried out at the laboratory or small pilot scale; only a few studies have been concerned with large- or full-scale applications. Most full-scale AnMBR installations were established in Japan. Kanai reported about 14 large-scale AnMBR implementations in the food and beverage industries in Japan (Kanai, Ferre, Wakahara, Yamamoto, & Moro, 2010).

A typical case study on the treatment of high-strength industrial wastewater using a full-scale AnMBR is presented here.

The study is the first AnMBR installation in North America and the largest AnMBR installation in the world. It was built at Ken's Foods in Massachusetts (Christian, Grant, McCarthy, Wilson, & Mills, 2011).

Due to lack of space, positive economics, and the ability to provide additional capacity for flow and organic load, the system was converted from Ken's Foods' existing anaerobic process to AnMBR in July 2008. It provides waste treatment, but also a large gain in energy production from salad dressing and barbeque sauce wastewater.

The process uses Kubota flat-plate membrane cartridges (with nominal pore size of 0.4 μm) that are submerged directly into the anaerobic biomass and completely block all suspended solids from escaping to the effluent. Figure 5.11 shows a general process flow diagram of the AnMBR process.

The design of this AnMBR system has an effluent flow rate of 475 m^3/day with 39,000 mg/L COD, 18,000 mg/L BOD, and 12,000 mg/L total suspended solids (TSS), under mesophilic conditions, ensured by an average operating temperature of

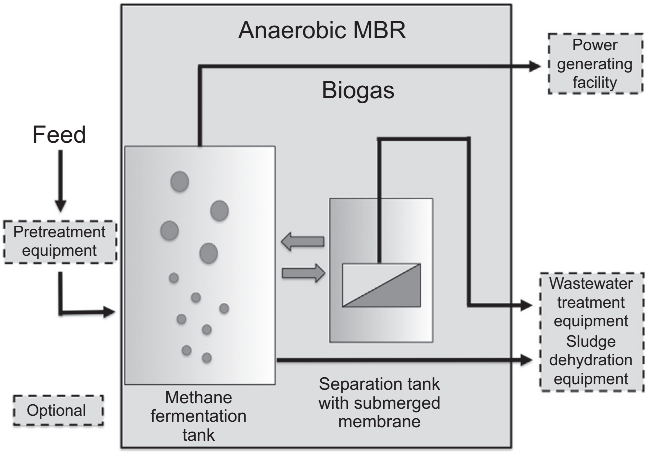

Figure 5.11 General process flow diagram of the AnMBR process.
Modified from Christian et al. (2011).

33 °C for all four anaerobic membrane tanks, a pH of 6.9 ± 0.1 for anaerobic sludge acclimatization, an operating volumetric flux rate in the range of 0.06–0.10 m^3/m^2 day, and a TMP fluctuating between 0.005 and 0.1 bar. Once the TMP reaches 0.1 bar, membrane cleaning is required (three of four membrane compartments were cleaned once during the first 20 months of operation). Table 5.5 presents the raw wastewater characteristics and average effluent quality after 20 months of running the pilot test.

In Table 5.5, this AnMBR process consistently provides an effluent with undetectable TSS concentrations and COD and BOD concentrations of 209 ± 39 and 16 ± 5 mg/L, corresponding to COD and BOD removals of 99.4% and 99.9%, respectively. By dint of biogas scouring across the membrane surface, a very low rate of membrane fouling is an important result in this study, because membrane fouling under anaerobic conditions is a considerable issue for the AnMBR process.

Table 5.5 **Raw wastewater and AnMBR effluent characteristics (July 2008 to April 2010)**

Parameter	Raw wastewater	AnMBR effluent	% Removals
Flow rate, m^3/day	300	300	–
BOD, mg/L	18,000	20	99.9
COD, mg/L	33,500	210	99.4
TSS, mg/L	10,900	<1	100
pH	–	7.05	–

Upgrading the existing anaerobic treatment system to an AnMBR demonstrated the simplicity and suitability of the process for a wastewater treatment system that previously experienced difficulty with solids management and sludge settling ability (Christian et al., 2011).

This installation at Ken's Foods can be considered an ideal technology for the development of renewable energy from waste, especially when containing a high suspended solids concentration.

5.5 Forward osmosis MBRs

The combination of FO and activate sludge treatment is a relatively new process. FO is a natural process driven by the osmotic pressure difference that retains solutes but allows water to permeate through a semipermeable membrane (Cath, Childress, & Elimlech, 2006). FO is attractive because of the high rejection efficiency of its membranes; hence, the drawback of conventional MF and UF MBRs can be overcome, which are limited in the retention of low-molecular-weight compounds (LMWC). To increase efficiency in LMWC removal, conventional MBRs need to be combined with downstream RO/NF units, which results in high capital cost and energy consumption (Alturki et al., 2010).

In FO-MBRs, treated water is drained without a pump by osmotic pressure into a draw solution with higher solute concentration than the feed solution; this results in dilution of the draw solution. Therefore, the draw solution needs to be concentrated by either mechanical (RO) or thermal processes (distillation). In doing so, the treated clean water can be drained off the system. Figure 5.12 shows a schematic of the process. FO-MBR offers the possibility of high cleaning efficiency in wastewater treatment and reuse. Achilli, Cath, Marchand, and Childress (2009) reported more than 99% of organic carbon and more than 98% of NH_4—N removal combining the biological and FO processes using flat-sheet cellulose triacetate FO membranes (Achilli et al., 2009). With this process, the draw solution is reconcentrated by RO.

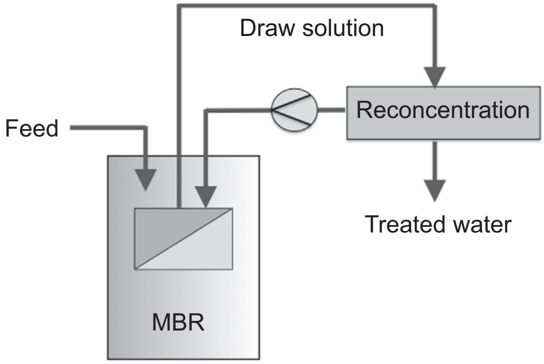

Figure 5.12 Schematic of FO-MBR system.

Most research work on FO-MBRs was conducted on the laboratory scale. There are only a few examples of larger pilot-scale studies. Quin et al. (2009) studied optimization of an FO-MBR on the pilot scale using NaCl and $MgSO_4$ salts in draw solutions. The NaCl performed at much higher efficiency than $MgSO_4$ as an osmotic agent, owing to a greater solute diffusion coefficient.

Chen et al. (2014) combined a submerged AnMBR with an FO membrane to treat synthetic low-strength wastewater. The FO-AnMBR showed greater than 96% carbon removal and 100% of total phosphorous and 62% of NH_4—N removal. This was better removal efficiency than for the conventional AnMBR. The most salient feature of FO-AnMBR is its ability to provide biogas that can be used as an energy source to drive the combined process.

5.6 Conclusion and perspectives

Over the past 2 decades, the development of MBRs has made great progress. In particular, the application of aerobic MBRs showed rapid growth in many municipal and industrial large-scale implementations. This is mainly because of their potential for recycling and reusing grey water and industrial effluents. Major improvements have been achieved for aerobic MBRs (Brepols, 2011):

- Improved module hydraulics and optimized process control helped reduce energy consumption for air scouring.
- Advances in membrane production led to improvement in materials stability and resilience, whereas market prices have come down.
- In terms of investment cost, today's MBR plants are not necessarily more expensive than comparable conventional activated sludge plants.

MBR technology is expected to grow in the near future because of the increasing scarcity of water worldwide, which makes wastewater reclamation necessary. This will be further aggravated by climate change. Based on the estimated global MBR market of US$838.2 million in 2011, the MBR market is projected to grow at an average rate of 22.4%, reaching a total market size of US$3.44 billion in 2018 (WaterWorld, 2012). The Chinese market is expected to grow at an even higher rate of 28.9%, with the key drivers of high economic growth rate, increased confidence in technology, and public awareness, as well as a strong need for wastewater reclamation (Sartorius, Walz, & Orzanna, 2013).

Besides China, the MBR market in Middle Eastern and North African countries is expected to witness a high growth trajectory in the next 5—10 years because of a large number of projects commissioned in medium and large range plants with capacities ranging between 5,000 and 50,000 m^3/day (Frost & Sullivan, 2012).

Future research and development should focus on further lowering energy demands (operating costs) and membrane costs (capital costs), as well as FO-MBRs, because of their advantages regarding the high rejection of low-molecular-weight contaminants and their lower fouling propensity.

List of abbreviations

AnMBR	Anaerobic MBR
BOD	Biological oxygen demand
CAT	Conventional anaerobic treatment
COD	Chemical oxygen demand
EPS	Extracellular polymeric substances
FS	Flat sheet
F/M	Feed to microorganisms
HF	Hollow fibre
HRARs	High-rate anaerobic reactors
HRT	Hydraulic residence time
iMBR	Immersed MBR
LMWC	Low molecular-weight compounds
MBR	Membrane Bioreactor
MF	Microfiltration
MT	Multi-tubular
MLD	Million liter per day
MLSS	Mixed liquor suspended solids
MW	Mixed wastewater
OLR	Organic loading rate
PCP	Pentachlorophenol
PE	Polyethylene
p.e.	Population equivalent
PP	Polypropylene
PES	Polyethylsulphone
PS	Polysulphone
PVDF	Poly vinylidene difluride
RO	Reverse osmosis
SL	Sludge loading
SMP	Soluble microbial products
sMBR	Side-stream MBR
SRT	Sludge retention time
TMP	Transmembrane pressure
TSS	Total suspended solids
TWW	Treated wastewater
UF	Ultrafiltration
WW	Wastewater

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Advances in electrodialysis for water treatment

6

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6.1 Introduction

Electrodialysis is a membrane process driven by a difference in electrical potential over a membrane stack, in which charged compounds are removed from a feed solution. It is a process with a relatively long history, with several papers published in the 1950s on applications such as the demineralization of sugar solutions (Anderson & Wylam, 1956), desalination (Dewhalley, 1958), and protein separation (Laurence, 1956), which are still among applications of interest more than half a century later. What is remarkable is that although the direction has not substantially changed, the interest in electrodialysis has boomed during the past decade. The number of publications on electrodialysis has doubled in 10 years and has increased by a factor of 10 in 30 years. Moore's law seems to be valid for electrodialysis as well. This is partly the result of the global tendency to publish more and more papers, not necessarily of higher or even the same quality. Nevertheless, it is interesting to observe the changes in research interest over the years. The most conservative conclusion from the numbers is that electrodialysis has remained a process of particular interest in terms of its potential for separation as well as in terms of applications over 6 decades. It was already considered a mature process in 1972 (Solt, 1972) and it is not surprising that the research topics have only partially shifted since the early days. Scaling problems, for example, were reported in one of the earliest publications on electrodialysis (Cooke, 1958) and are still on the research agenda today. Examples include the development of pretreatment methods such as pre-softening with a pellet reactor (Tran, Jullok, Meesschaert, Pinoy, & Van der Bruggen, 2013) and the use of electrochemical processes to remove scaling from membranes (Zaslavschi, Shemer, Hasson, & Semiat, 2013). The separation of proteins was already understood in earlier days to have potential (Laurence, 1956), although the breakthrough in this area came much later; many applications today are in the dairy industry for whey protein concentration, milk protein standardization, etc. (Daufin et al., 2001). Applications and methods, however, are much more advanced today. Electrodialysis with ultrafiltration membranes, for example, allows for advanced separation of peptides by exploiting the combined effect of charge and size separation by fine-tuning the pH and cutoff of the membrane (Firdaous et al., 2009; Roblet, Doyen, Amiot, & Bazinet, 2013). Electrodialysis in that context would touch the performance of a nanofiltration membrane, although the potential for specific separations is different (Langevin, Roblet, Moresoli, Ramassamy, & Bazinet, 2012). Coupling nanofiltration and electrodialysis (with

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ultrafiltration membranes) in a single process line would optimize the overall separation performance and allow the production of more specific peptide fractions. The principle of electrodialysis can be further extended in view of the improved separation of peptides. In the electrophoretic membrane contactor, a porous membrane is used to establish contact across two flowing liquids between which an electrically driven mass transfer takes place (Galier & Roux-de Balmann, 2011).

In terms of applications, comparison with the early days yields more surprises. Urine separation is currently a topic of considerable interest. Historically, the use of electrodialysis for salt separation was described in 1960 in a publication that appeared in *Nature* (Wood, 1960). At that moment, it did not attract much interest (it was cited an impressive three times), but today, urine separation has been revived. Scientific interest has shifted and the separation needed today is more challenging than only the removal of salts: the focus is rather on recycling of nutrients, while micropollutants should be kept out of the eventual product (Pronk, Biebow, & Boller, 2006). Electrodialysis is probably a critical process to achieve this, although none of the processes suggested for urine separation including electrodialysis have so far advanced beyond the laboratory stage; a combination of solutions may be needed to meet the requirements (Maurer, Pronk, & Larsen, 2006). A combination of electrodialysis, precipitation, and evaporation has perspectives of application in developing countries; this can be linked to local business development, which is an important prerequisite for the implementation of new technologies in developing countries (Pronk & Kone, 2009).

Despite the continuous presence of electrodialysis on the separations scene, it is by no means a static process. Apart from the logical shift in attention for various applications, the main advances in electrodialysis are related to the breakthrough of electrodialysis with bipolar membranes (which allows for integrated reactions, in situ combination of fermentation and electrodialysis, and, in general, the conversion of salts to their corresponding acids and base, in a wide range of applications), and the use of non-classical membrane materials and configurations for advanced separations. These are described in more detail in this chapter. Other advances are the integration of electrodialysis with traditional unit operations and other membrane separations in the chemical, biochemical, food, and pharmaceutical industries (Xu & Huang, 2008), the development of reverse electrodialysis to capture renewable energy from mixing salt and freshwater (Vermaas et al., 2013), and ionic liquid–assisted electrodialysis for concentrating, acidifying, and removing organic salts from aqueous solution (Lopez & Hestekin, 2013) or for the selective recovery of lithium from seawater (Hoshino, 2013).

In addition, even after over half a century, the fundamental understanding of all phenomena related to electrodialysis is still a point of attention. For example, mechanisms for overlimiting current and concentration polarization are not yet well understood, and only recently was a first-principles model involving the Nernst–Planck–Poisson equations fully coupled with the Navier–Stokes equations proposed (Urtenov et al., 2013). At the same time, the leaky membrane model was proposed as a simplified model based on the Nernst–Planck equation (Dydek & Bazant, 2013). Other efforts aim to translate the process fundamentals to a simulation model (Tanaka, 2013), which surprisingly has not yet converged for electrodialysis. To understand the flow in an electrodialysis stack, computational fluid dynamics can be used (Tamburini, La Barbera, Cipollina, Ciofalo, & Micale, 2012).

This chapter describes the fundamentals of electrodialysis in brief, with the aim of understanding the process principles (for a more in-depth analysis of the fundamentals, the reader is referred to the publications mentioned above), followed by a review of the advances of electrodialysis in water treatment as stated previously.

6.2 Fundamentals of electrodialysis for water treatment

Two kinds of membranes are used in electrodialysis: anion exchange and cation exchange. These two membrane types are alternated in a membrane stack so that a repeating unit is obtained consisting of a compartment with an anion exchange membrane on the left side and a cation exchange membrane on the right, followed by another compartment with an anion exchange membrane on the right side and a cation exchange membrane on the left.

Over this membrane stack, a difference in electrical potential is applied using electrodes at both ends of the stack. The feed solution is pumped through the stack. Cations migrate in the direction of the negatively charged cathode and are allowed to migrate through the first cation exchange membrane. The next membrane is an anion exchange membrane, so that the cation cannot migrate further. Anions migrate in the direction of the positively charged anode and can migrate through the first anion exchange membrane. The next membrane is a cation exchange membrane, so that the anion cannot migrate further (Figure 6.1). The membranes are in principle not permeable for water, although osmosis and electro-osmosis are known to occur in an electrodialysis stack.

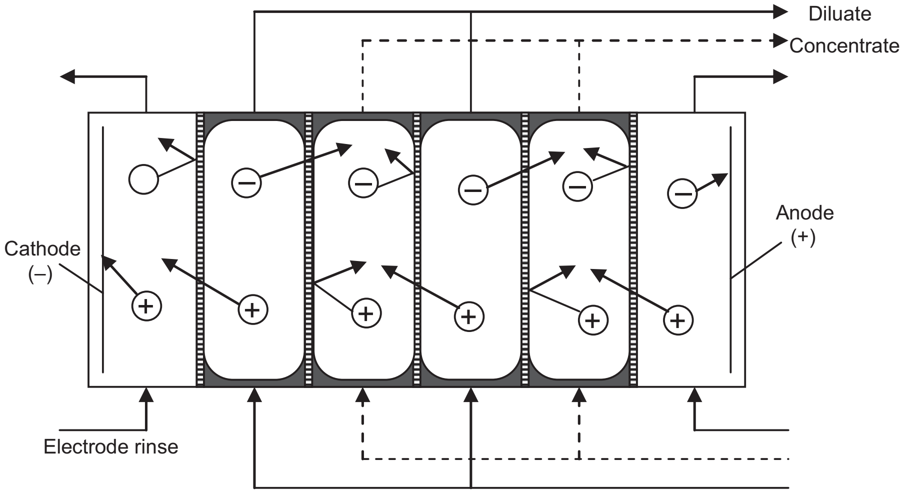

Figure 6.1 Ion migration in a salt solution through the membrane stack.

In this way, positive as well as negative ions are removed from the feed solution, whereas the neighboring compartments are concentrated.

The flow through the feed compartments is usually denoted as the diluate stream; the flow with increasing concentration is denoted as the concentrate stream.

The combination of a series of cells (consisting of an anion exchange and a cation exchange membrane, and a diluate compartment and a concentrate compartment) is necessary to decrease the time needed to purify a given stream (in a batch configuration with recycling) or decrease the size of the membranes in the system (in a flow-through system).

Because of the flow of ions through the stack, the electrical current is transferred. The extent to which the electrical current is effectively used for migration of ions that should be removed determines the efficiency of electrodialysis.

Apart from the diluate and concentrate flow, an electrode rinse solution is generally applied. The electrodes are positioned in separate compartments to protect the electrode material. At the cathode, hydrogen gas and hydroxyl ions may be formed owing to the dissociation of water (after application of a voltage). The hydroxyl ions may possibly damage the electrode when the electrode material is not carefully selected. An acid is usually added to the rinse liquid of the cathode to prevent damage.

At the anode, the electrode material is at risk because of the formation of metal oxides at the electrode surface (corrosion), which can then dissolve in an acid environment. Possible materials with sufficient resistance are graphite, stainless steel, nickel alloys, or a Platinum coating. Reactions with a metal M are:

$$\mathrm{M} + x\mathrm{OH}^- \Leftrightarrow \mathrm{M(OH)}_x + x\mathrm{e}^-$$

$$2\mathrm{M} + 2x\mathrm{OH}^- \Leftrightarrow \mathrm{M_2O}_x + x\mathrm{H_2O} + 2x\mathrm{e}^-$$

Because of the consumption of OH^-, hydrogen ions are left, which make the solution more acidic. This dissolves metal ions:

$$\mathrm{M(OH)}_x + x\mathrm{H}^+ \Leftrightarrow \mathrm{M}^{x+} + x\mathrm{H_2O}$$

$$\mathrm{M_2O}_x + x\mathrm{H}^+ \Leftrightarrow 2\mathrm{M}^{x+} + x\mathrm{H_2O}$$

H_2, Cl_2, and O_2 may be formed as a result of oxidation reactions at the anode. These cause negative effects. Therefore, it is important to make sure that negative ions (such as Cl^-) do not have access to the electrode compartments. For the cathode, this is not problematic because it repels anions, but the anode needs sufficient protection. This can be achieved by using two cation exchange membranes. The electrode rinse solution usually contains SO_4^{2-}, which would not cause problems at the anode.

Membranes are often exposed to aggressive compounds. Furthermore, because of the electrical resistance, the temperature may increase. Many feed flows (e.g., surface water) contain suspended solids. These may damage the membrane as the result of friction and scouring. The chemical, thermal, and mechanical resistance of the membranes is therefore an important parameter to consider.

Between the membranes, a spacer is positioned that is usually made of a polymer (polyethylene, polyvinylchloride (PVC), or specialty polymers). The spacers provide mechanical support to the membranes. They are made in a maze configuration that ensures the membranes are not pressed onto each other. They also provide good flow dynamics by promoting turbulence.

When the membranes are brought into the solution, a chemical potential difference arises between the solution and the inner structure of the membrane. This brings ions of the same sign as the fixed ions into the membrane. These are called co-ions. For the same reason, counter-ions migrate from the membrane to the bulk of the solution. Then, a dominant charge emerges in the membrane (co-ions and fixed ions have a higher concentration and the same charge), giving rise to an electrical potential that opposes the chemical potential. This electrical potential (the Donnan potential) limits the co-ion concentration in the membrane and the removal of counter-ions from the membrane.

When the electrical potential difference is applied over the electrodes, a current will arise in which the counter-ions and co-ions take part. Mainly counter-ions are transported, because their concentration is higher.

This also demonstrates that there cannot be an ideally selective membrane, because transport of ions always starts with the transport of co-ions. The co-ion concentration in the membrane is never zero at the startup. This selectivity is described by the permselectivity and therefore also by the transport number.

The selectivity of ion exchange membranes for anions or cations is related to the charge, which is in turn due to the presence of specific functional groups. Anion exchange membranes contain positively charged groups (typically quaternary ammonium salts) that attract anions. Cations, on the other hand, are repelled. Cation exchange membranes contain negatively charged groups (sulfonic acid or carboxylic acid groups) that attract cations. Anions, on the other hand, are repelled.

The selectivity of the membranes is determined by the transport number and permselectivity. A transport number of 1 for a cation exchange membrane means that it permeates all cations and retains all anions, and vice versa for an anion exchange membrane. In practice, membranes with a transport number of 0.9 are considered good.

The transport number t_i of a component c is defined as:

$$t_{\mathrm{c}} = \frac{j_{\mathrm{c}}}{i} \tag{6.1}$$

where j_{c} is the ion flow density and i is the current density.

The permselectivity P_+ is: $$P_+ = \frac{\bar{t}_+ - t_+}{1 - t_+} \tag{6.2}$$

where $\bar{t}_+$ is the value in the middle of the membrane. The permselectivity is concentration dependent; when the concentration in the electrolyte solution is high, more co-ions end up in the membrane.

The electrical resistance of a membrane largely determines the current losses occurring in the stack. The lower this resistance is, the less the temperature in the stack will increase, and therefore the fewer losses will occur. Thus, the electrical resistance of the membranes should be kept as low as possible to limit losses, because the resistance of the flows through the stacks cannot be changed. The order of magnitude of the electrical resistance of a membrane is 2−10 ohm/cm^2.

When the electrical potential of the process is increased, the current density increases as well. More ions are transported. This may lead to a total depletion of ions in the boundary layer at the diluate side of the membrane. Then the current density cannot increase further because no ions are left to transport the electrical current. This is called the *limiting current density*. At this point, the efficiency of the process has become low. The electrical energy is consumed to split water into its ions, which can transport the electrical charge and maintain the potential difference and current density. The electrical resistance has enormously increased. It is important not to exceed this limiting current density. The limiting current density can be determined experimentally using the method of Cowan and Brown, which involves measuring electrical resistance R as a function of the reciprocal current, I^{-1} (Figure 6.2). The intersection of the two lines tangential to the legs of the curves determines the limiting current (from which the limiting current density can be calculated).

Another phenomenon that may occur is back-diffusion. This occurs when the driving force of the concentration difference between the diluate and the concentrate compartment has increased so much that ions diffuse from the concentrate compartment back to the diluate compartment, against the electrical flow. This should be taken

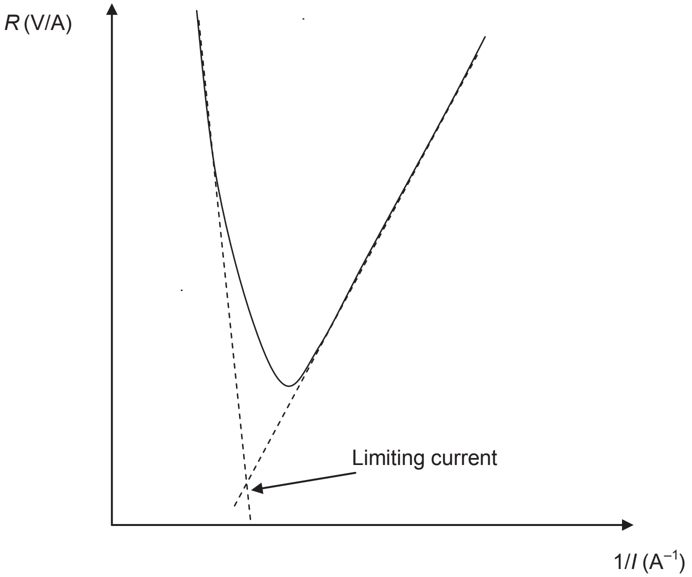

Figure 6.2 Determination of the limiting current and the limiting current density in electrodialysis.

into account when applying concentrated solutions to an electrodialysis unit. Electrodialysis allows one to obtain a concentration factor up to ca. 200–250.

At the diluate side, the ion concentration in the boundary layer (close to the membrane) is lower than in the bulk of the flow. At the concentrate side, the ion concentration in the boundary layer (close to the membrane) is higher than in the bulk of the flow. This is the result of diffusion. Both concentrations can be calculated as:

$$c_{\mathrm{m}} = c_{\mathrm{b}} - \frac{\left(t^{\mathrm{m}} - t^{\mathrm{bl}}\right)\cdot i\cdot \delta}{z\cdot F\cdot D}\,(\text{for the diluate side}) \tag{6.3}$$

$$c_{\mathrm{m}} = c_{\mathrm{b}} + \frac{\left(t^{\mathrm{m}} - t^{\mathrm{bl}}\right)\cdot i\cdot \delta}{z\cdot F\cdot D}\,(\text{for the concentrate side}) \tag{6.4}$$

The limiting current density in the boundary layer can be calculated from (e.g., at the diluate side):

$$i_{\mathrm{lim}} = \frac{z\cdot D\cdot F\cdot (c_{\mathrm{b}} - c_{\mathrm{m}})}{\delta\cdot \left(t^{\mathrm{m}} - t^{\mathrm{bl}}\right)} \tag{6.5}$$

where c_{b} is the bulk concentration of the solute at a distance δ from the membrane; c_{m} is the concentration of the solute near the membrane; F is the Faraday's constant (96,487 C/mol); D is the diffusion coefficient (m/s); z is the valence of the ion; δ is the thickness of the boundary layer (m); t^{m} is the transport number of the ion in the membrane; and t^{bl} is the transport number of the ion in the boundary layer

The limiting current density is reached when c_{m} goes to zero. The above equation for the current density for $c_{\mathrm{m}} = 0$ (limiting current density) is:

$$i_{\mathrm{lim}} = \frac{z\cdot D\cdot F\cdot c_{\mathrm{b}}}{\delta\cdot \left(t^{\mathrm{m}} - t^{\mathrm{bl}}\right)}$$

It has been experimentally demonstrated that the limiting current density of a solution increases linearly with temperature.

$$i_{\mathrm{lim}} = A + \varphi\cdot T$$

where A is the limiting current density (i_{lim}) at 0 °C; T is the temperature; and φ is the temperature coefficient for the limiting current density.

A and φ are constants for a given concentration and a given species. The concentration dependency for a given compound is linear as well.

The temperature in the stack increases during electrodialysis, so that during the process the limiting current density increases. The flow velocity also increases the maximal current.

Membrane fouling, however, will decrease the limiting current density. All of this should be taken into account to ensure that the limiting current density is not exceeded.

The limiting current density of the cation exchange and anion exchange membranes for a solution with a single salt is not necessarily the same. It is only the same when the cation and the anion have the same transport number. If not, the transport number of the cation is usually smaller than that of the anion, and in that case, the limiting current density will first be attained at the cation-selective membrane. In the $R{-}I^{-1}$ curve, two separate minima are then visible for the two types of membranes.

For solutions containing several solutes or a mixture of ions, each compound will have its own limiting current density.

6.3 Advances in membrane materials for electrodialysis for water treatment

Electrodialysis membranes are dense membranes that can be either heterogeneous or homogeneous. Heterogeneous membranes are made of an ion exchange resin, which is milled to a small grain size and then mixed with a solution of binding polymers (PVC, rubber, styrene/divinylbenzene copolymer, etc.). The ratio of resin grains and binding polymer determines the electrical and mechanical properties of the membrane. More binding polymer improves the mechanical strength, but also increases the electrical resistance. Heterogeneous membranes have a limited mechanical strength and a high electrical resistance, in general.

Homogeneous membranes are synthesized by adding ionizable functional groups to a polymeric film. The polymers that are used have to:

- induce a uniform charge distribution
- have good mechanical stability and low electrical resistance
- be cross-linked to reduce swelling when applied in water.

The more charges are introduced, the better is the conductivity, but this leads to swelling because the material becomes more hydrophilic. Cross-linking anchors the polymeric chains in the polymer by chemically linking the chains to one another; this reduces swelling.

Homogeneous membranes are thinner than heterogeneous membranes, which reduces their resistance. They are mechanically stronger because they are directly made as a film (unlike heterogeneous membranes).

The charge density of typical membranes is 1−2 mEq/g (dry polymer).

The membrane material contains functional groups that enable ion transport. The charged groups remaining on the membrane surface are the fixed ions; the ions that are dissociated from their functional group are the counter-ions. Both are hydrated when an aqueous feed is applied. Anion exchange membranes often contain quaternary ammonium groups as fixed ions; cation exchange membranes contain sulfonyl or carboxyl groups. Anion exchange membranes can be recognized by their transparent white color. Cation exchange membranes vary in color from amber-brown to white, depending on the type.

Regular ion exchange membranes are not selective. However, some anion exchange membranes have been developed with selectivity for monovalent ions (such as the

ACS series of anion exchange membranes of Eurodia Industrie S.A. (Wissous, France)). This allows for the selective removal of, e.g., nitrates compared with (divalent) sulfates. This is important to manage the total dissolved solids (TDS) of the product stream, which should not be too low for most applications including potable water, whereas nitrates should be removed to a larger extent. A typical outcome is a reduction of the nitrate concentration by 84% with a reduction in TDS by 49%. The advantage of this is that remineralization after nitrate removal is no longer necessary.

Whereas the number of ion-exchange membranes was limited until a decade ago, research efforts have resulted in a much wider range of polymeric membranes (even though these are generally not commercially available). Synthesis of anion exchange membranes includes poly(vinyltrimethoxysilane-*co*-2-(dimethylamine)ethylmethacrylate) copolymer (Chakrabarty, Prakash, & Shahi, 2013), membranes composed of 4-vinylbenzyl chloride, styrene, and ethylmethacrylate (Koo, Kwak, & Hwang, 2012), cross-linked polystyrene (Sachdeva, Ram, Singh, & Kumar, 2008), acrylonitrile/butadiene/styrene with activated carbon and silver fillers (Zendehnam, Robarmili, Hosseini, Arabzadegan, & Madaeni, 2013), and aliphatic-hydrocarbon–based anion exchange membranes prepared from glycidyl methacrylate and divinylbenzene (Tanaka, Nagase, & Higa, 2011), to name just a few. Such membranes may be applicable in other electromembrane applications such as fuel cells (Merle, Wessling, & Nijmeijer, 2011).

Cation exchange membranes include polystyrene and polyaniline blends (Amado, Gondran, Ferreira, Rodrigues, & Ferreira, 2004), heterogeneous polyvinylchloride/styrene–butadiene–rubber blends (Hosseini, Madaeni, Heidari, & Moghadassi, 2011), and monovalent selective membranes made of blends of sulfonated poly(ether sulfone) with sulfonated poly(ether ether ketone) (Gohil, Nagarale, Binsu, & Shahi, 2006). Furthermore, ceramic cation exchange membranes synthesized by impregnation of microporous ceramic supports with zirconium phosphate have been developed for aggressive wastewater applications (Marti-Calatayud, Garcia-Gabaldon, Perez-Herranz, Sales, & Mestre, 2013), and phosphotungstic acid–based membranes on graphite support intended for use as electrolyte-filled separators for batteries and super-capacitors (Seepana, Pandey, & Shukla, 2012).

This shows the large potential of various materials as anion exchange or cation exchange membranes, although commercialization today is still limited.

A bipolar membrane consists of a combination of a cation exchange and an anion exchange membrane (Figure 6.3). Between the two membranes a water film is present from which water is dissociated; the bipolar membrane is a source of anions (OH^-) as well as cations (H^+), although they end up in different compartments on both sides of the bipolar membrane.

Development and application of bipolar membranes have emerged especially in the past decade. Research on synthesis has resulted in, e.g., sulfonated polystyrene ethylene butylene polystyrene-poly(vinyl alcohol)–quaternized polystyrene ethylene butylene polystyrene bipolar membranes (Venugopal & Dharmalingam, 2013), poly(vinyl alcohol)–sodium alginate chitosan with TiO_2 and ZnO (Chen, Hu, Chen, Chen, & Zheng, 2011), and poly(vinyl alcohol)–poly(anetholesulfonic acid sodium salt) (cation selective) and poly(vinyl alcohol)–poly(diallyldiethylammonium bromide) (anion selective)

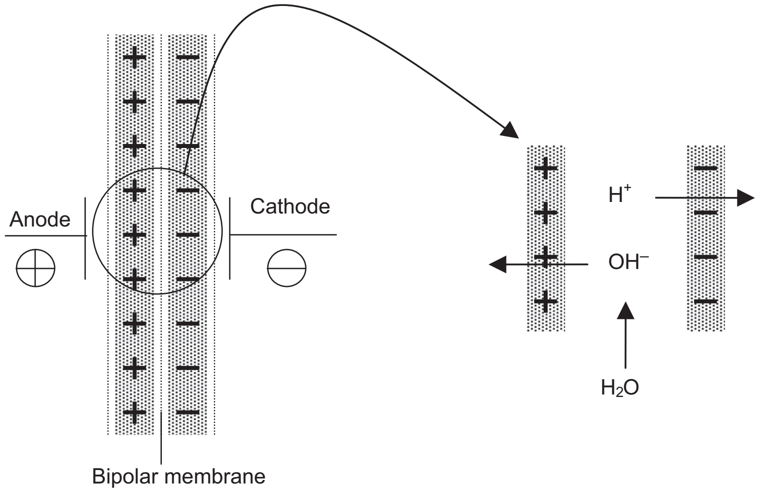

Figure 6.3 Representation of a bipolar membrane for electrodialysis.

bipolar membranes (Espinoza-Gomez, Flores-Lopez, Rogel-Hernandez, & Martinez, 2009). Several more examples can be found in the literature.

6.4 Advances in membrane modules and system configurations for electrodialysis for water treatment

The classical stacked module is still the standard configuration. Advances in module design are primarily related to the use of spacers in the stack. Spacers increase the electrical resistance, which translates into higher power consumption. Optimization of the fluid dynamics within the channels is still a problem, as demonstrated by computational fluid dynamics simulations to predict the fluid flow field inside a single channel inside an electrodialysis stack (Tamburini et al., 2012). An appropriate choice of net spacer material can influence the slip/no-slip condition of the flow on the spacer wires, thus significantly affecting the channel fluid dynamics in terms of pressure drops (Gurreri, Tamburini, Cipollina, & Micale, 2012). A conducting spacer instead of the traditional non-conducting spacer may help overcome electrical resistance (Zhang, Wang, & Goa, 2012), whereas fluid dynamics and electrical resistance may be improved simultaneously when using ion exchange membranes in which the spacer is formed directly on the membrane surface (Balster, Stamatialis, & Wessling, 2010), so that it is no longer a separate entity.

Further innovations are related to the stack configuration. The use of bipolar membranes, as described above, yields a four-compartment membrane stack, which is an extension of the classical three-compartment approach. Such configuration is also applied in selectrodialysis, a process using a four-compartment stack without bipolar

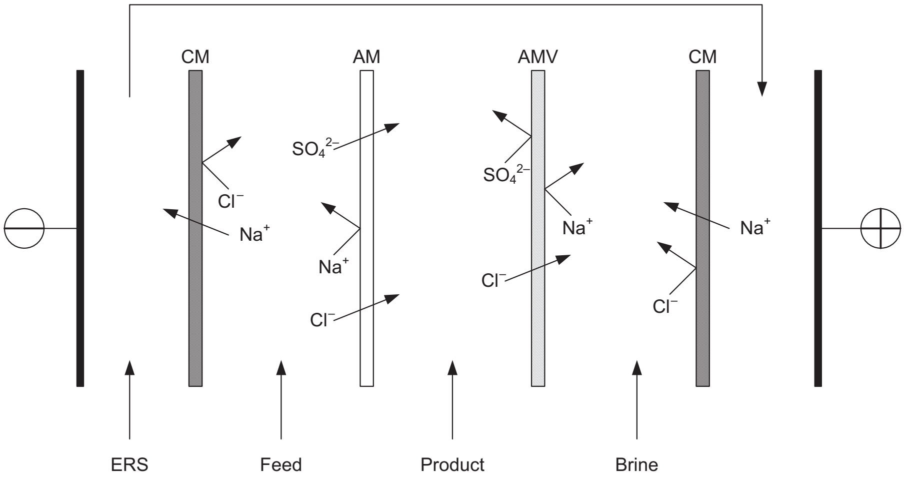

Figure 6.4 Selectrodialysis stack for ion fractionation. ERS, electrode rinse solution; CM, cation exchange membrane; AM, anion exchange membrane (nonselective); AMV, anion exchange membrane (selective for monovalent ions).

membranes but with a combination of selective and nonselective membranes to achieve fractionation of ions so that, for example, phosphates can be selectively removed from a feed stream (Zhang, Paepen, Pinoy, Meesschaert, & Van der Bruggen, 2012). This is shown in Figure 6.4.

A feed solution containing cations, monovalent anions, and divalent anions is pumped through the first compartment, which is sealed by a cation exchange membrane (CM) and an anion exchange-selective membrane (AM). The cations migrate under the influence of the applied electrical potential difference toward the cathode, passing the CM. The anions, monovalent as well as bivalent, migrate toward the anode and thus pass the AM. Thus, the solution of the middle compartment, the product, will be enriched with anions. At the same time, monovalent ions available in this product compartment migrate toward the anode, passing the AMV. This compartment is where the selection of the monovalent versus bivalent ions occurs, and is denoted as the selector. This compartment is enriched in bivalent anions; monovalent ions are removed. The third compartment (brine compartment) is enriched by the migrating monovalent anions. This process was shown to be feasible for concentrating phosphate ions selectively from wastewater (Zhang et al., 2013).

Other innovations relate to the flow through electrodialysis stacks. A co-current hydraulic flow mode of the salt solutions through the compartments of the stack is often applied, which requires a series of separation modules. This can be improved by changing the classical co-current hydraulic flow mode into a mixed flow mode, in which the internal hydraulic flow of diluate and concentrate is co-current in the stack compartments but is externally counter-current over the total series of stacks (Brauns et al., 2012).

Integrated processes may further extend the range of applications for water treatment. As an example, the separation of Co^{2+} and Ni^{2+} is discussed: two cations

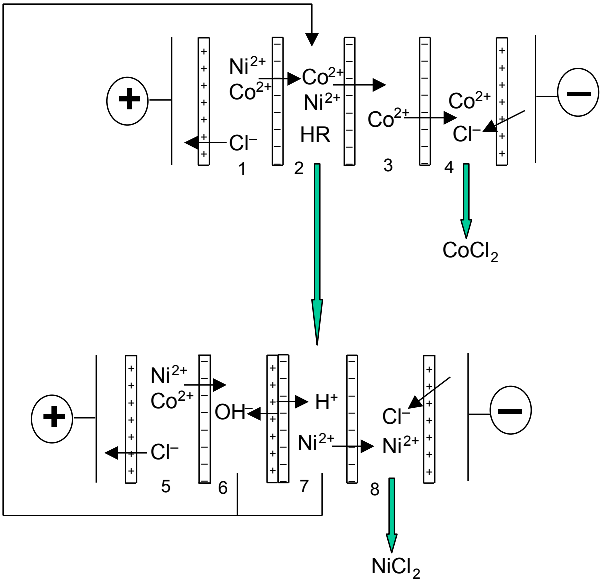

Figure 6.5 Separation of ions with the same charge and similar size using electrodialysis and electrodialysis with bipolar membranes (EDBM).

with the same charge and approximately the same size (Xu, 2001). Separation can be achieved by two electrodialysis stacks in series, the first one of which is a conventional electrodialysis unit followed by an electrodialysis unit with bipolar membranes (Figure 6.5).

A wastewater stream containing a mixture of Co^{2+} and Ni^{2+} is supplied to compartment 1. The positive ions, in this case Co^{2+} and Ni^{2+}, migrate through the cation exchange membrane to compartment 2. In this compartment, a complexing agent is present, denoted as HR. This agent selectively forms a complex with one of the two cations, according to the reactions:

$$Co^{2+} + 2R^- \overset{K_c}{\rightleftharpoons} CoR_2$$

$$Ni^{2+} + 2R^- \overset{K_c}{\rightleftharpoons} NiR_2$$

For the separation considered here, K_c is much larger for Ni^{2+} than for Co^{2+} so that only the nickel complex is formed. The cobalt ions are not complexed and can therefore migrate through the two consecutive cation exchange membranes to compartment 4. There, they combine with an anion to the corresponding metal salt. This concentrate stream contains only the cobalt salt and no nickel.

Nickel occurs now as a neutral complex in the solution and therefore cannot migrate to another compartment.

The solution in compartment 2 is fed to compartment 7 of the EDBM system. In this compartment, there is an excess of H^+ ions, so that the pH is sufficiently low for the following reaction to occur:

$$\mathrm{NiR_2} + 2\mathrm{H}^+ \overset{K_c}{\rightleftharpoons} \mathrm{Ni}^{2+} + 2\mathrm{HR}$$

At low pH, the Ni^{2+} ions are exchanged for protons and are again released. The protons come from the bipolar membrane. The free nickel ions can further migrate through the cation exchange membrane to compartment 8, where they can be separated as a metal salt.

The complexing agents from compartment 5 are recycled to compartment 2, together with the hydroxyl ions that are released in compartment 6 to increase the pH again to a neutral value. These hydroxyl ions are also generated by the bipolar membrane.

The net result is that the Co^{2+} ions accumulate in compartment 4 and the Ni^{2+} ions are collected in compartment 8.

The concentration difference between Ni^{2+} and Co^{2+} ions in the corresponding compartments can reach up to 1/20.

6.5 Applications of electrodialysis for water treatment

The dominant application of electrodialysis is still in desalination. This is a well-established application that can be readily applied. Emerging applications are therefore in (1) the use of electrodialysis for alternative feed waters, (2) ion fractionation, and (3) the use of bipolar membranes in a wide range of production or conversion processes.

A typical example of alternative feed water is concentrated brine from an reverse osmosis (RO) plant, in which electrodialysis is used as a technology to prevent damage to marine ecosystems (Jiang, Wang, Zhang, & Xu, 2014). Similarly, the concentrate resulting from RO of treated wastewater is applied to reduce the volume of salty water discharge (Zhang, Ghyselbrecht, Meesschaert, Pinoy, & Van der Bruggen, 2011). Electrodialysis was found to be a viable technology, but scaling may be a problem because of the enhanced concentration of carbonates after wastewater treatment. Industrial wastewater applications have been considered as well (Silva, Poiesz, & van der Heijden, 2013); electrodialysis is feasible in terms of the separation of monovalent and divalent ions, with energy requirements ranging from 6 to 11 kW h/m^3 of feed stream depending on the water reclamation rate.

Fractionation using electrodialysis has main applications for amino acids. Amino acids can be transported selectively across a double membrane system composed of a cation exchange and an anion exchange membrane via pH adjustment of the source phase solution (Tsukahara, Nanzai, & Igawa, 2013). Electrodialysis with commercially available ion exchange membranes was applied to isolate the basic amino acids L-lysine (Lys) and L-arginine (Arg) (Readi, Girones, Wiratha, & Nijmeijer, 2013). This has even more potential when electrodialysis is applied with ultrafiltration membranes. This was demonstrated in several applications such as the separation of a pepsin–pancreatin soy protein isolate hydrolysate (Roblet et al., 2013) and to recover and concentrate the active antibacterial fraction of a snow crab by-products hydrolysate, which is the result of a peptide with a molecular weight of about 800 Da (Doyen, Saucier, Beaulieu, Pouliot, & Bazinet, 2012). The attraction of using ultrafiltration membranes for electrodialysis applications is in the possibility of fine-tuning the separation on the basis of either charge separation or size exclusion, which allows for specific separation of charged organic compounds, typically related to peptides.

However, selective removal of other ions is also interesting. One example is the use of monovalent permselective membranes for selective removal of arsenic and monovalent ions from brackish water RO concentrate (Xu, Capito, & Cath, 2013). Monovalent permselective anion exchange membranes have high selectivity in removing monovalent anions over di- and multivalent anions. In general, transport of monovalent and divalent ions is different because of steric effects and different charge interactions; for example, a removal rate of more than 70% for monovalent ions might correspond to a removal rate below 50% for divalent ions (Silva et al., 2013). This can be exploited and optimized for, e.g., the removal of nutrients from wastewater.

The use of bipolar membranes has been considered in many studies. The most straightforward one is when concentrates from seawater desalination are used as feed. This yields a mixture of sulfuric acid and hydrochloric acid on the one side and sodium hydroxide on the other. A concentration of 1 mol/L can be obtained in realistic conditions, with a good prospect for long-term operation (Shen, Huang, et al., 2013). Similar observations were made for industrial saline water mainly composed of NaCl and KCl, which yielded an acid and a base stream with a concentration of around 2 mol/L (Ghyselbrecht et al., 2013). Bipolar membranes were used in another application on a pilot scale to recover glyphosate and the production of base/acid with high concentration in view of the zero discharge of wastewater (Yang, Gao, Fan, Fu, & Gao, 2014). Electrodialysis with bipolar membranes may be coupled with diffusion dialysis for two-step recovery, with electrodialysis as the second step to recover the remaining concentrations of acid (Zhuang et al., 2013). More applications include the production of morpholine (Jiang, Wang, & Xu, 2013); the separation of lithium and cobalt in view of the recycling of waste lithium—ion batteries, in a similar approach as described above for nickel and cobalt (Iizuka, Yamashita, Nagasawa, Yamasaki, & Yanagisawa, 2013); the production of tetrapropyl ammonium hydroxide on a pilot scale, with a perspective for full-scale industrial application (Shen, Yu, Huang, & Van der Bruggen, 2013); and the production of L-ascorbyl-2-monophosphate, a stable substitute of vitamin C (Song et al., 2012). Many more applications have been reported, which indicates the potential of electrodialysis with bipolar membranes as a versatile process. A complete overview, however, is beyond the scope of this chapter.

6.6 Future trends

Electrodialysis has been of interest for the past 5 decades, although for a limited range of applications such as the desalination of brackish water. This will not substantially change in years to come, although an increase in these applications is not expected because of competition with more cost-effective processes (at higher salt concentrations) such as RO and membrane distillation. Other applications related to selective removal of one or more ions, however, may become attractive when membrane materials are developed with better selectivity (e.g., for nitrate, specific peptides, or phosphate), or when alternative stack configurations are applied in which a fractionation effect can be obtained.

Since the turn of the century, bipolar membranes have been increasingly studied and applied. This opens up a new range of applications related to combined reaction and purification, owing to the acid—base splitting effect. Numerous applications can be based on this feature, and many more are on the agenda to be further developed in coming years. This will in turn stimulate the availability of bipolar membranes, with a further positive effect on the application market.

One question remains for electrodialysis, which is related to the sustainability of the system. Although the process is claimed to be a green technology, this may be argued from an energetic point of view, particularly when taking the exergetic value of the required electrical energy into account. Therefore, more attention to this aspect is critical. Combined systems based on renewable energy may overcome this issue, which then will allow, for example, remote applications of electrodialysis.

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Photocatalytic membrane reactors for water treatment

7

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7.1 Introduction

Heterogeneous photocatalysis is an advanced oxidation process (AOP) based on the use of a semiconductor (the photocatalyst). It has been extensively studied for about four decades, when Fujishima and Honda (1972) discovered the photocatalytic splitting of water on TiO_2 electrodes. It has been object of a large amount of studies related to environment recovery by the total degradation to innocuous substances of organic and inorganic pollutants (Hoffmann, Martin, Choi, & Bahnemann, 1995) and for synthesis (Molinari, Caruso, & Poerio, 2009; Palmisano et al., 2010). It is a discipline that includes a large variety of reactions (Molinari, Argurio, & Lavorato, 2013): partial or total oxidations, dehydrogenation, hydrogenation (e.g. hydrogen transfer), metal deposition, water detoxification, gaseous pollutant removal, bactericidal action, etc.

The main advantages of photocatalysis, making it a very promising 'green' process, consist in the mild operating conditions and the possibility to abate refractory, very toxic, and nonbiodegradable molecules (Molinari, Caruso, & Palmisano, 2010; Palmisano, Augugliaro, Pagliaro, & Palmisano, 2007). Besides, photocatalysis: (1) avoids the use of environmentally and unhealthy dangerous heavy metal catalysts by using safer photocatalysts (mainly TiO_2); (2) uses mild oxidants (O_2, in some cases from the air); (3) needs few auxiliary additives; (4) does not produce harmful chemicals; (5) offers a good alternative to the energy-intensive conventional treatment methods; and (6) can be combined with other physical and chemical technologies (e.g. membrane separations).

Because the photocatalyst is generally used as a powder suspended in a liquid medium, the catalyst-recovering step from the reaction environment is a pivotal stage in view of large-scale applications. Photocatalytic membrane reactors (PMRs) represent a promising approach to overcome this limitation. A PMR can be defined as a device existing in various configurations that combines a photocatalyst and a membrane to produce chemical transformations. A PMR improves the potentialities of classical photoreactors (PRs) and those of membrane processes with a synergy of both technologies, thus minimizing environmental and economic impacts (Molinari, Caruso, Argurio, & Poerio, 2008; Molinari et al., 2009). The membrane permits continuous operation in systems in which the recovery of the photocatalyst (immobilized or in suspension), the reaction, and the product separation simultaneously occurs, resulting in a device that is competitive with other separation technologies in terms of material

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recovery, energy costs, reduction of the environmental impact, and selective removal of the components. Higher energy efficiency, modularity, and easy scale-up are some other advantages of PMRs compared to conventional PRs.

Water treatment by removing both organic and inorganic pollutants represents the main use of the photocatalytic techniques. Water pollution, caused by hazardous organic chemicals used in industry and agriculture, is a serious problem. Environmental laws are severe, and they will become more and more restrictive in the next years. Furthermore, various directives suggest the use of green chemistry concepts and clean technologies inside the manufacturing processes to protect the environment. Traditional chemical and biological treatments (e.g. adsorption on active carbon, chemical oxidation, and aerobic biological treatments) to clean-up water often fail to remove most organic pollutants because of the high resistance of these compounds, resulting in high concentrations discharged in treated effluents. On the basis of this, in the last years, the attention of the international scientific community has been focused on the development of alternative methods. In this context, photocatalytic processes represent a promising alternative green process (Huo et al., 2013; Mozia & Morawski, 2006, 2012; Mozia, Tomaszewska, & Morawski, 2005, 2007) because, as a consequence of the highly unselective reactions involved in the photocatalytic processes, a wide range of organic pollutants can be totally degraded (i.e. mineralized) into small and harmless species (carbon to carbon dioxide, hydrogen to water, nitrogen to nitrate, etc.) without using chemicals, avoiding sludge production and its disposal.

In the pertinent literature, different studies, in which photocatalysis is coupled with pressure-driven membrane techniques such as nanofiltration (NF) and ultrafiltration (UF) for the degradation of organic pollutants, are reported (Molinari, Borgese, Drioli, Palmisano, & Schiavello, 2002; Molinari, Palmisano, Drioli, & Schiavello, 2002; Patsios, Sarasidis, & Karabelas, 2013; Zhang et al., 2013). Membrane fouling is one of the main drawbacks of these systems. On the basis of this, some authors proposed to couple photocatalysis with (1) membrane distillation (Huo et al., 2013; Mozia & Morawski, 2006; Mozia & Morawski, 2012; Mozia, Tomaszewska, & Morawski, 2007), obtaining an almost complete total organic carbon (TOC) removal, but requiring energy to activate the evaporation phenomenon; (2) dialysis (Azrague, Aimar, Benoit-Marquié, & Maurette, 2007), to mineralize organic compounds contained in artificial turbid water operating at ambient temperature; and (3) pervaporation (Camera-Roda & Santarelli, 2007; Camera-Roda et al., 2011), improving the detoxification efficiency of wastewater containing organic pollutants at low concentration levels.

In this chapter, the basic principles of photocatalysis and PMRs are reported, with the advantages related to their coupling, thanks to the synergistic effects. The importance in making a correct choice of membrane (type and material) is evidenced, discussing the choices made in literature and the criteria used for selection. Moreover, a classification of the PMRs based both on their configuration (pressurized and depressurized/submerged) and on the particular membrane separation with photocatalysis (pressure-driven membrane separation, membrane distillation, dialysis, and pervaporation) is also presented, providing evidence that the opportune choice of PMR configuration and membrane separation is a key step to limit membrane fouling.

Finally, some applications of PMRs for water treatment, in particular for pharmaceuticals removal, are reported, with evidence of the potentialities, the drawbacks, and the future trends.

7.2 Fundamentals of PMRs for water treatment

7.2.1 Basic principles of photocatalysis and types of photocatalysts and membranes

The main difference of photocatalysis compared to conventional catalysis is the photonic activation mode of the catalyst, which replaces the thermal activation (Herrmann, 2005). The electronic structure of a semiconductor is characterized by a valence band (VB) and a conduction band (CB), which are separated by an energy band gap (Eg). When a semiconductor particle is excited by irradiation with photons of energy (hν) equal or higher than its energy band gap (Eg), valence electrons (e^-) are promoted from VB to CB, thus leaving a positive hole (h^+) in the VB. For semiconductor TiO_2, this step is expressed as:

$$TiO_2 + h\nu \rightarrow TiO_2\left(e^- + h^+\right) \tag{7.1}$$

In the absence of suitable electron and/or hole scavengers, the photo-generated electrons and holes can recombine in bulk or on the surface of the semiconductor within a short time, releasing energy in the form of heat or photons. Electrons and holes that migrate to the surface of the semiconductor without recombination can reduce and oxidize, respectively, the substrates adsorbed on the semiconductor. A schematization of both the photonic activation of the photocatalyst and the photocatalytic oxidation and reduction reactions that take place onto a photo-activated semiconductor particle is reported in Figure 7.1.

The process in Figure 7.1 can be divided in four steps:

1. Absorption of light followed by the separation of the electron—hole couple;
2. Adsorption of the reagents;
3. Redox (reduction and oxidation) reaction;
4. Desorption of the products.

The redox reactions involving the species adsorbed onto the semiconductor surface occur only if the potentials of the redox couple to which the substrates belong (E_1^0, E_2^0) are compatible with both the VB and CB potentials (E_{VB}, E_{CB}). In particular, the redox potential of the species to be oxidized, E_2^0, should be less positive than E_{VB}, so that the photo-produced holes h^+ can oxidize the reduced form of this species ($red_2 \rightarrow ox_2$, see Figure 7.1). At the same time, the redox potential of the species to be reduced, E_1^0, should be more positive than E_{CB}, so that the photo-produced electrons e^- can reduce the oxidized form of this species ($ox_1 \rightarrow red_1$, see Figure 7.1). Only if both $E_2^0 < E_{VB}$ and $E_1^0 < E_{CB}$ conditions are met, both reduction and oxidation are thermodynamically favoured, and the overall photocatalytic process takes place.

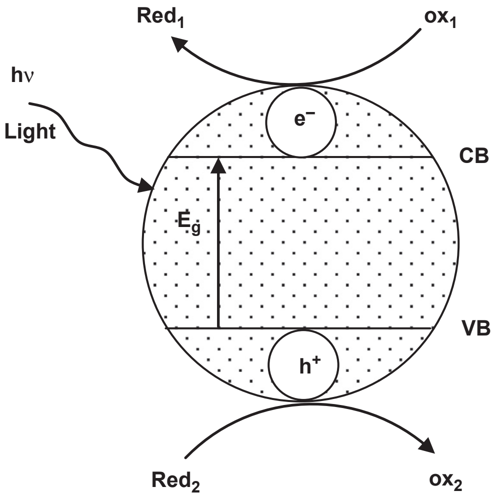

Figure 7.1 Schematization of the photocatalytic process that occurs on a photo-activated semiconductor particle. ox_1, red_1, ox_2, and red_2 represent, respectively, the oxidized and the reduced species of two different redox couples, indicated as 1 and 2.

The redox reactions that take place onto the semiconductor surface represent the basic mechanisms of photocatalytic water/air purification and photocatalytic hydrogen production/substrate hydrogenation, respectively. In the VB, photo-generated holes can oxidize surface hydroxyl groups into hydroxyl radical in the aqueous reacting environment:

$$OH^- + h^+ \rightarrow OH\bullet \tag{7.2}$$

As widely accepted, hydroxyl radicals are the primary oxidants that attack the substrates to be degraded by reducing them to their elemental form.

In the CB, photo-promoted electrons can reduce the molecular oxygen dissolved in the aqueous phase to superoxide radical, metal ions to their lower oxidation states or H^+ ions to $H\bullet$:

$$O_2 + e^- \rightarrow \bullet O_2^- \tag{7.3}$$

$$Me^{n+} + e^- \rightarrow Me^{(n-1)+} \tag{7.4}$$

$$H^+ + e^- \rightarrow H\bullet \tag{7.5}$$

The so-generated hydrogen radicals can follow two main fates: combination for H_2 production or hydrogenation of adsorbed substrate.

Thanks to (1) the favourable energetics of its band structure, (2) its relatively high quantum yield, (3) its stability under irradiation, and (4) its low cost and availability, TiO_2 represents the archetypical photocatalyst, a virtual synonym for photocatalysis.

Nevertheless, this material does not present photo-response under visible light illumination because of its wide band gap, taking advantage of only less than 6% of the solar energy. Thus its potential as a green technology cannot be entirely fulfilled. Consequently, in the last years, a great number of new photocatalysts have been synthesized and tested as possible alternatives to TiO_2 (Di Paola, García-López, Marcì, & Palmisano, 2012; Hernández-Alonso, Fresno, Suárez, & Coronado, 2009), particularly in view of the solar application. The most important requirements that such a material should possess are a suitable band gap, chemical and physical stability, nontoxic nature, good availability, and low cost. The most common materials used are oxides or sulfides, which redox potentials for the VBs and the CBs range are between $+4.0$ and -1.5 V versus a normal hydrogen electrode (NHE). Their photocatalytic properties depend mainly on the position of the energetic level and on the band gap. Table 7.1 summarizes the most common semiconductors used as photocatalysts, reporting their band gap and wavelength of the radiation needed for the activation.

The photoactivity of a semiconductor depends also on the mobility and lifetime of the photo-produced electron/hole couples, on the light absorbance coefficient, and on the method used to prepare the photocatalytic powder, which affects many physicochemical properties of the semiconductor such as surface area, distribution of particle size and crystallinity.

Despite the photocatalytic process offering interesting advantages with respect to other catalytic process (e.g. milder operating conditions, use of safer catalyst, etc.), its use in the industry is still limited for three different reasons (Ni, Leung, Leung, & Sumathy, 2007): (1) recombination of photo-generated electron/hole pairs that dissipate their energy as heat; (2) fast backward reaction; and (3) difficulty to use visible light, which limits the effectiveness of the use of solar energy.

Table 7.1 **Band gaps and wavelengths of the most common semiconductors used as photocatalysts**

Photocatalyst	Band gap (eV)	Wavelength (nm)
SnO_2	3.8	318
TiO_2 anatase	3.2	387
TiO_2 rutile	3.0	380
WO_3	2.8	443
Fe_2O_3	2.2	560
ZnO	3.2	387–390
ZnS	3.7	335–336
CdS	2.5	496–497
CdSe	1.7	729–730
GaAs	1.4	886–887

To solve these problems, continuous efforts have been made to enhance the photocatalytic activity and promote the visible light response.

A simple approach consists in the addition of electron donors or electron scavengers, able to react irreversibly with the photo-generated VB holes or CB electrons, respectively. Practically, electron scavengers or electron donors can be reduced by CB electrons or oxidized by VB holes, respectively; the remaining strong oxidizing VB holes or strong reducing CB electrons can oxidize/reduce the substrate. Operating in this way, the electron/hole recombination can be suppressed or reduced, and higher quantum efficiency can be achieved.

Another way to suppress or to reduce the recombination of photo-generated electron/hole pairs consists in doping the semiconductor with a noble metal like Pt, Au, Pd, Rh, Ni, Cu, and Ag. By using this method, photo-promoted electrons can be transferred from CB of the semiconductor to metal particles deposited on its surface, while photo-generated VB holes remain on the photocatalyst. Thus, the possibility of electron—hole recombination is greatly reduced, resulting in an enhancement of photocatalytic efficiency (Araña et al., 2008; Chen et al., 2008; Colmenares, Aramendía, Marinas, Marinas, & Urbano, 2006; Rosu, Suciu, Lazar, & Bratu, 2013; Wu et al., 2008; Yang et al., 2013). A combined effect of metal ion doping consists in the reduction of the band gap energy of the photocatalyst, thus shifting the radiation absorption towards higher wavelengths, permitting the use of visible light (Ge, 2008; Ling, Sun, & Zhou, 2008). The same effect also can be obtained by doping the catalyst with anions, such as N, F, C, S, and B (Collazzo, Foletto, Jahn, & Villetti, 2012; Di Valentin & Pacchioni, 2013).

Other ways to overcome previous limitations consist in dye sensitization, composite semiconductors, metal-ion implantation, etc.

PMRs are hybrid systems in which photocatalysis is coupled with a membrane separation. In general, a membrane can be defined as a barrier that separates two phases controlling the mass transport between them.

The most important classification of membranes is based on their morphological properties. In particular, a membrane can be porous, allowing the permeation through its pores, and then the transport mechanisms (sieving mechanism and/or Knudsen diffusion) depend on the pore size, or dense, in which the mass transport takes place by the so-called solution/diffusion mechanism, i.e. dissolution of the permeation species in the membrane phase and diffusion across the membrane thickness.

Another morphological classification of membrane distinguishes symmetric and asymmetric membranes. In a symmetric membrane, structural and transport properties are the same throughout its section, and the thickness of the entire membrane determines the flow. In asymmetric membranes, consisting of a dense thin layer supported by a porous layer that acts as mechanical support of the fragile skin layer, structural and transport properties change along the membrane thickness. In this way, the high selectivity of a dense membrane is combined with the high permeation rate of a thin layer membrane. Asymmetric membranes are mainly used in membrane separation processes that use hydrostatic pressure as the driving force (the so-called pressure-driven processes): reverse osmosis (RO), NF, UF, and microfiltration (MF) (Mulder, 1996).

In a PMR system, the appropriate choice of the membrane (material and type) and membrane module configuration is mainly determined by the type of photocatalytic reaction. Indeed, the membrane can assume many roles. The main purpose in coupling a membrane process with a photocatalytic reaction is the necessity to recover and reuse the catalyst. So, it is important to choose a membrane (type and material) with complete catalyst rejection, thus maintaining it in the reaction environment. Besides, when the process is used for the degradation of organic pollutants, the membrane must be able to reject the substrates and their intermediate products, which otherwise pass in the permeate. For example, when the photocatalytic process is used as a synthetic pathway, the main objective can be the selective separation of the product, e.g. minimizing its successive oxidation, which leads to undesirable byproducts.

In this context, the rejection (*R*) is a useful parameter that expresses the ability of the membrane to maintain the substrate and its intermediates in the reactive environment:

$$R = \left(C_f - C_p\right)/C_f = 1 - \left(C_p/C_f\right) \tag{7.6}$$

in which C_f and C_p are the solute concentrations in the feed and permeate, respectively.

The retention of the substrates and degradation byproducts is important also to control the residence time of substrates in the photocatalytic system. This parameter strongly influences the efficiency of photodegradation. Longer retention times, usually obtained by reducing the permeate flux, results in higher pollutant degradation, due to the greater contact time between the molecules to be degraded and the catalyst. However, since the PMR must be able to offer a high water permeate flux, it is important to find a good compromise among the permeate flux and the residence time to achieve a system for application purpose.

7.2.2 Membrane materials, development and design for photocatalysis

Because the main problem encountered when the photocatalytic process is coupled to a pressure-driven process such as MF and UF (which requires porous membranes) is the decrease of permeate flux caused by concentration polarization and fouling, the choice of membrane material is strongly determined by the need to limit these phenomena and by the chemical and thermal stability of the materials.

Polymeric membranes are generally used in photocatalysis, although inorganic ones, which generally present higher chemical and thermal stability, are attractive for PMR applications. But they have the disadvantage of a significantly higher cost compared to polymeric ones (Chin, Chiang, & Fane, 2006; Moritz, Benfer, Arki, & Tomandl, 2001). In view of this economic factor, suitable polymeric membranes should be sought for this application.

Molinari et al. (2000) reported an investigation of the stability, under ultraviolet (UV) irradiation, of some eligible commercial membranes composed by various materials. Tests of photo-resistance under UV light were carried out by irradiating the membranes immersed in distilled water. Samples were periodically withdrawn and analysed by TOC, optical microscopy (OM), and scanning electron microscopy (SEM) to verify any damage to the membrane surface. Membrane stability was also determined by measuring the changes in pure water permeation flux (WPF) before and after UV irradiation. Table 7.2 shows the main characteristic of the 11 commercial membranes used in the UV irradiation tests.

Membranes made of polyacrylonitrile (PAN), fluoride + polypropylene (PP), and polysulphone + PP seemed to be stable to UV light over a 24-h period of irradiation. PAN membrane was chosen to carry out some photo-reactivity experiments, because it showed the highest permeate flux, which was constant in the time. TiO_2 was immobilized on the flat sheet membrane by ultrafiltrating TiO_2 suspensions in water (600 mL) at 0.05, 0.1, 0.2, and 0.3 g/L; the amounts of immobilized TiO_2 were, respectively, 0.76, 2.04, 4.08, and 6.12 mg/cm^2 of membrane. The best uniform coverage was given by loading 4.08 mg/cm^2, although the best results for the photocatalytic reaction were obtained in a suspended TiO_2 system. 4-nitrophenol (4-NP) was used as model molecule, and 80% degradation was obtained in around 5 h by using 0.5 g/L of suspended TiO_2, whereas degradation around 51% was obtained with the same irradiation time in the system with deposited TiO_2, regardless of the amount of catalyst.

Some years later, Chin et al. (2006) reported a study focused on the selection of polymeric membranes for PMR applications providing a protocol, similar to that

Table 7.2 Types of commercial membranes used in the UV irradiation test

Type of membrane	Pore size	Polymer	Supplier
MPPS 0000 u002	15 kDa	Polysulphone	Separem
MPPS 0000 u006	40 kDa	Polysulphone	Separem
MPPS 0000 u20	2.5 kDa	Polyamide	Separem
MPPS 0000 u25	2.0 kDa	Polyamide	Separem
P-12-10	–	PEEK	Homemade
FS 50 PP*	50 kDa	Fluoride + PP	Dow
PES	40 kDa	Polyethersulphone	TechSep
PVDF	0.1 μm	Polyvinyldene fluoride	TechSep
GR 51 PP	50 kDa	Polysulphone + PP	TechSep
PAN	40 kDa	Polyacrylonitrile	TechSep
CA 600 PP	20 kDa	Cellulose acetate-PP	Dow

* Note: PP: polypropylene.
Source: Molinari et al. (2000).

one proposed by Molinari et al. (2000) for testing the stability of polymeric membranes before using them with photocatalytic reactions. Membrane stability was characterized by: (1) changes in WPF, before and after UV irradiation; (2) release of TOC in the 50 mL of Milli-Q water in which the membrane were immersed, before and after the predefined time of UV exposure; and (3) SEM to observe the surface morphology of the membranes before and after the exposure to UV light. The overall change in surface hydrophobicity or hydrophilicity of the membranes was determined by contact angle measurements (CAM). Ten types of polymeric membranes (Table 7.3) were subjected to the initial UV screening test. Polytetrafluoroethylene (PTFE), hydrophobic polyvinylidene fluoride (PVDFphobic), and PAN membranes were stable after 30 days of UV illumination. However, in a study of the oxidative stability of membranes (under UV, hydrogen peroxide [H_2O_2], and combined UV/H_2O_2 conditions), it was found that the stability of PAN membrane declined considerably when it was exposed to 10 days of 200 mM H_2O_2/UV conditions. Then the author concluded that on the basis of their UV and oxidative screening tests, PTFE and hydrophobic PVDF are the better choice for photocatalytic applications.

Different papers reported in the literature suggest the use of PVDF for PMRs. Fu, Ji, Wang, Jin, and An (2006) successfully used a submerged membrane photocatalytic reactor (SMPR), in which the MF module was made of PVDF hollow fibre membranes (pore size = 0.2 μm, filtration area = 0.2 m^2), for the degradation of fulvic acid by nanostructured TiO_2. Chin, Lim, Chiang, and Fane (2007) studied a low-pressure PVDF submerged hollow fibre membrane module to retain the TiO_2 particles in the photodegradation of bisphenol A (BPA), used as a model pollutant.

Table 7.3 **Types of commercial membranes used in the UV irradiation test**

Type of membrane	Pore size	Suppliers
Polyvinyldene fluoride (PVDF)	0.22 μm	Millipore
PVDF-MP	0.22 μm	Millipore
PVDF-Pall	0.1 μm	Pall filtration
Polycarbonate (PC)	0.1 μm	Millipore
Polysulphone (PS)	600 kDa	Osmonics
Polytetrafluoroethylene (PTFE)	0.2 μm	Cole Parmer
Polypropylene (PP)	0.1 μm	Osmonics
Polyacrylonitrile (PAN)	40 kDa	Cleanseas
Polyethersulphone (PES)	50 kDa	Millipore
Cellulose acetate (CA)	0.2 μm	MFS

Source: Chin et al. (2006).

Despite all the properties that make PVDF one of the most extensively applied UF membrane materials (e.g. antioxidation, good thermal, and hydrolytic stabilities as well as good mechanical and membrane-forming properties), the hydrophobic nature of PVDF often results in severe membrane fouling and permeability decline, since organic contaminants (hydrophobic) deposition on this materials results favoured due to chemical affinity. This has become a conspicuous drawback for their application in water treatment (Lang, Xu, Yang, & Tong, 2007). Many methods have been tested to improve the membrane performances. Among these ones, blending with inorganic materials, especially nanoparticles, has attracted great attention owing to the relatively easy preparation by the method of phase inversion, which is carried out under mild conditions (Shon et al., 2010; Wei et al., 2011). On the basis of this, Damodar, You, and Chou (2009) reported a study on the self-cleaning, antibacterial, and photocatalytic properties of TiO_2-entrapped PVDF membranes. The modified PVDF membranes were prepared by using the phase inversion method, adding different amounts of TiO_2 particles (0–4 wt%) into the casting solution. The TiO_2–PVDF membranes were tested for their antibacterial property by using *Escherichia* coliform, photoactive property using reactive black 5 (RB5) dye, and self-cleaning (antifouling) properties using 1% Bovine Serum Albumin (BSA) solution. Obtained results evidenced that the hydrophilicity and pore size of composite PVDF/TiO_2 membranes were varied by addition of different amounts of TiO_2. This also improves the permeability of modified PVDF/TiO_2 membrane. The PVDF/TiO_2 membrane showed better bactericidal ability as compared to neat PVDF membrane under UV light. The rate of RB5 removal was higher as compared to neat PVDF membrane. Among the tested membranes the ones with 2–4% PVDF/TiO_2 showed better antifouling/self-cleaning ability as compared to neat PVDF membrane.

On the same topic, Wei et al. (2011) proposed a new PVDF–TiO_2 nanowire hybrid UF membrane prepared via phase inversion by dispersing TiO_2 nanowires in PVDF casting solutions. Obtained results showed that the microstructure, mechanical property, thermal stability, hydrophilicity, permeation, and antifouling performance of hybrid membranes were improved significantly by addition of hydrophilic inorganic TiO_2 nanowires.

In a recent work, You, Semblante, Lu, Damodar, and Wei (2012) evaluated the antifouling and photocatalytic properties of a membrane in which polyacrylic acid (PAA) was plasma-grafted on commercial PVDF membrane to introduce functional groups on the membrane surface that can support the TiO_2 nanoparticles. Obtained results showed that the membrane hydrophilicity was tremendously enhanced by the self-assembly of TiO_2, following a direct proportionality to TiO_2 loading. However, greater hydrophilicity did not necessarily implicate better antifouling properties, since excessive nanoparticles plugged membrane pores. The membrane with 0.5% TiO_2 loading maintained the highest pure water flux and the best antifouling property. Beyond this concentration a significant permeate flux decline was observed. The TiO_2-modified membranes were able to remove 30–42% of 50 mg/L aqueous RB5 dye, and the degradation reaction was highly dependent on TiO_2 amount. The overall results evidenced that the fabricated membranes are good candidates for use in membrane reactors with high hydrophilicity, fouling mitigation, and photocatalytic capability.

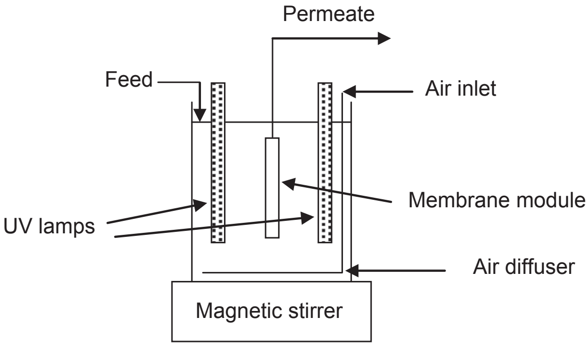

Figure 7.2 Schematization of the assembled photocatalytic membrane reactor (PMR). Adapted from Damodar and You (2010).

Chin et al. (2006) demonstrated that PTFE (a highly crystalline polymer that exhibits excellent thermal stability and high chemical resistance) membranes are also good candidates for PMR applications. On the basis of this, Damodar and You (2010) proposed a PMR assembled by integrating a novel flat plate PTFE membrane module that was placed at the centre of the tank and surrounded by two UV lamps (see Figure 7.2).

The performance of the assembled PMR was evaluated in the mineralization of RB5, and the efficiency of catalyst recycling and reuse was studied using batch and long-term continuous experiments. The obtained data showed that during continuous, long-term operations, the membrane module was able to maintain the catalyst effectively within the reactor, and the catalyst was also reused without much loss in dye degradation efficiency. Indeed, the catalyst that gradually deposited on membrane surface during continuous operation was effectively recycled by using simple and quick cleaning method, after which the original behaviour of the membrane and RB5 degradation performance were restored. The performance of the reactor was stable, with nearly 75−82% TOC removal and 85−90% chemical oxygen demand (COD) removal and showed similar trend for about five to six days after each membrane-cleaning step.

Raja et al. (2007) studied the discolouration of orange II on synthesized PTFE/Co_3O_4 films under visible light irradiation. An innovative way to prepare PTFE/Co_3O_4 supported catalyst by a suitable thermal treatment of the PTFE film in contact with the Co_3O_4 colloid was presented. The so prepared catalyst allowed the accelerated discolouration of orange II.

Another hydrophobic polymer largely used in PMR is PP. PP hollow fibre membranes were used by Erdim, Soyer, Tasiyici, and Koyuncu (2009) to study the effect of natural organic matter (NOM) fouling. Synthetic and natural raw waters were used in their photocatalytic experiments. The experimental data showed that the increase in NOM concentration increased the pressure, while raw water experiments showed a higher pressure increase and lower removal efficiencies compared to that of synthetic water.

Because of their hydrophobic nature, PP membranes can be used in MD (Mozia & Morawski, 2006; Mozia, Morawski, Toyoda, & Tsumura, 2010).

Many works are reported in literature on the coupling of the photocatalytic process with NF membranes, which have the advantage of retaining low molecular weight molecules better in comparison to low-pressure MF and UF modules.

Different NF membranes were tested in the photodegradation of different pharmaceuticals by Molinari, Pirillo, Loddo, and Palmisano (2006). Table 7.4 reports the main characteristic of these NF membranes.

Obtained results evidenced that membrane retention depended on both the pH of the aqueous solution to be treated and on the chemical characteristics of the particular pharmaceutical compound to be degraded. NF PES 10 at alkaline pHs, NTR 7410 at neutral and alkaline pHs, and N 30 F at acidic pHs were the membranes that showed

Table 7.4 Main characteristics of commercial membranes tested

Type of membrane	Material	Characteristics	Manufacturer
NTR 7410	Sulfonated polysulfone	Rejection 10% with 0.2% NaCl at 4.9 bar, 25 °C, and pH 6.5	Nitto Denko, Tokyo
PAN GKSS HV3/T	Polyacrylonitrile	Cut-off = 30 kDa; water flux 423.1 L/h/m^2 at 2 bar and 846.2 L/h/m^2 at 4 bar	GKSS, Germany
N 30 F	Modified polysulfone	Rejection 25–35% with 0.2% NaCl and 85–95% with 0.5% of Na_2SO_4; water flux 40–70 L/h/m^2 at 40 bar and 20 °C	Hoechst, Celgard, Germany
NF PES 10	Polyethersulfone	Rejection 10–20% with 0.5% NaCl and 40–70% with 0.5% of Na_2SO_4; water flux 200–400 L/h/m^2 at 40 bar and 20 °C	Hoechst, Celgard, Germany

Source: Molinari et al. (2006).

the best rejection percentages for furosemide, at pressures of 4—8 bar. NTR 7410 was the best membrane for ranitidine rejection, over the whole pH range, although its rejection at 8 bar was lower than that found for NF PES 10.

In another work (Molinari et al., 2002) NF PES 10 and NTR 7410 membranes were tested for the photocatalytic removal of 4-NP and benzoic acid from aqueous solutions. TiO_2 P25 Degussa was used as the catalyst, both suspended and deposited on the polymeric membranes. Obtained results showed that the treatment of 4-NP solution in acidic medium allowed the total removal of the substrate by using a continuous system. NTR 7410 was also an efficient NF membrane for separating two dyes, Congo red and direct blue, from aqueous solutions (Molinari, Pirillo, Falco, Loddo, & Palmisano, 2004).

7.3 Advances in membrane modules and system configurations for PMRs for water treatment

Despite the important advantages of the photocatalytic processes with respect to the traditional ones, their application at industrial level is limited by different drawbacks related to the involved reactions and reactor configuration.

With regard to the configuration of the reactor, and in particular by considering the photocatalyst, two operative configurations can be identified: the first one, in which the photocatalyst is suspended in the aqueous reacting phase, and another one with the photocatalyst immobilized on a support.

Slurry photocatalytic reactors, in which the catalyst is suspended in the aqueous reacting phase, have been widely used. In these reactors the nondegraded molecules or their byproducts are freely transported in the final stream. Photocatalyst recovery and recycle is another problem. The coupling with pressure-driven membrane separations in PMRs can solve these problems.

7.3.1 Pressurized membrane PRs

Different types of PMRs were built with the purpose of obtaining an easy separation of the catalyst from the reaction environment and an efficient removal of pollutants from aqueous media. The most studied configurations were pressurized systems, in which pressure-driven membrane processes, such as MF, UF, and NF, were combined to the photocatalytic process. In these systems the catalyst, used both in the suspended configuration and immobilized on the membrane, is confined in the pressurized side of the permeation cell.

In 2002, Molinari et al. (2002) reported some experimental results obtained by using two different pressurized PMR configurations for the degradation of 4-NP. In particular, the configurations studied were: (1) a first one, in which the irradiation of the catalyst was performed in the permeation cell containing the membrane, with three sub-cases: (a) catalyst in suspension; (b) catalyst deposited on the membrane; (c) catalyst entrapped in the membrane; and (2) a second one, in which the irradiation of the suspended catalyst was performed in the recirculation tank. The results showed that the second configuration appeared to be the most interesting for industrial applications in terms of irradiation efficiency and membrane permeability. For example, in reactor optimization, high irradiation efficiency, high membrane permeate flow rate, and selectivity can be obtained by sizing separately the 'photocatalytic system' and the 'membrane system' and taking advantage of all the best research results for each system.

In a successive work the same group Molinari et al. (2004) studied the photodegradation process of two commercial azo dyes, i.e. Congo red ($C_{32}H_{22}N_6Na_2O_6S_2$) and patent blue ($C_{27}H_{31}N_2NaO_6S_2$), in a membrane PR by using TiO_2 Degussa P25 as the photocatalyst and an NF membrane. Two different PR configurations, a cylindrical one with an external lamp and an annular one with an immersed lamp in the axial position (Figure 7.3), were studied, and the influence of some operational parameters such as the pressure in the membrane cell and the initial concentration of the substrates was determined. A comparison between suspended and entrapped TiO_2 was also done.

The rate of pollutant photodegradation was strongly affected by the UV irradiation mode. In particular, the rate of photodegradation with the immersed lamp resulted 50 times higher than that of suspended one (0.274 versus 0.00548 mg/min), although the power of the last was four times greater. Congo red was photodegraded with higher rate under the same experimental conditions, probably due to its higher adsorption onto the catalyst surface. The reactor containing the suspended photocatalyst was significantly more efficient than the reactor containing the catalyst entrapped into the membrane, as also found by other authors (Mascolo et al., 2007). The observed

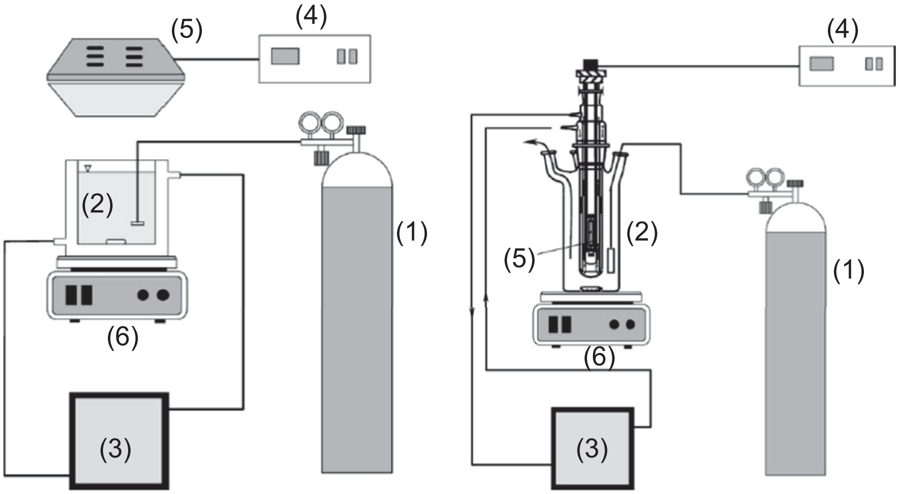

Figure 7.3 Scheme of the batch system with external lamp and with immersed lamp used in the experimental runs without membrane with the suspended catalyst: (1) oxygen cylinder; (2) cylindrical reactor with cooling jacket; (3) thermostatic baths with cooling water; (4) power supplies; (5) medium pressure Hg lamp; (6) magnetic stirrer (Reprinted from Molinari et al. (2004), with permission from Elsevier).

reduction of photoactivity was probably due to the lower available active surface area of the catalyst compared to the suspended immobilized system. The results evidenced that it was possible to treat successfully highly concentrated solutions (500 mg/L) of both dyes by means of a continuous process obtaining good values of permeate fluxes (30−70 L/m^2/h); this could be interesting for industrial applications.

7.3.2 Depressurized (submerged) membrane PRs

The main problem observed by coupling photocatalysis with a pressure-driven membrane process is the decrease of permeate flux caused by membrane fouling, due to catalyst deposition on the membrane. Submerged membrane systems represent one of the different approaches proposed to overcome this limitation. In this configuration, the catalyst is suspended in an open-air reaction environment, the membrane is immersed in the batch, and the permeate is sucked by means a vacuum pump.

Fu et al. (2006) reported the degradation of FA by using synthesized nanostructured TiO_2/silica gel catalyst particles in a submerged membrane photocatalytic reactor (SMPR) schematized in Figure 7.4. It was found that the photocatalyst at 0.5 g/L and airflow at 0.06 m^3/h were the optimal conditions for the removal of FA. The results showed a reduction of fouling phenomena when nanostructured TiO_2 was used as the photocatalyst.

An additional way to prevent photocatalyst deposition and then reduce membrane fouling consists in controlling the hydrodynamic conditions near the membrane surface. In this context, gas sparging at the bottom of the membrane represents a promising strategy. On this basis, Chin et al. (2007) studied the removal of BPA in water by using low-pressure submerged module, and they observed that the aeration, allowing a mechanical agitation, reduced the fouling of the membrane and maintained the TiO_2 well suspended in the solution. In addition, in this study another strategy to reduce membrane fouling was proposed: an intermittent membrane filtration, which permitted to maintain high flux at low aeration rate. Practically, when suction across

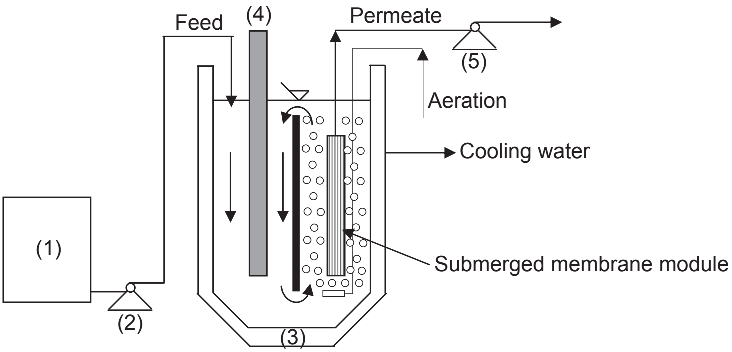

Figure 7.4 Schematic diagram of the submerged membrane photocatalytic reactor (SMPR) system: (1) feed tank; (2) feed pump; (3) thermostated jacket protoreactor; (4) UV lamp; (5) suction pump.
Reprinted from Fu et al. (2006), with permission form Elsevier.

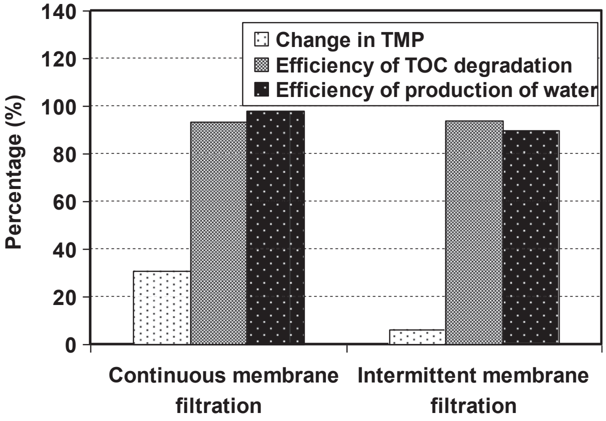

Figure 7.5 Comparison of the transmembrane pressure (TMP) change, total organic carbon (TOC) degradation and production of water between continuous and intermittent permeation operation.

Reprinted from Chin et al. (2007), with permission from Elsevier.

the membrane was stopped, the aeration could shear the membrane surface facilitating the detachment of catalyst particles. The results, summarized in Figure 7.5, showed that TOC photomineralization, by operating with intermittent operation, was similar to that ones obtained with continuous operation, i.e. 94% BPA reduction at 250 min. Moreover, it was found that with the intermittent mode, the transmembrane pressure (TMP) of the system decreased by five times compared to the continuous operation. Because TMP is proportional to the filtration energy cost, intermittent operation would reduce the operating cost of the continuous SMPR.

The advantages of this approach were also studied by Huang, Meng, Liang, and Qian (2007). They demonstrated that sedimentation of the suspended semiconductor can be controlled by applying fine-bubble aeration and intermittent membrane filtration.

Choi (2006) used the same intermittent approach studying the performance of a pilot-scale SMPR in the degradation of 4-Chlorophenol (4-CP). The results evidenced a complete degradation of the pollutant in 2 h. Besides, in continuous runs, no membrane fouling was observed when the intermittent operation was used.

Therefore, the SMPR with fine-bubble aeration and intermittent membrane filtration can be potentially applied in the photocatalytic oxidation process during drinking water treatment.

7.3.3 Coupling of photocatalysis and membrane distillation

Coupling of photocatalysis and MD could avoid fouling problems related to the use of pressure-driven membrane separations. MD is a separation process based on the principle of vapour—liquid equilibrium. The nonvolatile components (e.g. ions, macromolecules, etc.) are retained on the feed side, whereas the volatile components pass through a porous hydrophobic membrane, and then they condense in a cold distillate (usually distilled water).

The possibility on the way to use a PMR obtained by coupling photocatalysis and direct contact MD (DCMD) for degradation of azo dyes (acid red 18, acid yellow 36, and direct green 99) in aqueous solution was investigated by Mozia et al. (2007). The initial concentration of a dye was equal to 30 mg/L, and the catalyst (TiO_2 Aeroxide® P25, Degussa, Germany) loadings amounted to 0.1, 0.3, and 0.5 g/L. The results showed that the MD process was very effective in separation of photocatalyst particles. Indeed, after 5 h of the experiment, the turbidity of distillate was similar to that measured for ultrapure water, regardless of the TiO_2 amount in the reacting phase. The highest effectiveness of photodecomposition was obtained in the case of acid red 18, and the most difficult compound to be degraded was acid yellow 36, having the lowest molecular weight among all the dyes used (Figure 7.6).

A complete rejection of the dye and other nonvolatile compounds (organic molecules and inorganic ions) was achieved. Some volatile compounds crossed the membrane, as indicated by the measurements of TOC concentration into the distillate. However, the amount of these substances remained in the range 0.4—1.0 mg/L, so that it can be concluded that the product (distillate) was practically pure water. A permeate flux of 0.34 $m^3/m^2/d$ was obtained, similarly to those obtained during the process in which ultrapure water was used, regardless of the TiO_2 amount. This result evidenced that MD permitted to avoid the significant fouling observed when pressure-driven membrane processes were coupled with photocatalysis, although the higher energetic consumption of MD represents an important disadvantage.

Thus the hybrid process coupling the photocatalysis and DCMD is a promising method for the removal of organic compounds, such as azo dyes from water, because the MD membrane is a very effective barrier for the catalysts particles and the nonvolatile compounds present in the feed solution.

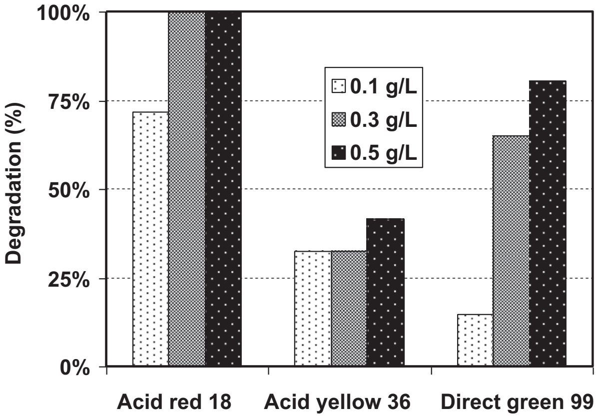

Figure 7.6 Photodegradation of Acid red 18, Acid yellow 36, and Direct green 99 in the PMR obtained by coupling photocatalysis and direct contact membrane distillation (DCMD) using different TiO_2 concentration in the reacting phase (evaluated on the basis of dyes concentration in the feed phase after 5 h of illumination).
Data from Mozia et al. (2007).

7.3.4 Coupling of photocatalysis and dialysis

The results summarized in the previous section show that only the combination of photocatalysis and MD avoids fouling, but it needs energy to reach evaporation phenomena.

On this basis, Azrague et al. (2007) proposed the combination of dialysis and photocatalysis to mineralize organic compounds (2,4-dihydroxybenzoic acid [2,4-DHBA] was used as a model pollutant) contained in artificial turbid waters obtained by using a natural clay named bentonite. In this PMR configuration, the dialysis membrane, used as a membrane contactor, permits to separate the polluted turbid water from the PR compartment (Figure 7.7).

Operating in this way, the membrane acts as a barrier for the photocatalyst particles, and it allows to extract the organic compounds from the turbid water, thanks to the concentration difference between the turbid polluted compartment and the one in which the photocatalytic reaction takes place. The absence of TMP avoids the formation of fouling, even in case of highly turbid water. Besides, the membrane permits: (1) to maintain the TiO_2 in the PR compartment avoiding a final filtration stage, and (2) to keep the bentonite away from the PR, thus avoiding the loss of efficient irradiations due to the scattering by bentonite particles.

All these advantages, combined with the complete removal of a high 2,4-DHBA concentration, demonstrate the effectiveness of the proposed PMR combining photocatalysis and dialysis. These results should lead to the design of a PMR working in a continuous mode.

7.3.5 Coupling of photocatalysis and pervaporation

Recently, it has been demonstrated that the integration of photocatalysis with PV is a promising method to improve the efficiency of the detoxification of water streams containing recalcitrant organic pollutants at a low concentration (Camera-Roda & Santarelli, 2007) as the integration of the two processes generates a synergistic effect. In PV, separation is not based only on the relative volatility of the components in the mixture,

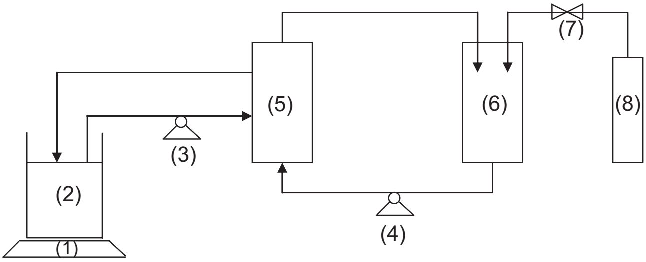

Figure 7.7 Schematization of the experimental set-up of the integrated photocatalysis−MD process: (1) magnetic stirrer; (2) feed (artificial turbid water) tank; (3) and (4) circulation pumps; (5) hollow fibre module or flat sheet membrane; (6) thermostated photoreactor; (7) pressure regulation valve; (8) oxygen cylinder.
Adapted from Azrague et al. (2007).

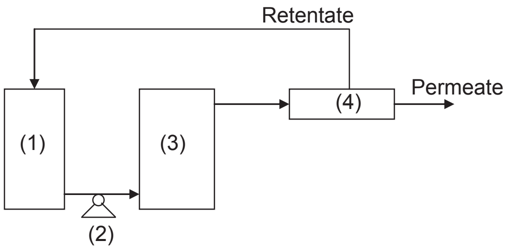

Figure 7.8 Schematization of the experimental set-up utilized for the integrated photocatalysis-PV process: (1) termostated feed tank; (2) membrane pump; (3) annular photocatalytic reactor (APR); (4) plane pervaporation module.
Adapted from Camera-Roda and Santarelli (2007).

but also depends on the relative affinity of the components with the membrane. Thus the choice of membrane material is important to obtain a selective separation of the molecules.

The experimental apparatus used for the integrated photocatalysis-PV process is schematically represented in Figure 7.8. The liquid is continuously recycled by a membrane pump to an annular photocatalytic reactor (APR) and kept at a constant temperature after passing through a small tank immersed in a thermostatic bath. Oxygen is continuously supplied inside the tank to maintain a constant concentration of 8 mg L^{-1} in the system. At the exit of the APR, the water passes through one or two plane PV modules (membrane surface area = 160 cm^2) through which the components permeate selectively, thanks to the vacuum (6 mbar) that is kept downstream.

The results (Figure 7.9) showed that the rate of disappearance of a model pollutant (4-chlorophenol, [4-CP]) is highly improved by using the integrated system as the

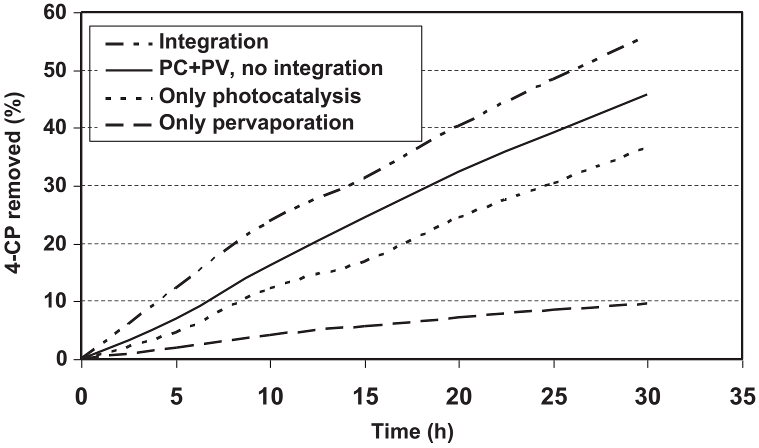

Figure 7.9 Percentage of 4-chlorophenol (4-CP) removed versus time in the integrated photocatalysis-PV process.
Adapted from Camera-Roda and Santarelli (2007).

membrane was efficient in continuously eliminating some intermediate products that could slow down the rate of the photocatalytic reaction, and, concurrently, the photocatalysis transforms the weakly permeable 4-CP into organic compounds that PV can remove at a high rate.

Process intensification by synergistic effect depends on the optimization of the ratio between the characteristic rates of the photocatalytic and PV processes.

Recently the use of a highly selective membrane allowed to recover some chemical products with high added value as vanillin starting from trans-ferulic acid (Camera-Roda et al., 2013).

7.4 Applications of PMRs for water treatment

In the last years, the interest in the presence of pharmaceutical active compounds (PhACs) and their metabolites in waterways has increased significantly (Jones, Voulvoulis, & Lester, 2002; Kasprzyk-Hordern, Dinsdale, & Guwy, 2008). Large amount of PhACs, in terms of thousands of tons, are annually used for therapeutic purposes or in animal farming in each European country and may be excreted both as unmetabolized and as active metabolites, thus reaching the aquatic environment. Besides, improper disposal of industrial waste may also contribute to their occurrence in aquatic environment. The wastewater is generally treated in sewage treatment plants (STP) that often fail to remove the majority of PhACs resulting in high concentrations discharged in treated effluents (Braga, Smythe, Schafer, & Feitz, 2005; Carballa et al., 2004; Castiglione et al., 2006; Colpin et al., 2002; Comeau, Surette, Brun, & Losier, 2008): so PhACs are detectable in the aquatic environment with concentration levels up to the μg/L. These amounts are much lower than maximum concentrations reported for typical industrial contaminants, but their toxicological chronic effects on aquatic environment, due to the continuous exposure to mixtures of pharmaceuticals, are unknown.

On this basis, the demand for developing efficient systems, alternative to the traditional purification methods, to remove PhACs from water has assumed a great research interest. PMRs could represent a useful solution to this problem.

The photodegradation of different pharmaceuticals (furosemide, ranitidine (hydrochloride), ofloxacine, phenazone, naproxen, carbamazepine, and clofibric acid) contained in aqueous medium at various pHs by using a batch PR and a PMR working in recirculation regime was studied by Molinari et al. (2006). The experimental tests were performed by using polycrystalline TiO_2 as the photocatalyst, determining the performances of different commercial membranes, mainly of the NF type (Table 7.4) in the PMR. To analyse the results of the photodegradation experiments in the PMR, the main factors involved in the overall performance of the PR were separately studied by carrying out the following tests: (1) adsorption tests on the TiO_2 particles; (2) degradation tests in the absence of the membrane; (3) membrane rejection by changing the operating pressures; and (4) degradation tests in the PMR. The results evidenced that the adsorption of the substrates onto the catalyst is affected by the pH, owing to the influence of this operating parameter on the hydrophilic/hydrophobic character of

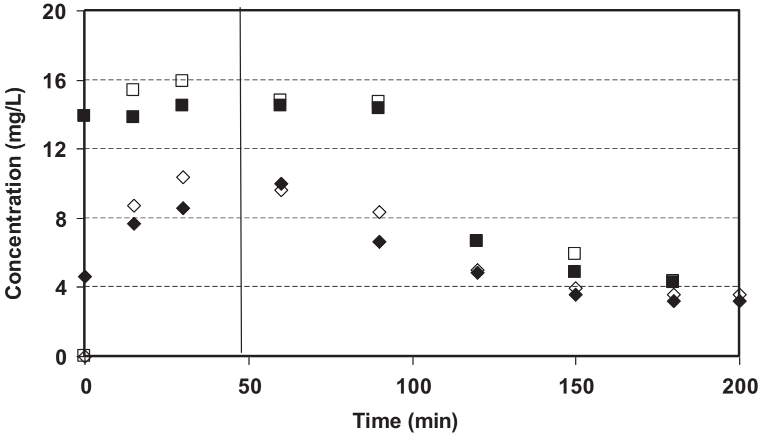

Figure 7.10 Substrate concentrations versus time for runs carried out by using the hybrid system with the NTR 7410 membrane at initial pH 3 ($TiO_2 = 1$ g/L; $O_2 = 22$ ppm; immersed lamp 125 W). Furosemide: (◆) retentate; (◇) permeate. Ranitidine: (■) retentate; (□) permeate.

Reprinted from Molinari et al. (2006), with permission from Elsevier.

the photocatalyst. All the seven considered molecules were successfully photodegraded in the batch reactor (without the membrane) with pseudo-first order kinetics.

Furosemide and ranitidine were selected to carry out the study of rejection and photodegradation in the PMR. During the photocatalytic tests in the PMR, the permeate flux through the NTR 7410 membrane had an average value of 45 L/h/m^2 at both acidic and alkaline pHs. Rejection values were in the range 10–60% for furosemide and 5–30% for ranitidine in the dark (without photoreaction), but a net decrease down to zero was observed in the contemporary presence of light, photocatalyst, and oxygen. Then, the degradation results in the PMR (Figure 7.10) showed that rejection measured in the presence of photocatalyst and oxygen, both in the dark and under irradiation conditions, was almost zero, so that the membrane in this case was beneficial only because it allowed the confinement of the photocatalyst.

In a successive work, the same group Molinari et al. (2008) reported the degradation of two pharmaceuticals (Gemfibrozil [GEM] and Tamoxifen [TAM]), selected as target molecule, using suspended TiO_2 as catalyst in two configurations of PMRs (pressurized and depressurized) operated in both batch and continuous mode. The latter mode consisted in the continuous withdrawn of the permeate from the reactor and its replacing by an equal volume of polluted water, until reaching a steady state (approximately 190 min) in terms of flux and rejection values of intermediates. The objective of these tests was to simulate the continuous photodegradation process that could be applied at industrial level. The experimental plant consisted of an annular PR with an immersed UV lamp connected to the permeation cell in which a pressurized flat sheet membrane or a submerged membrane module was located. The effects of parameters such as pH of the aqueous TiO_2 suspensions, pump flow rate, and membrane clean-up, on the efficiency of the PMR, were studied. Closed and continuous procedures were used to investigate the behaviour of the pressurized PMRs. The data obtained for the closed membrane system showed complete photodegradation of GEM and TAM, with an abatement of 99% after 20 min and mineralization higher than 90% after approximately 120 min.

Regard to the pressurized system, the membrane used (commercial flat sheet NF membrane NTR 7410, Nitto Denko, Tokyo) allowed to maintain the drug and the catalyst in the reaction environment, but it was not able to reject significantly the degradation intermediates which were also found in the permeate. A good operating stability was observed by operating in continuous mode, reaching a steady state for approximately 120 min (Figure 7.11), with a complete abatement of the drug and values of mineralization (60%) and permeate flux (38.6 L/h/m^2) that remained constant until the end of a run. A TOC rejection of about 62% at steady state confirmed the need to identify a membrane with higher rejection to the intermediate products. Catalyst deposition on the membrane surface and fouling caused a flux decline during the photocatalytic process.

The depressurized system, in which the submerged membrane module was located separately from the PR, and the oxygen was bubbled on the membrane surface could be of interest both to separate the photocatalytic zone from the separation zone and to reduce membrane fouling thanks to oxygen sparging. The UF membrane (PES commercial capillary membrane, 0.05—0.1 μm average pore size) used in the submerged system showed retention of only the catalyst in the reaction environment, while GEM and its oxidation products moved in the permeate. However, the submerged PMR permitted to obtain a steady-state flux of 65.1 L/h/m^2, higher than those obtained operating with the pressurized module, resulting it interesting for application purposes.

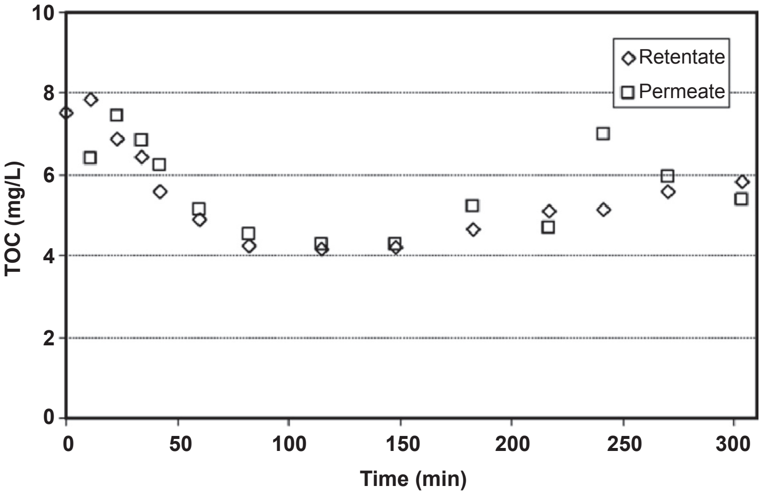

Figure 7.11 Total organic carbon (TOC) values versus the time in the degradation of Gemfibrozil (GEM) in the continuous submerged membrane photoreactor (continuous feed of GEM at concentration of 10 mg/L, Reprinted from Molinari et al. (2008), with permission from Elsevier).

The overall results reported by Molinari et al. (2006) and Molinari et al. (2008) confirmed that PMRs can be of interest in the removal of organic pollutants from water because they allowed the recovery and reuse of the catalyst, permitted to achieve a continuous process, and if a suitable membrane is found, it is possible to retain the pollutant and its degradation products in the reaction environment.

With regard to the possibility of using solar radiation to activate the photocatalyst, in 2005 Augugliaro et al. studied lincomycin (a common antibiotic) degradation in aqueous suspensions of polycrystalline TiO_2 Degussa P25 irradiated by sunlight. A hybrid system consisting of a solar PR coupled with a membrane module was tested with the aim to improve system sustainability and performance. The results of preliminary tests without the membrane separation step showed that lincomycin was successfully oxidized in the pilot plant solar PR. The presence of the membrane, which confined both photocatalyst and pollutants in the reaction environment, allowed operation in continuous mode. The data collected by using the hybrid system both in total recycle (batch) and in continuous mode (Figure 7.12) indicated that the presence of the membrane allows the reduction of both the substrate and intermediates down to low concentration levels.

Benotti, Stanford, Wert, and Snyder (2009) reported a study on the use of a PMR pilot system, using UV/TiO_2 photocatalysis, in the removal of 32 PhACs from water. The results showed that concentrations of all compounds decreased during the treatment. In particular, removal efficiency higher than 70% was obtained for 29 of the targeted compounds, while a removal efficiency lower than 50% was achieved for only three compounds. During the treatment of all the considered PhACs, no oestrogenically active transformation products were formed. Thus, the PMR developed in this work is a useful technology for water treatment as determined by pharmaceutical and endocrine-disrupting compound destruction as well as the removal of oestrogenic activity.

In 2012 Mozia and Morawski on the basis of their previous encouraging results obtained in dye removal from water, compared the efficiency of photodegradation of ibuprofen (IBU) sodium salt present in tap water in a PMR using DCMD under a

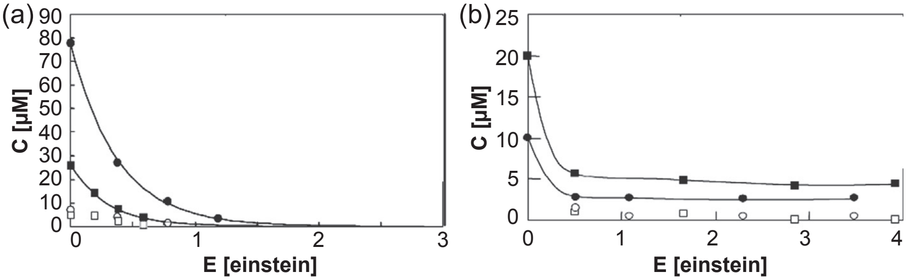

Figure 7.12 Lincomycin concentrations versus the cumulative photon energy, E, for runs carried out in (a) total recirculation regimens and (b) in continuous regimen by using the hybrid system at different initial lincomycin concentrations. Full symbol: retentate; open symbol: permeate.

Reprinted from Augugliaro et al. (2005), with permission from Elsevier.

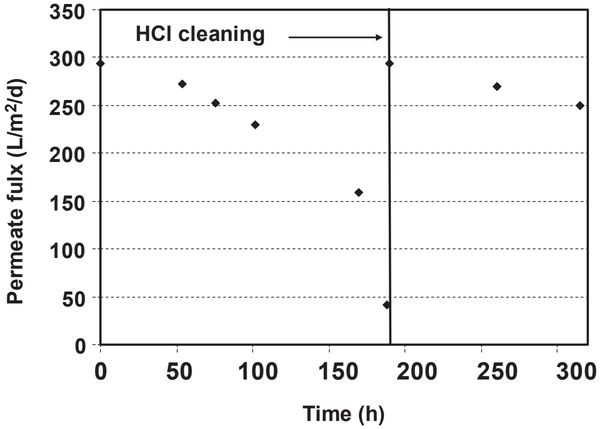

Figure 7.13 Changes of permeate flux during long-term operation of photocatalytic membrane reactor (PMR) using direct contact membrane distillation (DCMD) in continuous mode. Adapted from Mozia and Morawski (2012).

batch and continuous operation. The results revealed that the influence of the operation mode on the effectiveness of IBU decomposition and mineralization and on the product (distillate) quality was not significant. The permeate did not contain IBU, regardless of the process conditions. Despite that, the authors recommended the operation of the PMR in the continuous mode, due to its higher potential for a large-scale application.

Membrane scaling during a long-term process was also studied. The results, summarized in Figure 7.13, showed a decline of permeate flux during the long-term experiments. In particular, after 54 h of the PMR continuous operation, the flux was lower by approximately 7% compared to pure water flux (272 L/m^2/d versus 294 L/m^2/d), whereas after 188 h, an 86% flux decline was detected. The deposit layer formed on a membrane surface had a composite structure: on a thin porous TiO_2 layer the calcite and aragonite crystals were present. The application of cleaning with HCl solution allowed to dissolve the $CaCO_3$ scale deposit and to recover the flux. However, about 70 h after washing with HCl solution, the flux started decreasing with a similar rate as before cleaning.

In a successive work, the same authors (Mozia, Darowna, Przepiórski, & Morawski, 2013) reported the removal of a nonsteroidal anti-inflammatory drug (diclofenac sodium salt [DCF]) from water in two hybrid systems coupling photolysis or photocatalysis with DCMD. The results are summarized in Figure 7.14 in terms of TOC amounts in distillate (permeate) at the end of various experiments in comparison with the initial and final amounts of organic carbon in feed solutions. A complete DCF decomposition in the feed was obtained in both processes. In the case of the photolysis–DCMD hybrid system, the effectiveness of TOC mineralization after 5 h of irradiation ranged from 27.3% to 48.7%, depending on the DCF initial concentration. The addition of TiO_2 allowed the improvement of the efficiency of TOC removal. After 5 h of the hybrid photocatalysis–DCMD process, the mineralization efficiency was

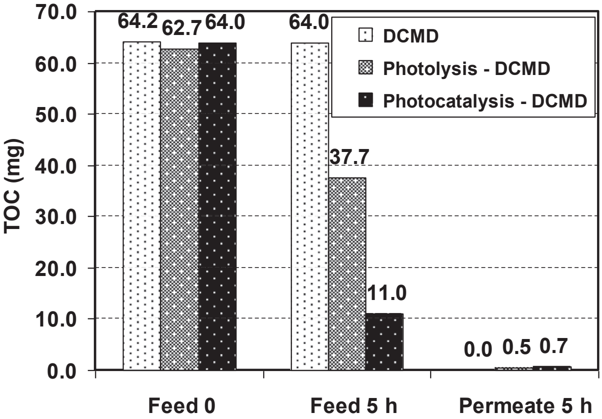

Figure 7.14 Comparison of TOC amounts in distillate (permeate) after 5 h of direct contact membrane distillation (DCMD), photolysis−DCMD, and photocatalysis−DCMD processes with the initial and final total organic carbon (TOC) amounts in feed solutions.
Data from Mozia et al. (2013).

in the range of 82.5−100%, the highest for the lowest DCF concentration. Application of DCMD in the hybrid systems ensured high efficiency of separation of DCF as well as the products of its degradation. Indeed, regardless of the process applied, distillate was high purity water: DCF was not detected, TOC concentration did not exceed 0.8 mg/dm^3, and conductivity was lower than 1.6 μS/cm.

The results obtained by Mozia and Morawski (2012) and Mozia et al. (2013) showed that, because the MD efficiently separated not only TiO_2 particles, but also organic contaminants present in feed solution, the PMR using DCMD represents a promising method for treatment of waters containing pharmaceuticals. Low permeate (distillate) flux assured relatively long residence time of contaminants, which resulted in high effectiveness of their photodegradation.

The overall results reported in this section confirm that PMRs can be of interest in the removal of organic pollutants (e.g. pharmaceuticals) from water, because the membrane: (1) separates TiO_2 particles efficiently, thus permitting the recovery and reuse of the catalyst; (2) permits the realization of a continuous process; and (3) allows the retention of organic pollutants and their degradation products, thus avoiding their release in the permeate and controlling the residence time of contaminants in the reaction environment. Then, PMRs can be considered a useful technology for water treatment as determined by PhACs destruction and the removal of oestrogenic activity. An important issue to take into consideration in developing photocatalysis−membrane hybrid processes is membrane fouling, mainly due to photocatalyst deposition on the membrane feed side. In this context, the approach proposed by Mozia et al., in which MD is coupled with photocatalysis, seems to be promising, because MD allows to obtain the points (1), (2), and (3) previously reported, and also permits the avoidance of the significant fouling observed when a pressure-driven membrane process is used, although the higher energetic consumption of MD could represent a limitation of this hybrid process.

7.5 Advantages and limitations of PMRs in water treatment

Based on the results summarized in the previous sections, the use of PMRs can be proposed as an attractive green process, because it is effective in abating harmful and recalcitrant substances present in aqueous effluents.

The main advantages related to the use of the PMRs to degrade pollutants are:

1. Possibility to be applied to a wide range of compounds in aqueous, gaseous, and solid phase;
2. Short reaction times and mild experimental conditions, usually ambient temperature and pressure;
3. Generally only oxygen from air without any additional additive is necessary;
4. Effectiveness with low concentration of pollutant(s);
5. Possibility to destroy a variety of hazardous molecules with the formation of innocuous products, solving the disposal pollutant problem associated to the conventional wastewater treatment methods;
6. Possibility to convert toxic metal ions in their nontoxic forms, which can be recovered and reused;
7. Synergistic effects by coupling the potentialities of classical PRs and those of membrane processes, i.e. catalyst recovery and reuse (immobilized or in suspension), rejection of the substrate, and/or separation of degradation products, thus allowing to perform the reaction of interest and the separation of the desired product(s) simultaneously in continuous mode;
8. Possibility to control the residence time of substrates in the photocatalytic system, thus verifying the contact time between the molecules to be degraded and the catalyst and then the photocatalytic degradation — this feature is very important when the process is used for synthetic purposes;
9. Possibility to use sunlight.

Despite these important advantages, the application of the photocatalytic process at industrial level is limited by different drawbacks, mainly related to the membrane fouling.

As reported in previous sections, the choice of the membrane is a key step for achieving a successful application of PMRs. For example, Molinari et al. (2006) and Mollinari et al. (2008) demonstrated the potentialities of PMR applications in both pressurized and submerged configurations in water detoxification, because they allowed the recovery and reuse of the catalyst and permitted the achievement of a continuous process, while the membrane rejection towards the pollutants was not very satisfactory. These results show the necessity to identify a membrane selective to intermediate products, to retain the pollutant and its degradation products in the reaction environment.

7.6 Conclusion

All the results reported in this chapter on coupling the photocatalytic process with membrane separations show numerous advantages derived from a synergistic effect of these two techniques. In particular, it has been shown that PMRs can be considered a useful technology for the removal of organic pollutants (e.g. pharmaceuticals) from water, thanks to PhAC destruction and the removal of oestrogenic activity.

An important limitation related to photocatalysis—membrane coupling is related to the decrease of permeate flux caused by concentration polarization and membrane fouling, mainly due to photocatalyst deposition on membrane surface. This drawback can be limited by appropriately choosing membrane material, which must also ensure adequate chemical and thermal stability, and type and PMRs configuration.

The ideal membrane process to be coupled with photocatalysis should possess these features: (1) complete retention of the catalyst and controlled fouling; and (2) good rejection of the substrates and of degradation byproducts, to avoid the release of dangerous substances in the treated water and to assure a residence time in the photocatalytic system sufficient for obtaining complete pollutant degradation and mineralization. Longer residence times are usually obtained by reducing the permeate flux, so it is important to find a good compromise among the permeate flux and the residence time to achieve a system for application purpose. In other words, the process intensification by synergistic effect depends on the optimization of the ratio between the characteristic rates of the photocatalytic and membrane separation processes.

Many methods have been tested to improve the membrane performances. Among these, blending with inorganic materials (e.g. immobilization of TiO_2) to increase the hydrophilic character of the membrane surface exposed to the reacting environment of TiO_2 is a promising approach that produces photocatalytic membranes with antifouling/self-cleaning ability. The so-prepared membranes are good candidates for use in membrane reactors for wastewater treatment and reuse processes.

Considering PMR configuration, the use of SMPRs with fine-bubble aeration and intermittent membrane filtration can be potentially applied in the photocatalytic oxidation process during drinking water treatment, because this approach significantly reduces membrane fouling.

The hybrid process obtained by coupling photocatalysis with MD seems very promising for the removal of organic pollutants from waters, because it possesses the ideal features previously reported. In particular, this coupling avoids fouling, but it needs energy to obtain evaporation. On the basis of this, the combination of dialysis and pervaporation with photocatalysis has been also reported, showing that this coupling also possesses the features of the ideal membrane process to be coupled with photocatalysis.

7.7 Future trends

The use of submerged membrane systems operated with fine-bubble aeration in the intermittent membrane filtration mode and the coupling of photocatalysis with MD, dialysis, and pervaporation represent some promising approaches for overcoming the limitation related to membrane fouling. In particular, the coupling with DCMD, seems to be more promising, as MD: (1) separates TiO_2 particles efficiently; (2) permits the retention of organic pollutants and their degradation byproducts (the MD distillate is practically high purity water); (3) permits the realization of a continuous process; and (4) allows the avoidance of membrane fouling, although the higher energetic consumption of MD could represent a limitation of this hybrid process.

On this basis, it is foreseen that hybrid system photocatalysis—membranes will have a significant impact in designing processes for the abatement of organic pollutants contained in waters.

7.8 Sources of further information

An exhaustive reference book on the fundamentals and applications of heterogeneous photocatalysis that was recently published is: *Clean by light irradiation: Practical applications of supported TiO2* by Augugliaro, V., Loddo, V., Pagliaro, M., Palmisano, G., & Palmisano, L. (2010). Cambridge (UK): RCS Publishing.

Fundamentals of photocatalysis and some interesting information about membrane PR regarding membrane materials and some operational issues can be found in: *Chapter 6* - Photocatalytic membrane reactors: Fundamentals, membrane materials and operational issues, by Mozia, S., Morawski, A.W., Molinari, R., Palmisano, L., & Loddo, V. (2013). In A. Basile (Ed.), *Handbook of membrane reactors - volume 2: Reactor types and industrial applications* (pp. 236–295). Cambridge (UK): Woodhead Publishing Limited. ISBN 978-0-85709-415-5.

Other interesting information about configuration and performance of PMRs and an example of this integrated technology in water treatment and chemical production can be found in: *Chapter 21* - Photocatalytic membrane reactors: Configurations, performance and applications in water treatment and chemical production, by Molinari, R., Palmisano, L., Loddo, V., Mozia, S., & Morawski, A.W. (2013). In A. Basile (Ed.), *Handbook of membrane reactors - volume 2: Reactor types and industrial applications* (pp. 808–845). Cambridge (UK): Woodhead Publishing Limited. ISBN 978-0-85709-415-5.

List of symbols

C_f	Solute concentration in the feed
C_p	Solute concentration in the permeate
$\mathbf{e}^-$	Photogenerated electron
Eg	Energy band gap
h	Plank's constant
$\mathbf{h}^+$	Photogenerated hole
ν	Frequency of light radiation

List of acronyms

E_1^0	Redox potential of the species to be reduced
E_2^0	Redox potential of the species to be oxidized
2,4-DHBA	2,4-dihydroxybenzoic acid
4-CP	4-Chlorophenol
4-NP	4-Nitrophenol
AOP	Advanced oxidation process
APR	Annular photocatalytic reactor
BPA	Bisphenol A
CAM	Contact angle measurement
CB	Conduction band

COD	Chemical oxygen demand
DCF	Diclofenac
DCMD	Direct contact membrane distillation
E_{CB}	Redox potential of the conduction band
E_{VB}	Redox potential of the valence band
FA	Fulvic acid
GEM	Gemfibrozil
IBU	Ibuprofen
MD	Membrane distillation
MF	Microfiltration
NF	Nanofiltration
NHE	Normal hydrogen electrode
NOM	Natural organic matter
OM	Optical microscopy
PAA	Polyacrylic acid
PAN	Polyacrylonitrile
PES	Polyethersulfone
PhAC	Pharmaceutical active compound
PMR	Photocatalytic membrane reactor
PP	Polypropylene
PR	Photoreactor
PTFE	Polytetrafluoroethylene
PV	Pervaporation
PVDF	Polyvinylidene fluoride
R	Membrane rejection
RB5	Reactive black 5 dye
RO	Reverse osmosis
SEM	Scanning electron microscopy
SMPR	Submerged membrane photocatalytic reactor
STP	Sewage treatment plants
TAM	Tamoxifen
TOC	Total organic carbon
UF	Ultrafiltration
UV	Ultraviolet irradiation
VB	Valence band
WPF	Water permeation flux

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Novel and emerging membranes for water treatment by hydrostatic pressure and vapor pressure gradient membrane processes

8

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8.1 Introduction

Membrane-based separation technologies are environmentally friendly separation processes that are designed to provide effective and economic solutions to a wide variety of environmental issues related to water and energy use, including climate change and global warming. The growth of membrane science and technology is mainly due to the impressive developments in materials used for membrane fabrication and modification, improvements in membrane modules, and the evolution of related systems, plants, and equipment.

In general, membranes are semipermeable barriers used for selective permeation of the desired species in liquid or gaseous phases by means of an appropriate driving force(s). One of the provided classifications of membrane separation processes is according to the nature of the membrane and the applied transmembrane driving force. Each membrane process exhibits its advantages and drawbacks, and as consequence it has its fields of applications. Providing that this chapter is focused on water treatment, Table 8.1 summarizes the common considered membrane separation processes in this field with the corresponding driving forces and their applications.

It is worth mentioning that membranes of different forms and characteristics are generally made from a wide variety of chemically and thermally stable polymers. Both single polymers and polymer blends are considered. Other materials, such as ceramics, metals, and glasses are also used, and mixed matrix membranes (MMMs) are fabricated. Various membrane fabrication techniques are being proposed and improved (i.e., phase inversion, sintering, stretching, track-etching, electrospinning, etc.). In addition, various methods have been developed for membrane modification (i.e., chemical modification, surface coating, grafting, etc.) to improve its performance.

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Table 8.1 Membrane separation processes used for water treatment with their driving force and main fields of applications

Membrane process	Transmembrane driving force	Main fields of applications
Microfiltration (MF)	Hydrostatic pressure gradient	Pre-treatment for other processes Clarification and biological stabilization in the beverage industry Analysis Sterilization in food and pharmaceutical industries Removal of bacteria, clarification
Ultrafiltration (UF)	Hydrostatic pressure gradient	Pre-treatment for other processes Separation of oil/water emulsion Dewaxing Deasphalting Electrophoretic paint Removal of macromolecules and virus
Nanofiltration (NF)	Hydrostatic pressure gradient	Drinking water production Removal of ions and small organics Chemical and pharmaceutical industry Concentration/dewatering Water softening Fractionation of monovalent and divalent cations
Reverse osmosis (RO)	Hydrostatic pressure gradient	Sea and brackish water desalination Drinking water production Wastewater treatment (industrial and municipal, pulp and paper, textile) Petroleum industry
Membrane distillation (MD)	Vapor pressure gradient (temperature gradient, downstream pressure)	Desalination and concentration of brines Ultrapure water production Near 100% separation of nonvolatile solutes present in water Extraction of volatile organic compounds Recovery of valuable compounds Food, medical, radioactive wastewaters
Pervaporation (PV)	Vapor pressure gradient (downstream pressure)	Dehydration of organic solvents Removal of organics from water Organic/organic separation
Electrodialysis (ED)	Electric potential gradient	Sea and brackish water desalination Ultrapure water production Demineralization of food products Table salt production Concentration of brines

Table 8.1 Continued

Membrane process	Transmembrane driving force	Main fields of applications
Reverse electrodialysis (RED)	Electric potential gradient	Power generation Sea and brackish water desalination
Osmotic distillation (OD)	Vapor pressure gradient (concentration gradient)	Near 100% separation of non-volatile solutes present in water Recovery of valuable compounds Food wastewaters
Forward osmosis (FO)	Concentration gradient	Sea and brackish water desalination Drinking water production
Pressure retarded osmosis (PRO)	Concentration gradient	Power generation Sea and brackish water desalination

Novel membranes with innovative materials and improved properties suitable for specific applications and compact module designs with better hydrodynamic flow channels and new areas of applications are continuously reported. Besides the high process performance of a given membrane that includes both the high liquid or vapor production rate and selectivity or separation efficiency, there are other basic properties that must be taken into account, such as operational simplicity, high energy efficiency, low cost, good stability under wide operating conditions, long-term durability, less fouling and scaling susceptibility, environment compatibility, customizable and adaptive between different membrane operations in integrated systems, easy control of its structure, and scale-up.

8.2 Pressure-driven membrane processes

In general, pressure-driven membrane processes (PDMPs) include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). These filtration processes can be distinguished by the size of the particles or molecules that the corresponding membrane is capable of retaining or passing through (Porter, 1988). This is roughly related to the membrane pore size, which is the main responsible parameter dictating the field of the process applications.

The membranes fabricated for each of the PDMPs exhibit specific characteristics according to the operating conditions and the subjected application. A common characteristic of the PDMP membranes is the high mechanical property to bear the applied hydrostatic pressure, especially for NF and RO. In the following sections, the recent progress made in each individual PDMP is thoroughly described with its novel and emerging membranes proposed for water treatment.

8.2.1 Microfiltration

As shown in Table 8.2, the pore size of an MF membrane ranges between 0.1 and 10 μm. The MF membranes must have a high porosity and a pore size distribution as narrow as possible. A large number of materials were considered for fabrication of MF membranes, both organic (hydrophilic or hydrophobic polymers) and inorganic materials (ceramics, metals, glasses). Some of the fabrication techniques, such as sintering, stretching, track-etching, and phase inversion, were used for fabrication of polymeric MF membranes.

Table 8.2 Characteristics of the different pressure-driven membrane processes

	Microfiltration (MF)	**Ultrafiltration (UF)**	**Nanofiltration (NF)**	**Reverse osmosis (RO)**
Pore size (nm)	100–10,000	1–100	0.5–2	<0.5
MWCO[a] (Da)	$>5\cdot10^5$	$2–5\cdot10^5$	$5\cdot10^2–2\cdot10^3$	$<5\cdot10^2$
Pressure (MPa)	0.1–2	1–10	10–30	15–30 (brackish) 40–80 (seawater)
Permeability (kg/m^2 s)	<278	2.5–278	0.5–8.5	<0.5
Membrane materials[b]	Ceramic, PS, PES, PVDF, CA	Ceramic, PS, PES, PVDF, CA, TF	CA, TF	CA, TF
Rejection	Particles Bacteria	Macromolecules Proteins Virus Colloids	High *Mw* compounds Multivalent ions Glucose	High and low *Mw* compounds Monovalent ions Inorganic ions Amino acids
Separation mechanism	Sieving	Sieving	Sieving, charge effects, diffusion	Solution diffusion

[a] MWCO = Molecular weight cut-off of the membrane (corresponding solute rejection 90%).

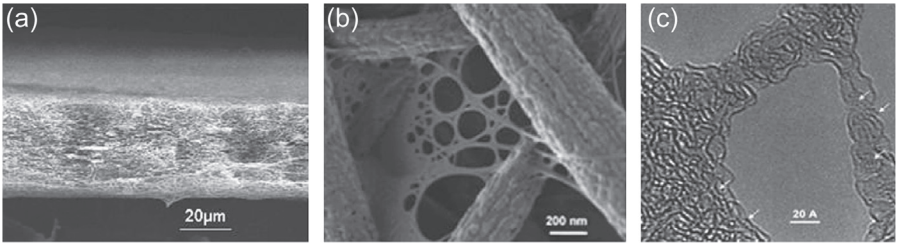
[b] PS, polysulfone; PES, Polyethersulfone; PVDF, polyvinylidene fluoride; CA, cellulose acetate; TF, thin-film.

The main problems of MF are the concentration polarization and fouling phenomena. Both reduce the water production rate and the efficiency of the whole process. Therefore, MF membranes are designed or modified taking into consideration both phenomena, and MF modules are cleaned periodically. It must be pointed out that the selection of a suitable material for MF is an important factor because solute(s) adsorption phenomenon also plays an important role in irreversible fouling effects.

Dong et al. (2012) used hydrophilic $Mg(OH)_2$ nanoparticles (NPs) as inorganic fillers to prepare polyvinylidene fluoride PVDF/$Mg(OH)_2$ MF hybrid membranes with enhanced antifouling property. Due to the addition of $Mg(OH)_2$ NPs, a large amount of hydroxyl (−OH) groups were formed. This results in an increase of the hydrophilicity of the prepared hybrid membrane, reducing the permeate flux losses caused by membrane biofouling of *Escherichia coli* and bovine serum albumin (BSA).

Wu, Tang, and Wu (2014) developed a novel silica (SiO_2)−graphene oxide (GO) nano-hybrid/polysulfone (PS) membrane, which exhibited excellent antifouling ability and improved water permeability, maintaining a high rejection factor to egg albumin. These results were attributed to the specific properties of SiO_2−GO nanohybrid such as the high hydrophilicity and the good dispersion derived from SiO_2 NPs.

Wang, Guan, et al. (2013) developed novel nanofibrous MF composite membranes, consisting of a two-layered electrospun polyacrylonitrile (PAN)/polyethylene terephthalate (PET) fibrous scaffold infused with oxidized or modified cellulose nanofibers, which were subsequently grafted by amine, such as polyvinylamine (PVAm), polyethyleneimine (PEI), or ethylenediamine (see Figure 8.1). These membranes have a web-like structure with high charge density, high porosity, and large surface area per unit volume. These characteristics enabled the membranes to simultaneously remove bacteria, viruses and/or toxic heavy metal ions maintaining a good permeation flux.



PAN layer CNF in PAN layer Cellulose nanofibers

Figure 8.1 SEM images of electrospun polyacrylonitrile/polyethylene terephthalate (PAN/PET) membrane (a) electrospun polyacrylonitrile/polyethylene terephthalate (PAN/PET) membrane (cross-section) and (b) PAN/PET membrane infused with polyvinylamine (PVAm) grafted CNF (top view). (c) TEM image taken at a small section of the cellulose network containing pores and individual polymer chains with spaghetti-like configuration. Reprinted from Wang, Guan, et al. (2013), with permission from Elsevier.

8.2.2 Ultrafiltration

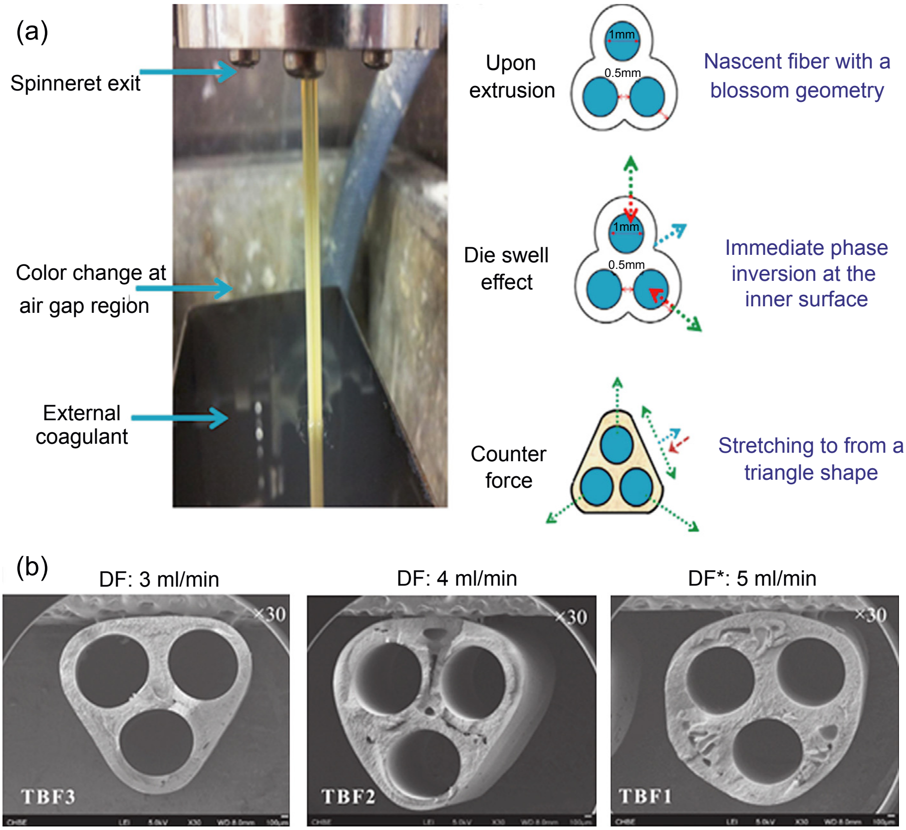
UF is a PDMP placed between MF and NF. However, MF and UF both ivolve similar membrane processes based on the same separation principle, being the difference between both the structure of the membrane, which is asymmetric for UF membrane with a much denser top layer, and consequently a much higher hydrodynamic resistance than MF. UF is commonly used to retain macromolecules and colloids from aqueous solutions and to remove un-dissolved, suspended or emulsified solids from water. Cellulose acetate (CA) and polyelectrolytes are among the first synthetic polymers used for UF membranes. Today, UF membranes are made from a wide variety of chemically and thermally stable synthetic polymers, including PS, PAN, polyethersulfone (PES), polyvinyl chloride (PVC), polycarbonate (PC), aliphatic and aromatic polyamides (PA), polyimides (PI), polyarylsulfone (PAS), and PVDF.

Kong et al. (2014) studied the effect of adding hydrophilic TEMPO-oxidized cellulose nanofibrils (TOCNs) as a modifying agent on the structure and performance of cellulose triacetate (CTA) UF membranes. The obtained results showed that the incorporation of TOCNs to CTA membranes enhanced its mechanical properties (tensile strength and break—elongate ratio) and its hydrophilicity, resulting in higher permeate fluxes and better antifouling performance.

Another innovative and interesting study was performed by Wang, Luo, and Chung (2014), who developed tri-bore UF hollow fiber membranes made from Matrimid® and PES polymers with round-shape bore channels and a regular triangle-shape outer geometry. Figure 8.2 shows the mechanism of formation of these UF membranes together with their scanning electron microscopy (SEM) cross-section images. This particular geometry is claimed to be advantageous in terms of uniform mechanical strength and enhanced permeation properties due to the evenly distributed membrane wall thickness.

Recently, a variety of inorganic particles or fillers such as SiO_2 (Wu, Mansouri, & Chen, 2013; Yu, Zhang, Zhang, Liu, & Zhang, 2013; Zhang, Wang, et al., 2014), silver (Ag) (Li et al., 2013), ferrous ferric oxide (Fe_3O_4), alumina (Al_2O_3) (Arsuaga et al., 2013), zirconia (ZrO_2) (Arsuaga et al., 2013; Arthanareeswaran & Thanikaivelan, 2010; Pang et al., 2014), titania (TiO_2) (Arsuaga et al., 2013; Hamid et al., 2011; Razmjou, Mansouri, & Chen, 2011; Razmjou, Resosudarmo, et al., 2012; Zhang, Lu, et al., 2013; Zhao, Wang, Wang, Sun, & Zhang, 2012), zinc oxide (ZnO) (Hong & He, 2014), and zeolites (Leo, Ahmad Kamil, Junaidi, Kamal, & Ahmad, 2013) have been used to develop novel UF MMMs or organic—inorganic hybrid membranes with improved permeabilities, mechanical strengths, and fouling resistant ability.

Among the different inorganic NPs blended with polymeric membranes, TiO_2 has also been used in numerous studies due to its superhydrophilic, photocatalytic, and antibacterial properties under ultraviolet (UV) irradiation. Rahimpour, Jahanshahi, Mollahosseini, and Rajaeian (2012) performed an approach to improve the properties, structure, and performance of PVDF/sulfonated polyethersulfone (SPES) blend UF membranes by using self-assembly of TiO_2 NPs on the membrane surface followed by UV irradiation to activate their photocatalytic property. The water contact angle



*DF: Dope flowrate

Figure 8.2 (a) Mechanisms of formation of triangle-shape tri-bore hollow fiber membranes. (b) SEM images of Matrimid® tri-bore hollow fiber membranes using different dope compositions. Adapted from Wang et al. (2014), with permission from Elsevier.

measurements showed that the hydrophilicity of PVDF/SPES membranes was strongly improved by TiO_2 deposition and UV irradiation. The initial permeate fluxes of both pure water and BSA aqueous solutions were lower for the TiO_2 deposited membranes compared to the PVDF/SPES membranes. However, the fouling propensity (bacterial activity) was significantly reduced, and the long-term permeate flux stability was enhanced.

As was mentioned previously, SiO_2 is another common NP used for membrane modification. SiO_2 has the advantage to improve the membrane mechanical properties and membrane porosity. Yu et al. (2013) used modified SiO_2 NPs grafted with N-Halamine to develop novel hydrophilic PES UF membranes. By SEM image analysis and contact angle measurements, it was confirmed that the addition of this modified SiO_2 exerted a slight influence on the microstructure of the PES membrane, but significantly improved its surface hydrophilicity and permeability.

Song and Kim (2013) prepared PS composites UF membranes with poly(1-vinylpyrrolidone) (PVP)-grafted SiO_2 NPs (PVP-g-SiO_2) by phase inversion method (see Figure 8.3). The resulted UF membranes exhibited higher water permeate flux than PS membranes without scarifying the solute rejection factors when the amount of PVP-g-SiO_2 was less than or equal to 5 wt% in the casting solution. The hydrophilicity of the PVP-g-SiO_2 membranes was increased with increasing PVP-g-SiO_2 content, and the PVP-g-SiO_2 membranes exhibited enhanced fouling resistance toward non-ionic surfactants.

Multifunctional inorganic ZnO NP has also attracted a significant attention due to its outstanding physical and chemical properties, including promising catalytic activity and efficient antibacterial and bactericidal capabilities. ZnO as an additive NP is more economical than TiO_2 and Al_2O_3 (Liang, Xiao, Mo, & Huang, 2012). Hong and He (2014) successfully prepared PVDF UF membrane blended with ZnO NP via phase inversion method. The photocatalysis tests clearly showed that the modified PVDF membranes had significant photocatalysis self-cleaning capability, which was due to the addition of nano-ZnO on the inner surface of the membrane (i.e., the pore wall). The water permeate flux of nano-ZnO/PVDF blend membranes was higher than that of single PVDF membrane, decreasing the membrane fouling resistance.

Mehrparvar, Rahimpour, and Jahanshahi (2014) prepared novel modified PES UF membrane for humic acid removal by blending different concentrations of two hydrophilic organic monomers, 3,5-diaminobenzoic acid (DBA) and gallic acid (GA), with PES. Experimental results showed that the different component ratios of each monomer affected the structural property of the blended membranes and the top surface roughness. As can be seen in Figure 8.4, with the addition of DBA and GA, the size of the macrovoids became smaller, and a denser surface was formed at the top membrane surface. The addition of DBA and GA monomers in the casting solution increased the water content and the hydrophilicity of the membranes. Moreover, the modified membranes exhibited better antifouling properties, and the best membrane was prepared with 8 wt% DBA and 6 wt% GA.

During the last 5 years, GO nanosheets, a two-dimensional carbon material, have received tremendous attentions thanks to its fantastic properties, such as good hydrophilicity, easy to be modified, and its ability to be dispersed in water, yielding to a prolonged and stable suspension. Wang et al. (2012) used GO nanosheets to develop novel organic—inorganic nanocomposite GO/PVDF-blended UF membranes. The GO addition played an important role in the membrane microstructure due to the affinity of GO with many types of hydrophilic groups, which increase the rapid mass transfer between the solvent and non-solvent during phase inversion. When the GO content increased up to 0.30 wt%, lateral pore structures appeared within the GO-blended PVDF membranes (Figure 8.5). These features enhanced the hydrophilicity, mechanical properties, and water permeate flux recovery ratio compared to the PVDF membrane. Yu, Zhang, Zhang, Liu, Zhang, & Song (2013) also developed a novel hyperbranched polyethylenimine (HPEI)-GO/PES blend UF membrane with enhanced antifouling and antibacterial performance via the phase inversion method.

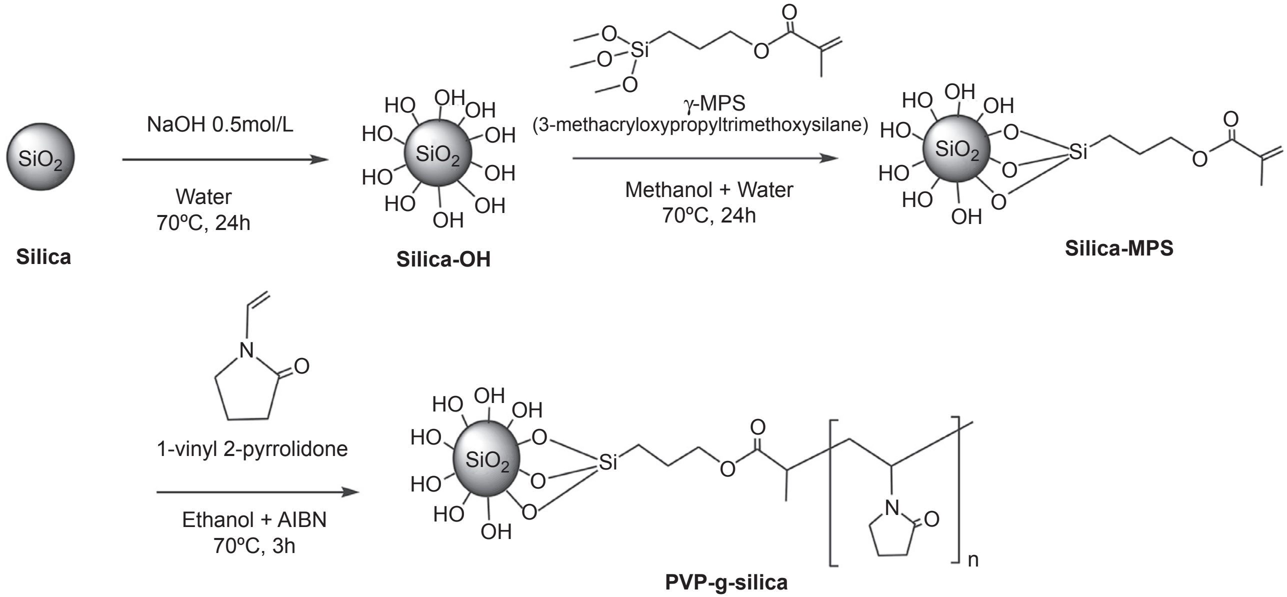


Figure 8.3 Reaction procedure for preparation of PVP grafted silica nanoparticles (PVP-g-SiO_2). Reprinted from Song and Kim (2013), with permission from Elsevier.

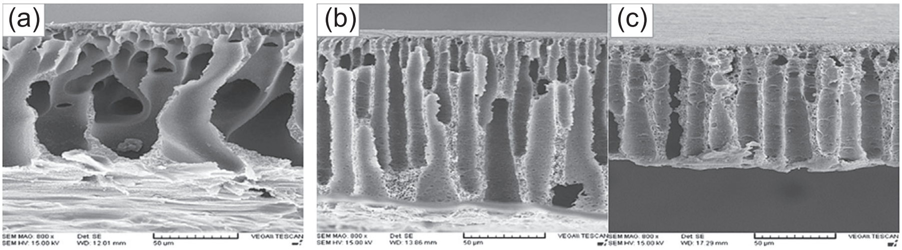


Figure 8.4 SEM cross-section images of: (a) neat polyethersulfone (PES) membrane and PES membrane with (b) 15 wt% diaminobenzoic acid (DBA) and (c) 15 wt% gallic acid (GA).
Reprinted from Mehrparvar et al. (2013), with permission from Elsevier.

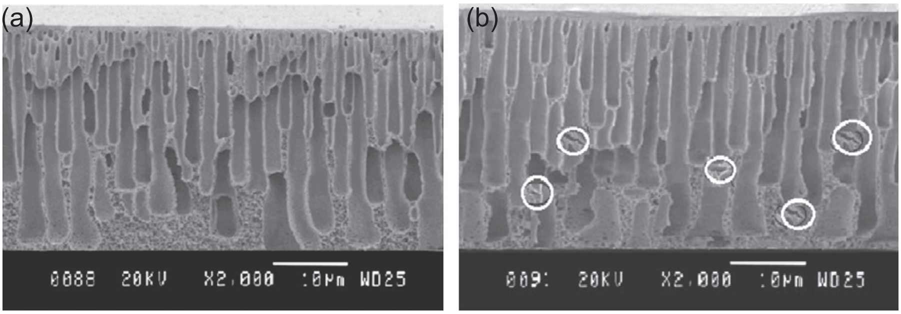


Figure 8.5 SEM cross-section images of the GO-blended polyvinylidene fluoride (PVDF) membranes with (a) 0 and (b) 0.3 wt% graphene oxide (GO).
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8.2.3 Nanofiltration

NF is a PDMP using semipermeable membranes with a molecular weight cut-off (MWCO) in the range of 0.5–2 kDa and pore sizes in the range of 0.5–2.0 nm (see Table 8.2). The origin of NF dates back to 1970s, when efforts started to be made developing RO membranes with reasonable water permeate fluxes at relatively low pressures (Li, Fane, Ho, Matsuura, et al., 2008). The NF process exhibits separation characteristics between RO and UF. The specific features of NF membranes are mainly the combination of very high rejection factors for multivalent ions (99%) with low to moderate rejection factors for monovalent ions (0–70%), and high rejection factors (90%) for organic compounds with molecular weights above that of the membrane MWCO. The major separation mechanisms of NF involve a steric (i.e., size exclusion) effect and an electrostatic partitioning interaction (i.e., Donnan exclusion) between a given NF membrane and a feed aqueous solution (Sun, Hatton, Chan, & Chung, 2012). In general, the traditional materials used for fabrication of NF membranes are polymers using the phase inversion or the interfacial polymerization (IP) techniques. The phase inversion membranes are homogeneous and asymmetric, and they are often made of CA or PES, while the NF membranes made by IP are heterogeneous, consisting of a thin-film composite (TFC) layer on the top of an UF substrate. Typically used polymers are (aromatic) PA, PI, PS, PES, sulfonated PS, and poly(piperazine amide), among others.

Recently, there has been a growing interest in developing novel NF hollow fiber membranes because of their flexibility and they are self-supporting and easy to pack in modules with high membrane area per unit module volume (Nunes & Peinemann, 2001; Yu, Cheng, et al., 2013). Most NF membranes have a TFC structure because of various key advantages compared to asymmetric membranes. Sun et al. (2012) developed a TFC NF dual-layer hollow fiber membrane via IP of HPEI and isophthaloyl chloride on a Torlon® polyamide-imide (PAI) dual-layer hollow fiber substrate. This NF membrane exhibited a double repulsion effect, a negatively charged substrate and a positively charged selective layer, resulting in superior rejection factors (>99%) for both positively and negatively charged dye molecules. This type of membrane was suggested to recycle valuable products and reuse water for textile, pharmaceutical, and other industries. Fang, Shi, and Wang (2013) prepared TFC NF hollow fiber membranes for water softening under low operating pressure (<2 bar) using IP of PEI and trymesoyl chloride (TMC) on the inner surface of a PES UF membrane substrate. The prepared membrane showed a pure water permeability (*PWP*) of about 17 L/m^2 h bar, an MWCO of around 500 Da (i.e., effective pore radius of about 0.65 nm), an $MgCl_2$ rejection factor of 96.7%, and an $MgSO_4$ rejection factor of 80.6%. Wei, Kong, Sun, and Chen (2013) prepared also TFC NF hollow fiber membranes by IP of piperazine (PIP) and TMC on PS/PES UF supporting membranes. The fabricated composite NF hollow fiber membranes had a relatively hydrophilic surface with an MWCO of approximately 520 Da, a *PWP* of 11.9 L/m^2 h bar, and rejection factors of 39.8% and 96.2% to NaCl and Na_2SO_4, respectively. Zheng et al. (2013) followed the dip-coating method to prepare positively charged TFC NF hollow fiber membranes for cationic dyes removal using polypropylene (PP) hollow fiber MF membrane as support, PVA and polyquaternium-10 as coating materials, and glutaraldehyde (GLA) as a crosslinking agent. The prepared membrane had an MWCO of 650 Da, a *PWP* of 8.6 L/m^2 h bar, and rejection factors of 92.8% and 35.0% to $CaCl_2$ and NaCl, respectively.

Not only hollow fiber membranes have been proposed for NF, but also flat sheet membranes. Guan, Zhang, Han, Zhang, and Jian (2013) developed TFC NF flat sheet membranes with improved thermal stability and high performance by coating sulfonated copoly (phthalazinone biphenyl ether sulfone; SPPBES) on poly(phthalazinone ether sulfone ketone) UF membranes used as support. The prepared SPPBES composite membranes exhibited a *PWP* of 7.3 L/m^2 h bar and 84% Na_2SO_4 rejection factor. TFC NF flat sheet membranes were also prepared by Han (2013) following the IP of melamine and TMC on a PEI UF membrane reinforced on PP non-woven fabric as a backing material. The membranes prepared under the optimum preparation conditions achieved a *PWP* of 3.4 L/m^2 h bar and a rejection factor to Na_2SO_4 of 77.8%.

As occurred with membranes designed for UF, different polymers and inorganic NPs have been used to improve the NF performance of TFC membranes. For instance, to solve the biofouling problem, Ag NPs were used. Kim, Hwang, Gamal El-Din, and

Liu (2012) used Ag NPs to enhance the antifouling and antibacterial property of the surface of NF membranes. Recently, a stable Ag-doped fly ash/polyurethane (Ag-FA/PU) nanocomposite multifunctional spider-web-like membrane was prepared by Pant et al. (2014) via one-step electrospinning process using fly ash particles. It was suggested that the direct reduction of the Ag metal precursor ($AgNO_3$) into Ag NPs caused by the solvent of PU (*N,N*-dimethylformamide) in the blend solution could be the responsible of the simultaneous formation of spider-web-like nanonets and deposition of Ag NPs on the surface of the fibers during electrospinning (Figure 8.6). These features enhanced absorption capacity to remove carcinogenic arsenic and toxic organic dyes, with the antibacterial properties reducing biofouling of the membrane.

Mollahosseini and Rahimpour (2014) tried to improve the antibacterial and antifouling property of TFC NF membranes by first coating TiO_2 NPs on an UF PS membrane support followed by the IP of *m*-phenylenediamine (MPD) and TMC monomers on the coated TiO_2 layer. With increasing TiO_2 content in TFC membranes, smoother and thicker surfaces appeared on the selective PA layer, reducing the probability of membrane fouling by macromolecules.

A novel β-cyclodextrin (β-CD)/polyester TFC NF membrane was prepared by Wu, Tang, and Wu (2013b) via in situ IP of TMC and triethanolamine (TEOA) in presence of β-CD. By adding an appropriate amount of β-CD, the membrane NF performance was improved in terms of water permeability, hydrophilicity, water permeate flux, rejection factor, and antifouling property. To enhance acid stability of TFC NF membranes, Yu, Zhou, et al. (2013) followed the IP of TMC and naphthalene-1,3,6-trisulfonylchloride (NTSC), and PIP to modify a PS UF membrane used as support. It was observed that the increase of the NTSC content in TMC-organic solution resulted in a more hydrophilic and negatively charged membrane surface, with an increase of both MWCO and *PWP* up to 660 Da and 10.6 L/m^2 h bar, respectively. Wu, Tang, and Wu (2013a) performed an improved process to develop high-performance thin-film nanocomposite (TFN) membranes using IP of TEOA and TMC on PS UF supporting membrane in presence of multiwalled carbon nanotubes (MWCNTs). By

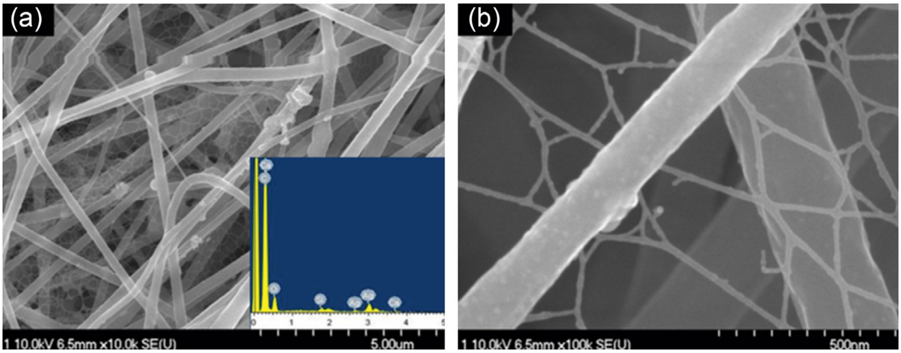

Figure 8.6 Field-emission scanning electron microscopy (FESEM) images of Ag/FA/PU (M1) mat (obtained from 1 h stirring solution) at different magnifications (a) lower magnification, (b) higher magnification (inset is FESEM EDX of Ag/FA/PU (M1) mat).
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using an adequate amount of MWCNTs, an appropriate surfactant, and a proper reaction time, MWCNTs/polyester nanocomposite membranes can be fabricated with both high permeation flux and excellent selectivity.

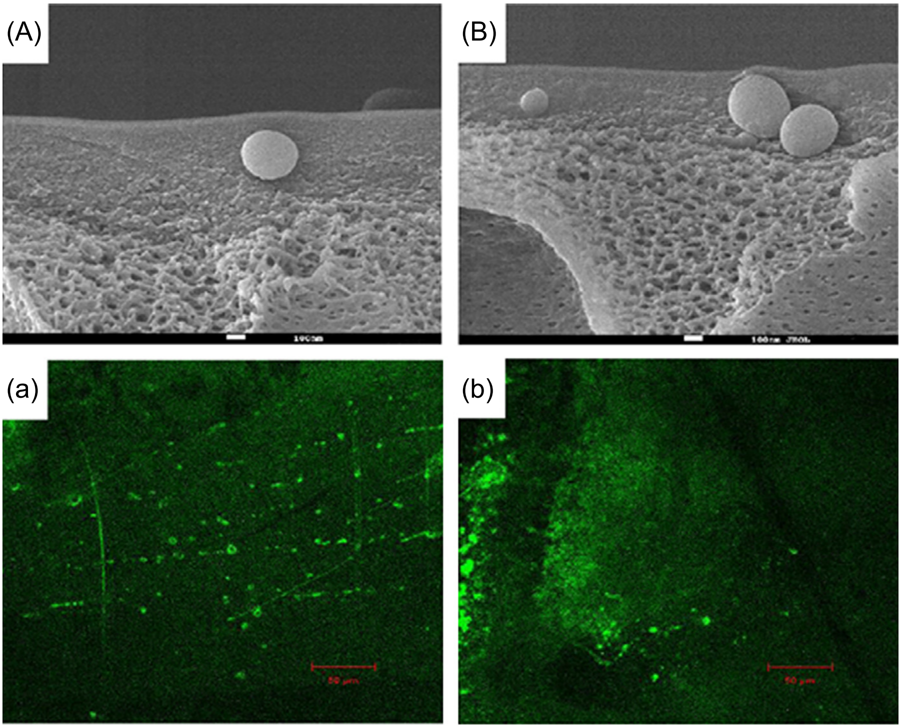
A novel antifouling mixed matrix PES NF membrane was prepared by Zinadini, Zinatizadeh, Rahimi, Vatanpour, and Zangeneh (2014) by embedding GO nanoplates in PES matrix. The modified GO/PES membranes showed a wider finger-like structure in comparison to those of the unmodified PES membrane, with a significantly higher water permeate flux, higher hydrophilicity, higher dye removal capacity, and higher retention factor. In addition, it was found that the membrane prepared with 0.5 wt% GO exhibited the best antibiofouling property with the highest mean pore size, porosity, and therefore the greater water permeate flux.

Recently, positively charged composite NF membranes were prepared via crosslinking modification with an active PEI layer and a PAN substrate (Feng, Xu, Li, Tang, & Gao, 2014). The PAN/PEI membrane with a PEI layer crosslinked with 12.0 wt% epichlorohydrin at 65 °C for 15 h exhibited an optimum NF performance with relatively high salt rejection factor and a high permeate flux (i.e., salt rejection factors of 92.82%, 69.76%, and 61.31% for feed aqueous solutions containing 2000 mg/L of $MgCl_2$, $MgSO_4$, and NaCl, respectively, with the corresponding *PWP*: 1.63, 1.60, and 1.79 L/m^2 h bar).

Another type of NF membranes, aquaporin (AQP)-based biomimetic membrane, has attracted increasing attention during the last two years because of its potential application for water purification and seawater desalination, attributed to the exceptionally high permeability and selectivity of AQPs. In late 2013, Li et al. (2014) introduced a novel and simple method to prepare an aquaporin Z (AQP-Z)-based biomimetic NF membrane consisting first on the deposition of polydopamine (PDA)-coated proteoliposomes on the surface of a substrate and then crosslinking PEI with the PAI substrate to encapsulate these deposited proteoliposomes (Figure 8.7). The resultant AQP-Z-based membrane prepared under the optimal conditions achieved 95% $MgCl_2$ rejection factor and a *PWP* of 3.7 L/m^2 h bar (50% higher than the control membrane with inactive AQPs). This type of membrane could preserve its activity even under harsh environmental conditions such as a high thermal treatment at 343 K for 2 h (Li et al., 2014).

8.2.4 Reverse osmosis

RO is a PDMP used to separate dissolved solids, such as ions, high and low molecular weight compounds, and amino acids from water-based solutions. More details on RO membrane and process applications are summarized in Tables 8.1 and 8.2. Currently, RO is the most important desalination technology. Different types of membranes were proposed for the RO process, but the most common ones are CA membranes and aromatic PA composite membranes. The first was an asymmetric CA-based RO membrane invented by Loeb and Sourirajan in 1960 (Hasson, 2010). Today, TFC membranes are the most used in RO applications. However, the main drawbacks of RO membranes are the “trade-off” between permeability and salt rejection factors, the membrane fouling, and the chlorination problem resulting in a significant



AQPs (LPR 400)

Mutants (LPR 400)

Figure 8.7 FESEM images (A and B, scale bar 100 nm) and confocal fluorescence microscopy images (a and b, scale bar 50 mm) of different membranes with AQP-Z incorporated membrane (called LPR 400).
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membrane degradation by the presence of chlorine in feed water solutions (Xu, Wang, & Li, 2013). As a consequence, research studies considered these three obstacles in developing novel suitable membranes for different RO applications (Misdan, Lau, & Ismail, 2012).

Innovative RO membrane engineering is still required because of the continuous increasing demands of desalination and membrane wastewater treatments with enhanced water production rates, greater salt rejection factors, and overall higher resistance to fouling (Li & Wang, 2010). Various strategies have been explored to tackle these needs, among which surface modifications (e.g., surface coating) and incorporation of specific additives, nanoparticles, and/or co-solvents in the aqueous/organic phase during the IP have been identified to be the most effective (Xu et al., 2013).

Wang, Dai, Zhang, Li, and Zhang (2013) prepared TFC RO membranes through IP of TMC, 2,4,4′,6-biphenyl tetraacyl chloride, 2,3′,4,5′,6-biphenyl pentaacyl chloride, and 2,2′,4,4′,6,6′-biphenyl hexaacyl chloride with MPD. The RO membrane skin layer became more negatively charged, thinner, and smoother as the functionality of the acid chloride monomer increased. The lower permeate flux of the highly functional acid chloride-based membrane owing to the greater extent of carboxylic acid groups on the membrane surface, lower surface roughness, and lower mobility of the crosslinked PA chains was observed. A novel high permeability PA TFC RO membrane was synthesized by Zhao, Chang, and Ho (2013) by introducing four different hydrophilic additives (*o*-aminobenzoic acid-triethylamine salt, *m*-aminobenzoic acid-triethylamine salt, 2-(2-hydroxyethl) pyridine, and 4-(2-hydroxyethyl) morpholine) in the MPD aqueous solution for IP. The obtained optimum membrane exhibited a stable desalination performance over a one-month test with a salt rejection factor of 98.8% and a permeate flux of 107.2 L/m^2 h.

Functionalized polyethylene glycol (PEG)-based polymers also have been synthesized and used to modify the PA TFC RO membrane surface to enhance its antifouling properties. A comb-like amphiphilic copolymer, methylmethacrylate-hydroxypoly (oxyethylene) methacrylate, was synthesized by Choi, Park, Tak, and Kwon (2012) via free-radical polymerization and used to modify the surface of the PA TFC RO membrane by the dip-coating method. In addition, to introduce antifouling quality in RO membranes without compromising their separation properties, a new type of polymer coating made from hydrophilic dendritic polymers was used to modify the surface of PA TFC RO membrane, rendering it more hydrophilic (Sarkar et al., 2010). As it can be seen in Figure 8.8, the hydrophilic dendritic polymers were crosslinked to form a network, and this was modified with hydrophilic linear chains (e.g., PEG, polyvinyl alcohol (PVA), and polyacrylamide) to form polymer brushes, which can help to prevent formation of biofilm. Moreover, antimicrobial metal ions such as Ag, Zn, or potassium could be chelated into the polymer network to further prevent biofouling. Examples of dendritic polymers are hyperbranched polymers or dendrimers. The chosen dendrimers were NH_2-terminated PAMAM (PAMAM G2) and PAMAM G2-PEG. Both dendrimers polymers can be crosslinked with glycidyl ether-functionalized α,ω-telechelic PEG to from the PAMAM G2-PEG networks, which were then used as hydrophilic coating layers.

Zwitterionic materials can bind water molecules more strongly than other hydrophilic materials via electrostatically induced hydration. Therefore, zwitterionic-based materials have been developed as promising candidates for preparation of antifouling surfaces (Xu et al., 2013). In this sense, Azari and Zou (2012) incorporated red-ox functional amino acid 3-(3,4-dihydroxyphenyl)-L-alanine onto commercial PA TFC RO membranes to create a zwitterionic surface resistant to membrane fouling. It was found that the coated membranes exhibited remarkably improved hydrophilicity, which resulted in an increase of the membrane water permeability preserving the salt rejection factor.

For the purpose of improving the antifouling properties of RO membranes, Ishigami et al. (2012) used the layer-by-layer (LbL) assembly to modify their surfaces by poly (sodium 4-styrenesulfate) (PSS) and poly(allylamine hydrochloride) forming a thin polyelectrolyte coating layer. This antifouling capability increased with increasing the number of layers due to the enhanced hydrophilicity and smoothness of the membrane surface. The obtained optimal layer number, based on the highest obtained water permeability when BSA was used as a foulant solute in water, was found to be four.

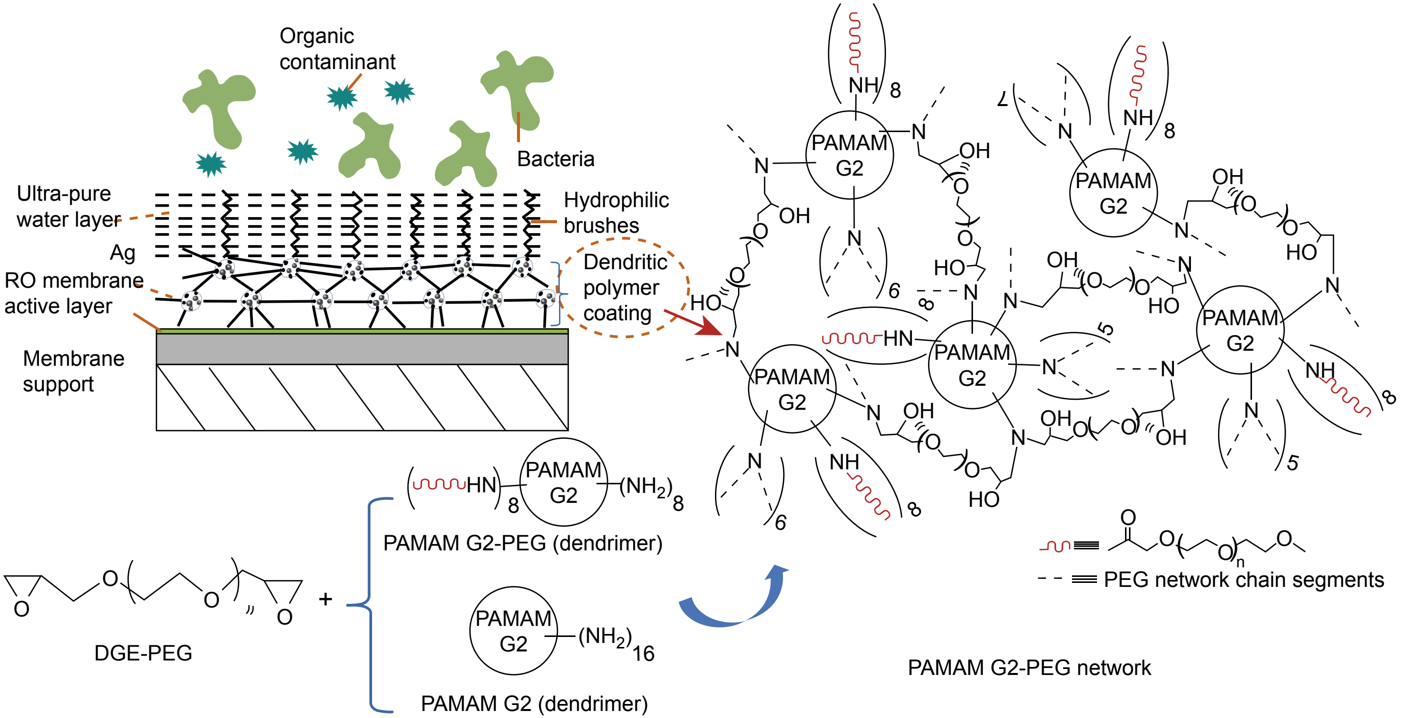

Figure 8.8 Schematic illustration of hydrophilic coating with dendritic polymers on the polyamide (PA) active layer of thin-film composite reverse osmosis (TFC RO) membrane.
Reprinted from Xu et al. (2013) and Sarkar et al. (2010), with permission from Elsevier.

It was concluded that LbL assembly on a membrane surface could reduce fouling not only by electrostatic repulsion between foulant and membrane surface, but also by electrostatic attraction due to the fact that the surface charge could be controlled by alternatively choosing the outer polyelectrolyte.

As was pointed out previously, chlorination is another trade-off for PA TFC RO membranes. Several researchers focused their studies to enhance chlorine tolerance of PA TFC RO membranes. For instance, Zhang, Wang, Wang, and Wang (2013) modified a commercial TFC aromatic PA RO membrane (RE2521-TL, Woongjin Chemical Co., Ltd., Korea) via free-radical graft polymerization of 3-allyl-5,5-dimethylhydantoin (ADMH) followed by crosslinking by *N*,*N*′-methylenebis(acrylamide) (MBA). After graft polymerization, it was observed that the ADMH/MBA modified membrane was more hydrophilic, with higher salt rejection factors but lower permeate flux than the unmodified membrane. Recently, Ni, Meng, Li, and Zhang (2014) synthesized a novel hydrophilic random terpolymer, poly(methylacryloxyethyldimethyl benzyl ammonium chloride-r-acryl-amide-r-2-hydroxyethyl methacrylate), via simple free-radical copolymerization using as a coating material a commercial PA TFC RO membranes (LCLE and BW30, DOW Chemical Co. Ltd., Minneapolis, USA) to improve their membrane antifouling performance and chlorine resistance (Figure 8.9). This innovative membrane modification method was demonstrated to be an effective way to render the PA TFC RO membrane more hydrophilic with antimicrobial properties and more resistance to chlorine and fouling.

The introduction of NPs with multifunctionalities in RO TFC membranes could lead to another breakthrough in membrane desalination by further enhancing water permeability without scarifying the salt rejection factors (Misdan et al., 2012). Recently, a number of organic–inorganic TFC nanocomposite membranes containing NPs such as zeolite (Kim, Hyeon, Chun, Chun, & Kim, 2013; Liu & Chen, 2013), SiO_2 (Bao, Zhu, Wang, Wang, & Gao, 2013; Park, Kim, Chun, Chun, & Kim, 2012), Ag (Nisola, Park, Beltran, & Chung, 2012), TiO_2 (Kim, Kwak, Sohn, & Park, 2003), ZnO (Schwartz et al., 2012), organo-selenium compounds (Vercellino et al., 2013), and carbon nanotubes (CNTs) (Baroña, Lim, Choi, & Jung, 2013; Zhao et al., 2014) have been investigated for their potential use in RO applications. Hydrophilic polyether-block-polyamide copolymer solutions with different contents of Ag NPs were used to prepare dense films and coating layers to improve the biofouling resistance of commercial PS UF membranes (Nisola et al., 2012). ZnO NPs in biocompatible poly(*N*-isopropylacrylamide) (PNIPAAm) hydrogel layers were used by Schwartz et al. (2012) to prepare novel antimicrobial composite membranes via mixing the PNIPAAm prepolymer with ZnO NPs, followed by spin-coating and photocrosslinking. It was also found that these ZnO/hydrogel nanocomposite coated films exhibited differential toxicity between bacterial and cellular species, which qualified them as promising candidates for novel biomedical device coatings.

It must be pointed out that different types of zeolite NPs such as NaA zeolite (Huang, Qu, Dong, Zhang, & Chen, 2013), NaX zeolite (Fathizadeh, Aroujalian, & Raisi, 2011) and A zeolite (Pendergast, Ghosh, & Hoek, 2013) have been added in PA active layer of TFC RO membranes to improve their RO performance.

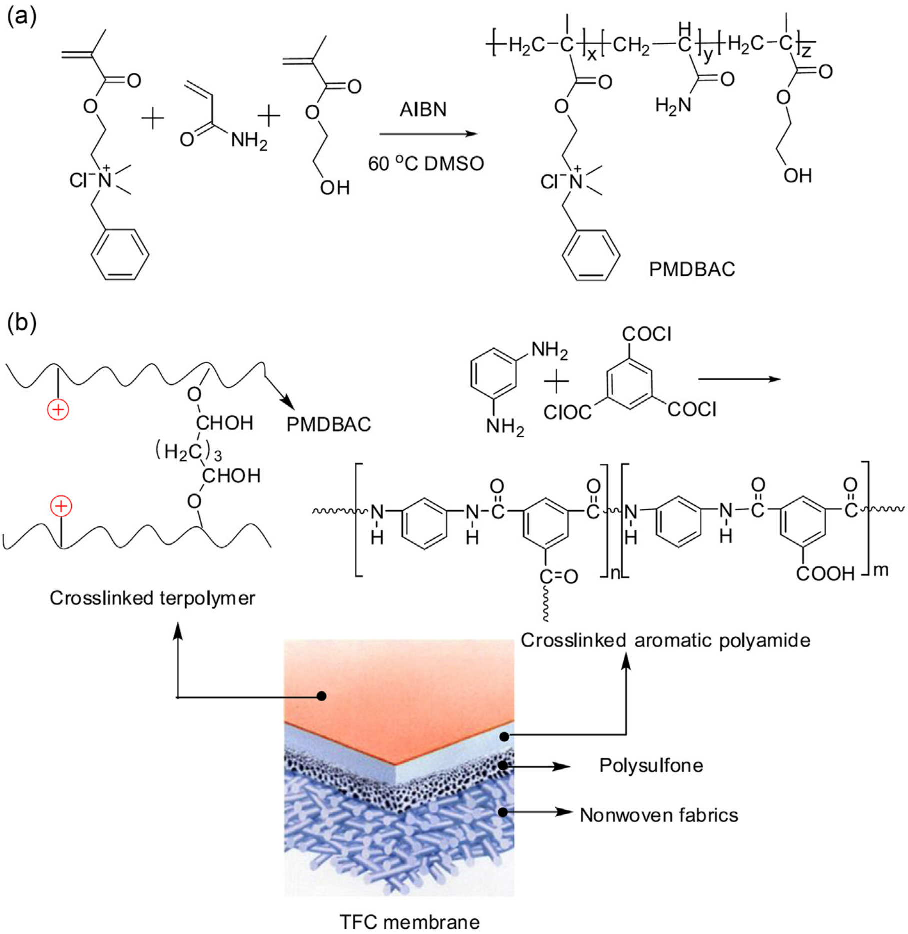

Figure 8.9 Schematic diagram for synthesis of the terpolymer P(MDBAC-r-Am-r-HEMA) (a) and surface modification of reverse osmosis (RO) membranes (b).
Reprinted from Ni et al. (2014), with permission from Elsevier.

Carboxy-functionalized MWCNTs were incorporated by Zhao et al. (2014) in PA TFC RO membranes via IP of MPD and TMC to improve their RO performance. The developed nanocomposite membranes were more negatively charged than the MWCNTs-free PA membrane, and the increase of MWCNT concentration in the membrane resulted in a higher permeate flux (50% higher) with almost the same solute rejection factor.

Surface topography modification of TFC RO membranes has been shown to be another potential approach for fouling mitigation. Functional TFC RO membrane with well-controlled surface patterns was reported by Maruf, Grenberg, Pellegrino, and Ding (2014). As it shown in Figure 8.10, this membrane fabrication procedure consisted on the formation of a dense PA layer via IP with TMC and

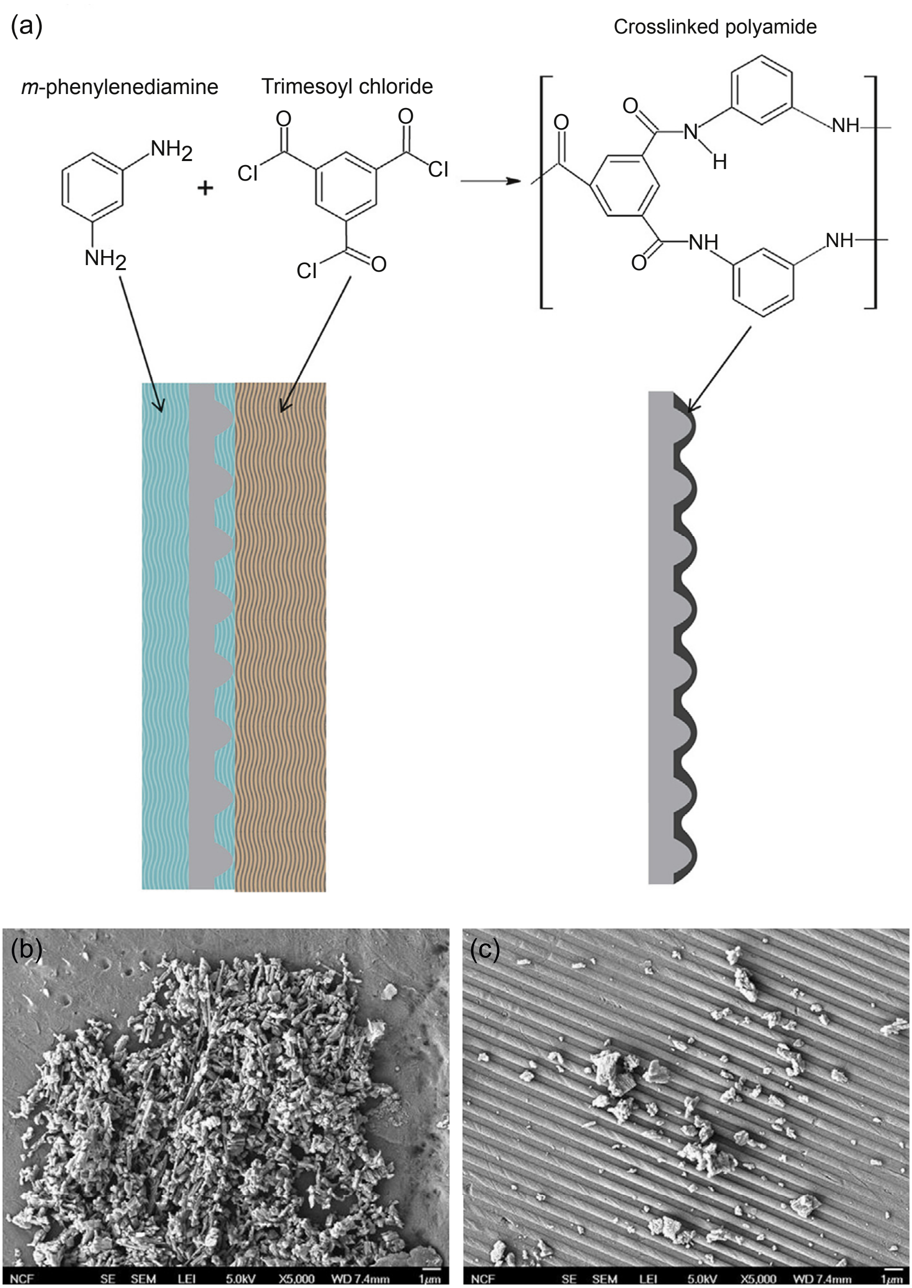

Figure 8.10 (a) Schematic diagram of the interfacial polymerization process used to fabricate the patterned thin-film composite (TFC) membranes. The monomers *m*-phenylenediamine and trymesoyl chloride (TMC) react to form a highly crosslinked polyamide (PA) layer at top of the patterned polyethersulfone (PES) ultrafiltration (UF) membrane used as a support. SEM images of the non-patterned (b) and patterned (c) TFC membrane surface after 24 h of $CaSO_4$ filtration experiment.

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MPD solutions on a nano-imprinted commercial PES UF support membrane (PW, GE Water and Infrastructure). The results showed that the patterned TFC membrane had a separation performance comparable to the current commercial TFC RO/NF membranes (i.e., commercial TFC RO membranes: XLE-440 (DOW Filmtec), CPA 3 (Hydranautics), ACM 2 (Trisep), TM-700 (Toray), and commercial TFC NF membranes: NF 270 (Hydranautics) and ES-10 (Nitto Denko)). It is important to note that the surface patterns induced hydrodynamic secondary flow at the membrane-feed interface, which is an effective way to decrease concentration polarization and reduce scaling effects.

8.3 Vapor pressure gradient driven membrane processes

8.3.1 Membrane distillation

In contrast to the previous reported PDMPs (MF, UF, NF, and RO) technology, which is isothermal, membrane distillation (MD) is a non-isothermal separation process in which only molecules in the vapor phase are transported from the feed to the permeate through a porous hydrophobic membrane, being the driving force the transmembrane vapor pressure (Alkhudhiri, Darwish, & Hilal, 2012; Khayet & Matsuura, 2011). Simultaneous heat and mass transfer occur in MD, and different MD configurations can be used to establish the driving force. The difference between the MD configurations is localized only in the permeate side of the membrane module. In direct contact MD (DCMD), sweeping gas MD (SGMD), and air gap MD (AGMD), the temperature difference induces the necessary vapor pressure difference. There is also another configuration termed vacuum MD (VMD), in which the permeate side of the membrane is kept at lower pressure by a vacuum pump to establish the transmembrane vapor pressure.

MD is applied in different fields (desalination, treatment of wastewaters containing non-volatile contaminants including radioactive wastes, recovery of valuable compounds, production of distilled and ultrapure water, food, medical, etc.). Compared to RO separation process, MD does not require the application of a high hydrostatic pressure (atmospheric pressure is enough), can process very high salinity brines including those generated by RO, and produce water with very high quality, which means almost total rejection factors of non-volatile contaminants. Moreover, MD can be combined with other processes in integrated systems such as MF, UF, NF, RO, and forward osmosis among others, making MD promising for various industrial applications (Khayet & Matsuura, 2011). However, MD technology also suffers some drawbacks such as the low membrane permeability, low thermal efficiency, high water production cost, temperature and concentration polarization effects, risk of membrane pore wetting, fouling, and scaling phenomena (Alkhudhiri et al., 2012; Khayet & Matsuura, 2011).

MD membranes are porous with a high porosity (void volume fractions), low pore tortuosity, low thermal conductivity, and hydrophobic. More details of the membrane requirements for an effective MD application were outlined by Khayet (2011). The most common used techniques for preparation of MD membranes are phase inversion, stretching, track-etching, sintering, dry/wet spinning or wet spinning, electrospinning, or membrane surface modification by physical or chemical techniques such as coating, grafting, and plasma polymerization. Most of the MD membranes are made via phase inversion methods because of its simplicity.

Some authors focused their MD membrane engineering toward the preparation of dual-layered membranes. Wang, Teoh, and Chung (2011) investigated the morphological architecture of dual-layer PVDF hollow fiber membranes consisting of a fully finger-like macrovoid inner-layer and a totally sponge-like outer-layer. Edwie and Chung (2012) also designed novel hollow fiber membranes with improved wetting resistances for desalination and salt recovery from highly concentrated NaCl aqueous solution by DCMD and crystallization. Three types of hollow fiber membranes were fabricated, single-layer PVDF, dual-layer hydrophobic−hydrophobic PVDF, and dual-layer hydrophobic−hydrophilic PVDF/PAN membranes. The single-layer PVDF membrane had a superior wetting resistance compared to other types of dual-layer membranes, in addition to the smallest reduction of membrane permeability (17.7%) and the highest purity of product water (1.1−1.3 μS/cm).

Su, Teoh, Wang Su, and Chung (2010) performed experimental and theoretical studies to investigate the effect of the inner-layer thermal conductivity on the DCMD permeate flux of hydrophobic−hydrophilic dual-layer hollow fiber membranes prepared by dry/wet spinning technique. Graphite particles and MWCNTs were embedded in the inner hydrophilic layer (Figure 8.11). It was found that incorporating graphite alone led to only a minor improvement of the thermal conductivity, but using both graphite and MWCNT, the thermal conductivity was increased from 0.59 to 1.30 W/m K. This enhancement of the thermal conductivity was attributed to the network formed by the MWCNT, which bridges the polymer nodules. As a consequence of the improved thermal conductivity of the inner-layer, a higher vapor pressure difference was established between both sides of the hydrophobic porous layer (see Figure 8.11(b) and (c)), and therefore a significant increase of the DCMD permeate flux was observed from 41.2 to 66.9 kg/m^2 h when using an inlet feed temperature of 80.4 °C.

Polytetrafluoroethylene (PTFE) is an attractive membrane material for MD due to its superior hydrophobicity, chemical resistance, thermal stability, and mechanical strength compared to PP and PVDF. It has also excellent stability in many organic and inorganic solvents. Teoh, Chung, and Yeo (2011) prepared PVDF/PTFE dual-layer composite hollow fiber membranes for seawater desalination by DCMD. The incorporation of PTFE particles in the PVDF spinning solution could efficiently suppress the formation of macrovoids and enhance the outer surface hydrophobicity of the membranes. Recently, Zhu et al. (2013) also used PTFE for the preparation of novel PTFE hydrophobic hollow fiber membranes for VMD by a cold pressing method including extrusion, stretching, and sintering. It was observed that the PTFE hollow fiber membranes with four stretching ratios (120%, 160%, 180%, and 220%) showed microstructures of nodes interconnected by fibrils (Figure 8.12) and achieved salt rejection factors of 99.9%. The increase of the stretching ratio

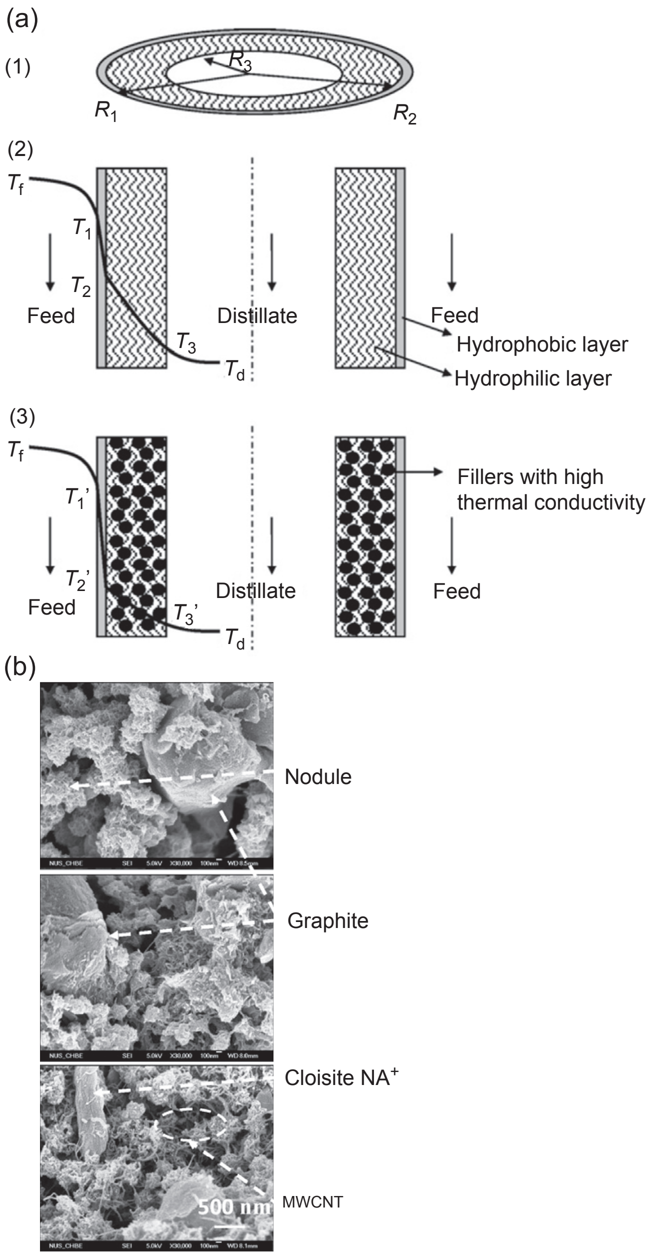

Figure 8.11 (a) Schematic dual-layer hydrophobic/hydrophilic hollow fiber membranes: (1) Cross-section of dual-layer hollow fiber membranes, (2) temperature distribution across dual-layer hydrophobic/hydrophilic membranes, and (3) temperature distribution across dual-layer hydrophobic/hydrophilic membranes filled with high thermal conductivity fillers blended into the inner-layer. (b) SEM images of the inner-layer filled with graphite, Cloisite NA$^+$ and MWCNT.
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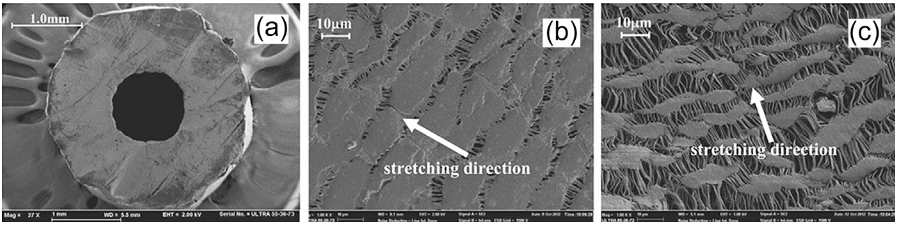

Figure 8.12 SEM images of the polytetrafluoroethylene (PTFE) hollow fiber membrane prepared by a stretching ratio of 220%: (a) X27 cross-section, (b) X1000 inner-surface, and (c) X1000 outer-surface.
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significantly increased the pore size and porosity and therefore improved the permeate flux, but decreased the water entry pressure in the pores and reduced the mechanical property of the membrane.

It is well known that ceramic membranes exhibit excellent chemical, structural, and thermal stabilities. Therefore, it would be interesting to explore this type of membranes in MD applications. Fang, Gao, Wang, and Cheng (2012) developed a novel hydrophobic porous alumina ceramic hollow fiber membrane by phase inversion and sintering method for desalination by VMD process. When using a feed salt aqueous solution (4 wt% NaCl) at 80 °C and a vacuum pressure of 4 kPa applied in the lumen side of the hollow fibers, a water permeate flux as high as 42.9 L/m^2 h was achieved, with a salt rejection factor over 99.5%, which was comparable to polymeric membranes.

Yang, Wang, Shi, Fane, and Debowski (2011) proposed plasma or chemical modification of the surface of PVDF hollow fiber-based membranes. The plasma coating involved a surface activation by exposing the membrane to a continuous plasma and a polymerization with the vapor of activated monomer. On the other hand, the chemical modification involved the hydroxylation of the PVDF membrane by an aqueous lithium hydroxide solution and successive reduction with an organic sodium borohydride ($NaBH_4$) solution followed by crosslinking with a perfluoro-compound of perfluoropolyether containing ethoxysilane terminal groups. Compared to the unmodified PVDF hollow fiber membrane, both modified membranes showed a greater hydrophobicity, higher liquid entry pressure (*LEP*) values, better mechanical strengths, smaller maximum pore sizes, and narrower pore size distributions with reasonably high DCMD permeate fluxes over a long-term operation (one month) as well as a high water quality. Wei et al. (2012) also used plasma surface modification approach to develop suitable membranes for MD. The surface of asymmetric hydrophilic PES flat sheet and hollow fiber membranes were modified by CF_4 plasma polymerization to form a hydrophobic layer with a water contact angle up to 120°. DCMD results proved that these plasma-modified PES membranes were good membranes for MD, with high water permeate fluxes up to 66.7 kg/m^2 h using 4 wt% NaCl as feed aqueous solution, and the salt rejection factors were as high as 99.97%. A comparative compilation of DCMD performance for different novel hollow fiber membranes is summarized in Table 8.3.

Table 8.3 **Direct contact membrane distillation (DCMD) performance of different single and dual-layer hollow fiber membranes fabricated in the literature**

				Feed parameters			Distillate parameters		
Membrane (reference)	**Thickness (μm)**	**Hollow fiber porosity (%)**	**Mean pore size (μm)**	**Solution**	**Inlet temperature (°C)**	**Flow rate (m/s)**	**Inlet temperature (°C)**	**Flow rate (m/s)**	**DCMD flux (kg/m^2 h)**
Accurel PP S6/2[a] (Gryta, 2007)	400	73.0	0.22	Concentrated tap water	90	0.96	20	0.29	34.0
PVDF single-layer HF[b] (Teoh and Chung, 2009)	140	86.0	0.16	3.5 wt% NaCl	79.5	1.9	17.5	0.9	46.1
PVDF single-layer HF (Wang et al., 2009)	180	86.7	–	3.5 wt% NaCl	81.3	1.8	17.5	1.2	79.2
PVDF single-layer HF (Yang et al., 2011)	275	83.0	0.145	3.5 wt% NaCl	70	–	25	–	54.0
PVDF single-layer HF (Edwie and Chung, 2012)	127.5	69.6	0.23[c]	3.5 wt% NaCl	80	0.7	17	0.7	35.1
PVDF single-layer HF (Hou et al., 2009)	130	79.7	0.28	3.5 wt% NaCl	81.8	0.5	20	0.15	40.5

PVDF single-layer HF (Song et al., 2012)	180	71.9	0.28	3.5 wt% NaCl	80.0	–	20	0.04	27.5
PVDF single-layer HF (Bonyadi et al., 2009)	120	80.0	0.44	3.5 wt% NaCl	79.9	1.6	19.4	0.8	54.3
PVDF single-layer HF (Drioli et al., 2013)	230	83.4	0.32	Distillate water	70	–	25	–	22.0
Si_3N_4 single-layer HF (Zhang, Fang, et al., 2014)	–	50	0.74	4 wt% NaCl	80	–	20	–	10.8
PES single-layer HF (Wei et al., 2012)	210	79.0	<0.07	4 wt% NaCl	73.8	2	20	0.68	66.7
PVDF/PAN dual-layer HF (Bonyadi and Chung, 2007)	340	80.0	0.41	3.5 wt% NaCl	78.2	1.6	16.6	0.8	37.4

Continued

Table 8.3 **Continued**

Membrane (reference)	Thickness (μm)	Hollow fiber porosity (%)	Mean pore size (μm)	Feed parameters: Solution	Feed parameters: Inlet temperature (°C)	Feed parameters: Flow rate (m/s)	Distillate parameters: Inlet temperature (°C)	Distillate parameters: Flow rate (m/s)	DCMD flux (kg/m^2 h)
PVDF/PAN dual-layer HF (Su et al., 2010)	271	70.0	0.41	3.5 wt% NaCl	80.4	1.8	15.3	0.7	66.9
PVDF/PAN dual-layer HF (Edwie, Teoh, and Chung, 2012)	153	75.4	0.47[c]	3.5 wt% NaCl	80	1.4	17	0.7	83.4
PVDF/PTFE dual-layer HF (Wang et al., 2011)	141	84.0	–	3.5 wt% NaCl	79.8	1.4	17	0.7	98.6
PVDF/PTFE dual-layer HF (Teoh et al., 2011)	145	82.5	0.26[c]	3.5 wt% NaCl	80	1.9	17.5	0.9	50.9

[a] Accurel PP S6/2: Commercial membrane from GmbH, Germany.

[b] HF = hollow fiber.

[c] Maximal pore size, others are mean pore size.

Novel and emerging flat sheet membranes were also developed for MD. Khayet, Mengual, and Matsuura (2005) proposed for the first time the use of double-layered porous hydrophobic/hydrophilic composite membranes for DCMD using fluorinated surface modifying macromolecules (SMMs) and the phase inversion method. This promising type of membrane exhibited a thin hydrophobic layer of about 10 μm, higher permeate flux than the commonly used commercial membranes, and very high salt rejection factors. Then a series of studies were performed using different types of SMMs and hydrophilic host polymers, such as PES and PS (Essalhi & Khayet, 2012; Khayet, 2013; Khayet & Matsuura, 2011; Peng et al., 2013; Qtaishat, Rana, Khayet, & Matsuura, 2009; Suk, Matsuura, Park, & Lee, 2010). Recently, Khayet (2013) used this type of membrane in nuclear technology for the treatment of low- and intermediate-level radioactive liquid wastes.

Dumée, Sears, Finn, Duke, and Gray (2010) explored the possibility of developing novel self-supporting CNT Bucky-Paper (BP) membranes via vacuum filtration for DCMD desalination. CNTs have exceptional mechanical, electrical, and thermal properties. It was reported that the CNT-BP membranes exhibited a high water contact angle (113°), a high porosity (90%), and relatively low thermal conductivity (i.e., 2.7 kW/m^2 h). However, a decline of the DCMD permeate flux and delamination of BP membranes due to the formation of micro-cracks were observed. To optimize this type of BP membrane, Dumée, Sears, Schütz, et al. (2010) developed novel CNT-BP-based composite and supported membranes with significantly improved MD performance. Furthermore, the same researchers also coated the CNT-BP membranes with a thin layer of PTFE to enhance their hydrophobicity and improve their mechanical stability without drastically changing their average pore size and porosity (Dumée et al., 2011).

Various studies have been focused on the preparation of more hydrophobic membranes for MD to reduce the risk of pore wetting. A variety of techniques such as plasma treatment, lithography, sol-gel technology, NP deposition on both smooth and rough substrates, fluoroalkylsilane coatings, and phase separation of a multicomponent mixture were considered for fabrication of superhydrophobic surfaces (i.e., water contact angles higher than 150°). Razmjou, Arifin, Dong, Mansouri, and Chen (2012) prepared a superhydrophobic PVDF membrane for MD applications with a 163° water contact angle, by generating a hieralchical structure with multilevel roughness and reducing the surface free energy of the membranes via TiO_2 coating through a low-temperature hydrothermal process followed by fluorosilanization of the surface with 1H, 1H, 2H, 2H-perfluorododecyltrichlorosilane (FTCS) (Figure 8.13). The multilevel hierarchical structure was attributed to the templating agent, which was found to be decisive in the final wettability of the membrane surface. Moreover, TiO_2 coating layer on the membrane provided sites for covalent bonding with hydrolyzed silane coupling agents. The modified FTCS$-$$TiO_2$$-$PVDF membranes showed good thermal and mechanical resistance, while both the *LEP* and water contact angle of the membrane were increased.

During last five years, novel flat sheet nanofibrous membranes prepared by electrospinning were proposed for MD because of their attractive characteristics for MD, such as the high void volume fraction, high hydrophobicity, high roughness, high

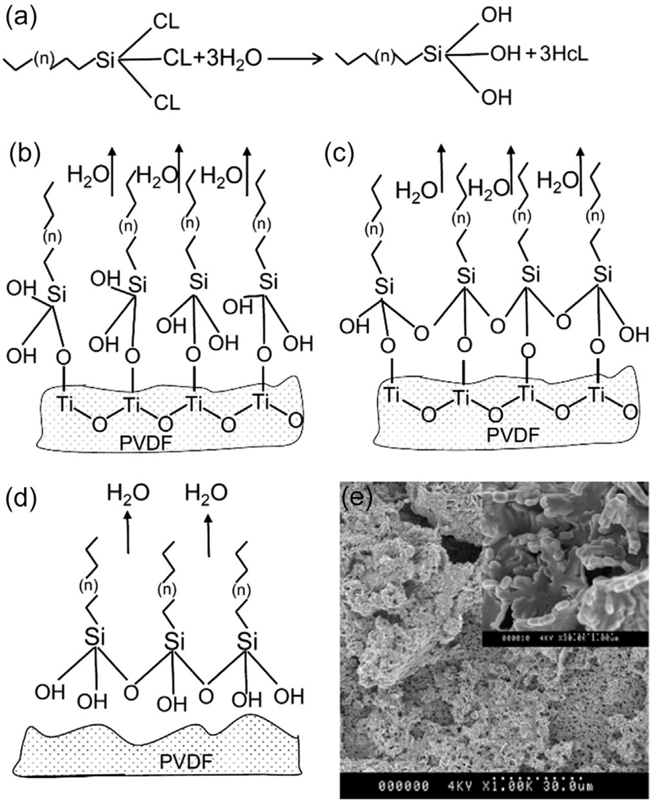

Figure 8.13 Mechanism for the fluorosilanization on the surface of polyvinylidene fluoride (PVDF) membranes with and without TiO_2. (a) Hydrolyzation of 1H, 1H, 2H, 2H−perfluorododecyltrichlorosilane (FTCS), (b) interaction of the hydroxyl groups with the surface of TiO_2 can form covalent bonds of Si−O−Ti, (c) the intermolecular crosslinking between the tri-silanols can lead to a 2D network of polysiloxane, (d) condensation of tri-silanols in the solution in absence of TiO_2 coating, and (e) surface SEM image of FTCS−PVDF membrane.

Reprinted from Razmjou, Arifin, et al. (2012), with permission from Elsevier.

surface-to-mass (volume) ratio, interconnected open space between nanofibers, low thermal conductivity, etc. (Khayet & García-Payo, 2011). Self-sustained electrospun nanofibrous membranes (ENMs) were prepared varying the PVDF concentrations in the solvent mixture acetone (Ac)/*N*,*N*-dimethylacetamide from 15 to 30 wt% and the electrospinning time (Essalhi & Khayet, 2013a, Essalhi & Khayet, 2014). The optimum PVDF concentration and electrospinning time for ENM formation was found to be 25 wt% and 2 h, respectively. This ENM exhibited a DCMD permeate flux of 12.15×10^{-3} kg/m^2 s, and the NaCl rejection factor was higher than 99.99%. The permeate flux of the ENMs was lower for longer electrospinning time. Essalhi and Khayet (2013b) developed a novel theoretical model that considered the gas transport mechanisms through the inter-fiber space of ENMs to predict the DCMD permeate flux of ENMs.

Maab et al. (2012) used both the phase inversion technique and the electrospinnig method to prepare a novel flat sheet porous membrane for MD based on hydrophobic synthesized aromatic fluorinated polyoxadiazoles and polytriazoles. By combining the high polymer hydrophobicity (i.e., 162° water contact angle), the high void volume fraction, and the *LEP* of about 0.9 bar, the salt rejection factors of these membranes were as high as 99.95%, and the water permeate fluxes were as high as 85 L/m^2 h for a feed temperature of 80 °C and a permeate temperature of 22 °C. Similarly, Prince et al. (2012) developed novel ENMs consisting of PVDF blended with clay nanocomposite for DCMD. An increase of the surface hydrophobicity with the addition of clay nanocomposite was also observed, and the prepared PVDF-clay ENMs showed good DCMD performance.

Lalia, Guillen-Burrieza, Arafat, and Hashaikeh (2013) also prepared ENMs for MD using the copolymer polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP). To fuse the fibers together and enhance the ENMs structural integrity with the mechanical properties, the ENMs were hot pressed. Among all prepared ENMs, the one fabricated with 10 wt% PVDF-HFP in the electrospinning solution had the optimum properties for MD application with 0.26 μm mean pore size, 58% porosity, 125° water contact angle, and a *LEP* value of 131.7 kPa.

To further improve the hydrophobicity of the PVDF ENMs used in MD, the electrospinning technique was followed by surface modification (Liao, Wang, & Fane, 2013). As shown in Figure 8.14, this procedure included PDA surface activation to improve the adhesive force between the fibers and Ag NPs, Ag NP deposition to optimize the morphology and roughness of the membrane, and hydrophobic treatment with 1-dodecanethiol. Compared to the unmodified ENM, the integrally-modified membrane could achieve a stable MD permeate flux of 31.6 L/m^2 h using a 3.5 wt% NaCl feed aqueous solution at 60 °C and permeate temperature of 20 °C.

To enhance the MD performance of the ENMs, Prince, Anbharasi, Shanmugasundaram, and Singh (2013) prepared PVDF ENM on a porous PVDF supported membrane fabricated by the immersion precipitation method and used it for desalination by AGMD configuration. The addition of the nanofiber layer on the PVDF supported membrane was found to increase the permeate flux, the salt rejection factor, and the AGMD long-term performance.

8.3.2 Pervaporation

PV is a membrane process in which an organic solvent/water mixture or an organic solvent mixture can be selectively separated by a dense membrane placed between the liquid feed mixture and a downstream permeate maintained by a vacuum pump. PV technology is similar to VMD, the difference being the characteristics of the membrane used, which is porous and hydrophobic for VMD. There is also a similarity between PV and SGMD when PV is carried out by gas stripping. Both a solution diffusion model and a pore flow model were considered in PV, in which the phase change of the diffused species takes place inside the membrane, and the desorption step occurs at

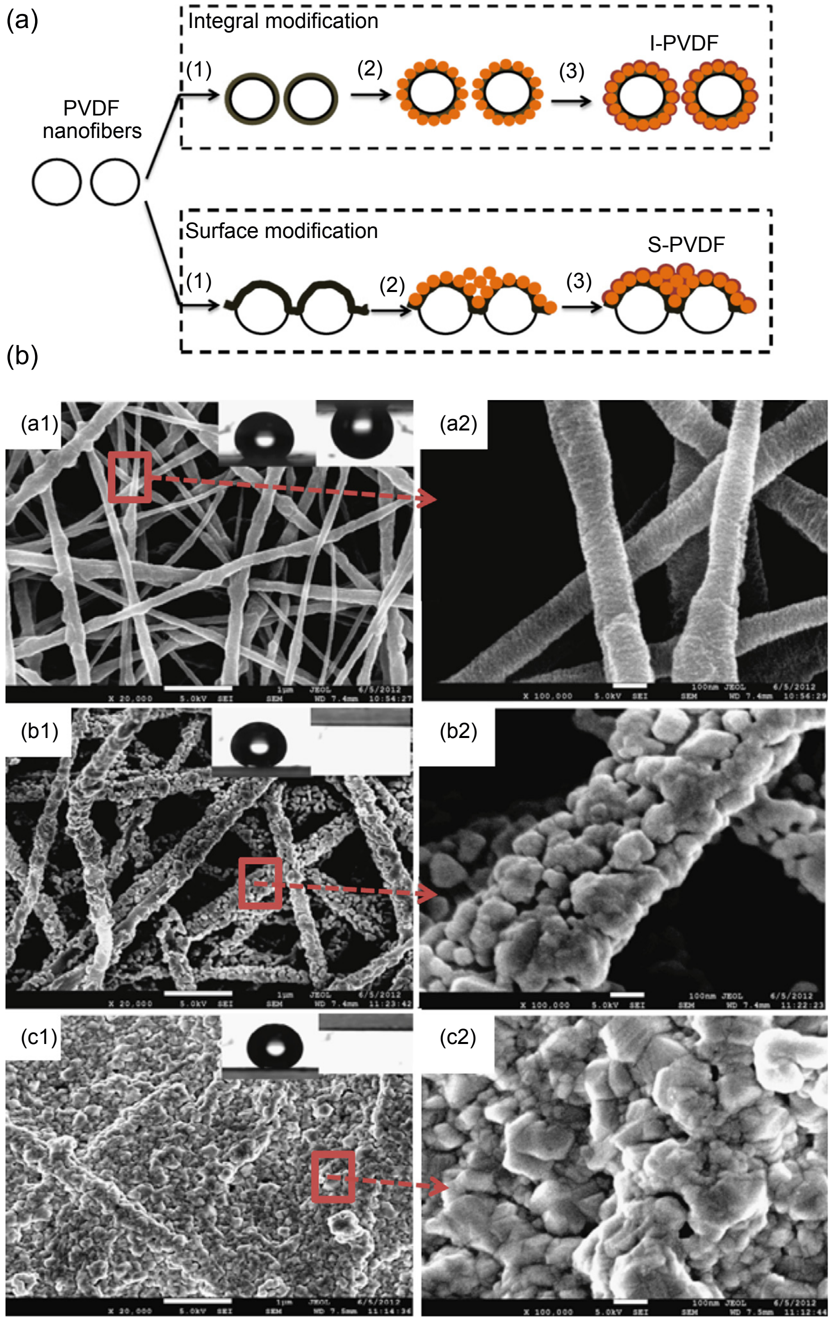

Figure 8.14 (a) Schematic method used for preparation of superhydrophobic polyvinylidene fluoride electrospun nanofibrous membranes (PVDF ENMs) ((1) PDA-modification; (2) silver nanoparticle coating; (3) 1-dodecanethiol hydrophobic modification). (b) SEM images of unmodified PVDF ENMs ((a1), (a2)), integral modified PVDF ENMs (I-PVDF (b1), (b2)), and surface modified PVDF ENMs (S-PVDF (c1), (c2)).
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the permeate side of the membrane. There are mainly two PV applications, those involving hydrophilic membranes used for the dehydration of organic/water mixtures such as PVA and NaA zeolite membranes (Liu, Wei, Jin, & Xu, 2012), and those involving hydrophobic membranes used to extract organic solvents or volatile organic compounds from water such as polydimethylsiloxane (PDMS) and silicalite-1 membranes (Liu et al., 2012).

Zuo, Wang, Sun, and Chung (2012) developed high-performance hollow fiber membranes for PV dehydration of isopropanol (IPA) consisting of a TFC PA selective layer and a porous Torlon® 4000T-MV PAI (Solvay Advanced Polymers) substrate prepared via IP of MPD or HPEI with TMC. The TFC membrane prepared from HPEI showed a higher hydrophilicity and fractional free volume than that made from MPD, which exhibited a better permeability. The TFC membrane fabricated under the optimum IP conditions from HPEI having a molecular weight of 2 kg/mol showed the best selectivity (i.e., 624), with a total permeate flux of 1.3 kg/m^2 h and a permeate water concentration of 99.1 wt% using a feed composition of 85/15 wt% IPA/water at 50 °C.

Wang, Gruender, and Chung (2010) developed high-performance dual-layer polybenzimidazole (PBI)/PEI hollow fiber membranes for ethylene glycol dehydration by PV process. Three types of membranes were prepared: PBI flat sheet dense membranes, which had the lowest PV separation performance due to its severe swelling; PBI single-layer hollow fiber membranes, which showed better PV separation performance, but had very low tensile strains; and PBI/PEI dual-layer hollow fiber membranes, which exhibited the best PV separation performance. An enhancement of the separation performance of PBI/PEI dual-layer hollow fiber membrane after exposing it to 75 °C thermal treatment was also detected. A novel approach to prepare multilayered membranes with excellent PV dehydration of different solvent/water mixtures has been performed by Zhang, Dai, and Ji (2011). This approach is based on a dynamic pressure-driven LbL technique to obtain a covalent assembly of GLA-crosslinked PEI multilayers on the inner surfaces of PAN hollow fiber porous substrate membranes. The dynamic pressure-driven LbL assembly was demonstrated to be an effective way to fabricate a defect-free selective layer only on a single side of the hollow fiber, which has the advantage of reducing the membrane transport resistance compared to the membranes made with traditional LbL process. Zhang, Song, Ji, Wang, and Liu (2008) prepared novel polyacrylic acid (PAA)/PEI multilayer polyelectrolyte complex (PEC) films on the inner side of hydrolyzed PAN hollow fiber membranes by the dynamic negative pressure LbL technique. Others papers also proposed an electric field enhanced method to fabricate multilayered PEC membranes by using modified PA RO membranes as supports, and poly(diallyl dimethylammonium-chloride) (PDDA), PEI, PSS, PAA as assembly components (Yin et al., 2010; Zhang, Qian, et al., 2008, 2009; Zhao, An, Ji, Qian, & Gao, 2011). Zhao, Qian, An, and Sun (2010) used charged PEC colloidal aggregates as novel LbL building blocks to prepare LbL multilayered membranes for PV dehydration.

As mentioned previously, the hydrophilicity of the PV membrane is necessary for the dehydration of organic solvents. The more hydrophilic the membrane is, the higher are the water sorption selectivity and water permselectivity. To improve the membrane hydrophilicity, many polymer materials were modified using different methods, such as sulfonation, quaternization, grafting, etc. However, an increase of the membrane hydrophilicity might increase the membrane swelling excessively, leading to a membrane with an open structure, which reduces the membrane strength. Crosslinking with an organic chemical reagent, such as GA, PAA, maleic acid, formaldehyde, or fumaric acid is an effective way to reduce membrane swelling. Zhang, Liu, Zhu, Xiong, and Ren (2009) synthesized quaternized PVA by grafting with (2,3-epoxypropyl) trimethylammonium chloride, to enhance the hydrophilicity, and then crosslinked by GLA to restrict its swelling in an aqueous ethanol solution. Rachipudi, Kariduraganavar, Kittur, and Sajjan (2011) also developed PV membranes for IPA dehydration by crosslinking sulfonated-PVA membranes with sulfophthalic acid (SPTA). The membrane prepared with 15 wt% of SPTA showed the highest water separation selectivity of 3452 with a total permeate flux of 3.51×10^{-2} kg/m^2 h.

Novel chitosan (CS)/TiO_2 nanocomposite membranes were prepared by Yang, Li, Jiang, Lu, and Chen (2009) using an in situ sol–gel process using tetrabutyl titanate as precursor and acetyl acetone as chelating agent controlling the forming rate of TiO_2 NPs. Compared to CS and CS/TiO_2 blended membranes, CS/TiO_2 nanocomposite membranes exhibited better PV performance for ethanol dehydration. CS-wrapped MWCNTs incorporated in sodium alginate membranes were prepared by Sajjan, Jeevan Kumar, Kittur, and Kariduraganavar (2013) for the separation of water/IPA mixtures. CS was chosen to wrap MWCNTs to improve their hydrophilicity. The PV membranes containing the highest amount of CS-wrapped MWCNTs (2 wt%) showed a water selectivity of 6419 and a permeate flux of 21.76×10^{-2} kg/m^2 h at 30 °C and 10 wt% of water in the feed solution.

UV/O_3 surface modification technology was used by Lai et al. (2012) to develop PDMS PV membranes for the treatment of 90 wt% aqueous ethanol mixture. Water contact angle measurements demonstrated that the hydrophilicity of PDMS membranes surface was significantly improved due to the change in its chemical structure from siloxane to silica. PV results indicated that both the treatment time and the working distance during the UV/O_3 treatment were important variables affecting the PV performance of the PDMS membrane.

To improve the PV permeate flux of polymeric membranes, Xiangli, Chen, Jin, and Xu (2007) prepared PDMS/ceramic composite membrane by depositing uniformly a crosslinked PDMS layer on the top of tubular non-symmetric ZrO_2/Al_2O_3 porous ceramic supports. The resulted PDMS/ceramic composite membranes exhibited a total permeate flux of 19.5 kg/m^2 h and an ethanol selectivity of 5.7 when using a 4.3 wt% ethanol feed aqueous mixture. Liu, Hou, Wei, Xiangli, and Jin (2011) used these PDMS/ceramic composite membrane for butanol removal from its dilute aqueous solution and obtained a total permeate flux of 0.457 kg/m^2 h with an acceptable butanol selectivity of 26.1 using a 1 wt% butanol in the feed solution at 40 °C. Because of the good long-term stability of these PDMS/ceramic composite membranes, Liu, Wei, et al. (2011) decided to use them for recovering biobutanol from biomass acetone-butanol-ethanol (ABE) fermentation broth exhibiting a high average total flux of 0.670 kg/m^2 h and an applicable ABE selectivity of 16.7. The performance of PDMS/ceramic composite PV membranes was improved by a homogeneous dispersion of ZSM-5 zeolite in PDMS via a surface graft/coating approach (Liu, Xiangli, Wei, Liu, & Jin, 2011). Lue, Chien, and Mahesh (2011) also prepared a heterogeneous PDMS MMMs containing 10 μm sized zeolite (TZP-9023, Tricate Zeolites, Bitterfeld, Germany) for PV of ethanol/water solutions.

Zhu, Xia, Liu, and Jin (2010) synthesized hydrophilic crosslinked PVA/CS layers on tubular asymmetric ZrO_2/Al_2O_3 ceramic supports and demonstrated that these ceramic-supported PVA/CS composite membranes were suitable candidates for PV dehydration of alcohol/water and ester/water mixtures. The composite membrane exhibited excellent PV performance, achieving a permeate flux of 1.25 kg/m^2 h and a water selectivity larger than 10,000 for 3.5 wt% ethyl acetate/water mixture.

To achieve higher membrane stability and improve the PV performance, various attempts have been made to develop blend membranes of PVA with other polymers. Mixed matrix blend membranes of PVA/PVP loaded with phosphomolybdic acid (PMA) were prepared for ethanol dehydration by Magalad, Gokavi, Raju, and Aminabhavi (2010). It was demonstrated that the extent of PMA loaded in the membrane affected the PV performance. 4 wt% of PMA particles in PVA/PVP blended matrix resulted in an enhancement of the PV performance, but higher PMA amounts (8 and 12 wt%) did not result in any improvement of PV performance.

It is worth mentioning that there are few research studies on homogeneous polyelectrolyte complex membranes (HPECMs), although these membranes exhibit good PV performance for dehydration of different organic aqueous solutions containing IPA, ethanol, Ac, etc. The required PECs to prepare HPECMs were synthesized by PAA, sodium carboxymethyl cellulose (CMCNa) as anionic polyelectrolyte, and PDDA, CS, poly(2-methacryloyloxy ethyl tri-methylammonium chloride) (PDMC), and poly(N-ethyl-4-vinylpyridiniumbromide) (PEVP) as cationic polyelectrolyte. For example, the PECs were first synthesized in aqueous hydrochloric acid. Then, the obtained solid PECs were dissolved in aqueous NaOH, and subsequently the HPECMs were made by casting the solution on a clean and smooth porous PS UF membrane. All the fabricated HPECMs from CMCNa−PDDA PECs (Zhao, Qian, An, Yang, & Zhang, 2008; Zhao, Qian, An, Gui, et al., 2009), PAA−PDDA PECs (Zhao, Qian, An, Yang, & Gui, 2009), CMCNa−CS PECs (Zhao, Qian, An, Gao, et al., 2009), CMCNa−PDMC (Zhao, An, et al., 2010), and CMCNa−PEVP (Jin, An, Zhao, Qian, & Zhu, 2010) were used in PV dehydration of aqueous IPA or ethanol solutions and showed very high water selectivity and high permeability (see Table 8.4). Attempts were also made to improve the mechanical properties of the HPECMs by modification using inorganic SiO_2 (Zhao, Qian, Zhu, An, Xu, et al., 2009) and MWCNTs (Zhao, Qian, Zhu, & An, 2009), but even under the optimal membrane fabrication conditions the elongations at break were maintained low, whereas the tensile strengths increased. In addition, CMCNa−PDDA PEC (Zhao, Qian, An, Zhu, et al., 2009), PDDA−PAANa PEC (Zhu, Qian, Zhao, An, & Li, 2010), and CMCNa−PDMC PEC (Zhu et al., 2011) were blended with the commercial PVA to increase both the mechanical properties and the PV performance of the HPECMs. It was found that the PEC/PVA blended membrane with PVA content of 30 wt%

Table 8.4 Pervaporation performance of various polyelectrolyte membranes (PECMs) for dehydration of isopropanol (IPA) and ethanol (EtOH) at 70 °C

Membrane	Feed solution	Water selectivity	Permeation flux (kg/m^2 h)	Reference
CMCNa-PDDA HPECM5.5	10 wt% water/IPA	960	2.47	Zhao et al. (2008)
CMCNa-PDDA HPECM2.6	10 wt% water/IPA	1791	1.92	Zhao et al. (2008)
CMCNa-PDDA HPECM0.19	10 wt% water/IPA	1049	2.47	Zhao, Qian, An, Gui, et al. (2009)
CMCNa-PDDA TPECM	10 wt% water/IPA	148.4	1.49	Zhao, Qian, An, Gui, et al. (2009)
PDMC-CMCNa PECM0.46	10 wt% water/IPA	1641	4.25	Zhao, An, et al. (2010)
PDMC-CMCNa PECM0.36	10 wt% water/IPA	1641	3.85	Zhao, An, et al. (2010)
CMCNa-PDDA/5 wt% SiO_2	10 wt% water/IPA	2186	2.1	Zhao, Qian, Zhu, An, Xu, et al. (2009)
CMCNa-PDDA/5 wt% MWCNTs	10 wt% water/IPA	2565	2.35	Zhao, Qian, Zhu, & An (2009)
PDDA-PAANa/30 wt% PVA	10 wt% water/IPA	978	2.36	Zhu, Qian, et al. (2010)
CMCNa-PDMC/30 wt% PVA	10 wt% water/IPA	2084	2.12	Zhu et al. (2011)
CS-CMCNa HPECM0.39	10 wt% water/IPA	1657	2.17	Zhao, Qian, An, Yang, et al. (2009)
PERVAP 2510[a]	10 wt% water/IPA	810	0.75	Chapman et al. (2008)
CMCNa-PDDA TPECM	10 wt% water/EtOH	188	0.49	Zhao, Qian, An, Gao, et al. (2009)
CS-CMCNa HPECM0.025	10 wt% water/EtOH	1062	1.14	Zhao, Qian, An, Gao, et al. (2009)

Table 8.4 **Continued**

Membrane	Feed solution	Water selectivity	Permeation flux (kg/m^2 h)	Reference
PECM0.284	10 wt% water/ EtOH	1419	0.93	Jin et al. (2010)
PECM0.440	10 wt% water/ EtOH	782	1.32	Jin et al. (2010)

[a] PERVAP 2510: commercial membrane from Sulzer Chemtech GmbH, Linden, Germany.

(PEC/PVA70-30) achieved the best mechanical properties with a tensile strength, Young's modulus, and elongation at break of about 1.5, 3.6, and 1.4 times those of the original HPECM, respectively.

8.4 Conclusions

The growth of membrane science and technology for water treatment is mainly due to the developments of materials used for membrane fabrication and for their modification. A wide variety of innovative materials such as chemically and thermally stable polymers, ceramics, metallics, etc., are used for preparing novel membranes of different configurations and characteristics. Moreover, various membrane fabrication techniques are being proposed and improved (i.e., phase inversion, sintering, stretching, track-etching, dry/wet spinning or wet spinning, electrospinning, LbL assembly, lithography, sol-gel, etc.), and various methods have been developed for membrane modification (i.e., IP, chemical modification, surface coating, grafting, crosslinking, plasma polimerization, polymer sulfonation or quaternization, nanoparticles (NPs) deposition, etc.) to improve both the properties of the membranes and the performance of the specific processes and their applications.

It has been observed that the incorporation of different additives, polymers, and inorganic NPs or fillers (i.e., zeolite, organo-selenium compounds, SiO_2, Fe_3O_4, Al_2O_3, ZrO_2, TiO_2, ZnO, CNTs, MWCNTs, GO, TOCNs, β-CD, zwitterionic materials, etc.) on the MF, UF, NF, and RO membranes has improved their antifouling and antibacterial ability, has increased their hydrophilicity and water permeability preserving or improving the solute rejection factors, and in some cases has enhanced membrane mechanical properties, porosity, and thermal stability.

In contrast to PDMP technology, MD is a non-isothermal separation process, which uses porous hydrophobic membranes for water treatment. In general, there is a growing interest on MD membrane engineering. In particular, various researchers are developing composite hollow fiber membranes for MD with a dual-layered configuration (hydrophobic—hydrophobic or hydrophobic—hydrophilic) to reduce membrane pore wetting, temperature and concentration polarization effects, fouling, and scaling phenomena. The addition of different materials and NPs (i.e., graphite particles, PTFE, Al_2O_3, ZrO_2, TiO_2, ZnO, CNTs, MWCNTs, SMMs, etc.) resulted in greater membrane hydrophobicity and thermal conductivity, higher *LEP* values, water quality, and long-term operation, and also better mechanical strengths, permeate fluxes, and salt rejections.

High permeate fluxes and water selectivities were achieved when ceramic-supported composite membranes and HPECMs have been used for PV dehydration of organic alcohol/water and ester/water mixtures containing solvents such as IPA, ethanol, Ac, etc. Some attempts were made to improve the mechanical properties of HPECMs using inorganic SiO_2 and MWCNTs or blending their PEC with PVA.

8.5 Future trends

Although the current use of membrane technology for water treatment is constantly growing thanks to the discovery and development of novel and advanced materials for membrane fabrication and modification, there are still some involved phenomena with effects that need to be reduced further (e.g., temperature and concentration polarization phenomena, membrane fouling, long-term operation, etc.).

Innovative membrane engineering is required because of the still continuous increasing demands of desalination and treatments of different and emerging types of wastewaters with improved water production rates, greater salt rejection factors, and higher resistance to fouling.

PMDPs and MD technologies can be adequately integrated for water production offering a wide range of industrial water treatment applications.

List of acronyms

β-CD	β-cyclodextrin
ABE	Acetone-butanol-ethanol
Ac	Acetone
ADMH	3-allyl-5,5-dimethylhydantoin
Ag	Silver
AGMD	Air gap membrane distillation
Al_2O_3	Alumina
AQP	Aquaporin
AQP-Z	Aquaporin Z
BP	Bucky-Paper
BSA	Bovine serum albumin
CA	Cellulose acetate
CMCNA	Sodium carboxymethyl cellulose
CNTs	Carbon nanotubes
CS	Chitosan
CTA	Cellulose triacetate

DBA	3,5-diaminobenzoic acid
DCMD	Direct contact MD
EDX	Energy-dispersive X-ray spectroscopy
ENMs	Electrospun nanofibrous membranes
FA	Fly ash
Fe_3O_4	Ferrous ferric oxide
FESEM	Field-emission scanning electron microscopy
FTCS	1H, 1H, 2H, 2H-perfluorododecyltrichlorosilane
GA	Gallic acid
GLA	Glutaraldehyde
GO	Graphene oxide
HPECMs	Homogeneous polyelectrolyte complex membranes
HPEI	Hyperbranched polyethylenimine
IP	Interfacial polymerization
IPA	Isopropanol
LbL	Layer-by-layer
LEP	Liquid entry pressure
MBA	*N*,*N*′-methylenebis(acrylamide)
MD	Membrane distillation
MF	Microfiltration
MMMs	Mixed matrix membranes
MPD	*m*-phenylenediamine
MWCNTs	Multiwalled carbon nanotubes
$NaBH_4$	Sodium borohydride
NF	Nanofiltration
NPs	Nanoparticles
NTSC	Naphthalene-1,3,6-trisulfonylchloride
PA	Polyamides
PAA	Polyacrylic acid
PAH	Poly (allylamine hydrochloride)
PAI	Polyamide-imide
PAMAM G2	NH_2-terminated PAMAM
PAMAM	Amine-functional polyamidoamine
PAN	Polyacrylonitrile
PAS	Polyarylsulfone
PBI	Polybenzimidazole
PC	Polycarbonate
PDA	Polydopamine
PDDA	Poly(diallyl dimethylammoniumchloride)
PDMC	Poly(2-methacryloyloxy ethyl tri-methylammonium chloride)
PDMS	Polydimethylsiloxane
PEC	Polyelectrolyte complex
PEG	Polyethylene glycol
PEI	Polyethyleneimine
PES	Polyethersulfone
PET	Polyethylene terephthalate
PEVP	Poly(N-ethyl-4-vinylpyridiniumbromide)
PI	Polyimides
PIP	Piperazine

PMA	Phosphomolybdic acid
PNIPAAm	Poly(N-isopropylacrylamide)
PP	Polypropylene
PS	Polysulfone
PSS	Poly(sodium 4-styrenesulfate)
PTFE	Polytetrafluoroethylene
PU	Polyurethane
PVA	Polyvinyl alcohol
PVAm	Polyvinylamine
PVC	Polyvinyl chloride
PVDF	Polyvinylidene fluoride
PVDF-HFP	Polyvinylidene fluoride-co-hexafluoropropylene
PVP	Poly(1-vinylpyrrolidone)
PWP	Pure water permeability
RO	Reverse osmosis
SEM	Scanning electron microscopy
SGMD	Sweeping gas MD
$\mathbf{SiO_2}$	Silica
SMMs	Fluorinated surface modifying macromolecules
SPES	Sulfonated polyethersulfone
SPPBES	Sulfonated copoly (phthalazinone biphenyl ether sulfone)
SPTA	Sulfophthalic acid
TEOA	Triethanolamine
TFC	Thin-film composite
TFN	Thin film nano-composite
$\mathbf{tio_2}$	Titania
TMC	Trymesoyl chloride
tocns	TEMPO-oxidized cellulose nano-fibrils
UF	Ultrafiltration
VMD	Vacuum MD
ZnO	Zinc oxide
$\mathbf{ZrO_2}$	Zirconia

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Novel and emerging membranes for water treatment by electric potential and concentration gradient membrane processes

9

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9.1 Introduction

Recently, salinity gradient power (SGP) has been recognized as a renewable and sustainable alternative technology for energy generation. This approach is able to convert osmotic pressure difference of salt solutions (i.e., high-concentrated and less-concentrated salt solutions) into mechanical or electrical energy by using selective membranes (Brauns, 2009). The worldwide availability of SGP is considered to be a huge energy resource, with an estimated potential power of 2.4–2.6 TW when the total discharge of all rivers in the world is taken into account (Hong, Zhang, Luo, & Chen, 2013). Each cubic meter of water in the river can generate 1.5 MJ of energy when mixed with equal amounts of seawater (comparable to 0.5 mol/L NaCl) and more than 16.9 MJ when mixed with brine solution (5 mol/L NaCl) (Post, Hamelers, & Buisman, 2008). Pressure retarded osmosis (PRO) and reverse electrodialysis (RED) are the most frequently studied membrane-based processes for energy conversion of salinity gradient energy (Hong et al., 2013). While PRO is a mechanical process that uses water selective membranes and turbines to produce electrical energy, RED is an electrochemical process that uses ionic selective membranes and electrodes for electricity production (Burheim, Seland, Pharoah, & Kjelstrup, 2012). Furthermore, RED is often considered to be more favorable for power generation because of its greater energy efficiency and reduced sensitivity to membrane fouling compared with PRO (Post et al., 2007).

Electrodialysis (ED) is an electrochemical process in which ions migrate through ion-selective exchange membranes (IEMs) as a result of their attraction to two electrically charged electrodes. ED is able to remove most charged dissolved ions and is used to produce potable water from saline aqueous solutions.

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The interest in osmotically driven membrane processes, such as forward osmosis (FO) and PRO, has increased during last decade (Alsvik & Hägg, 2013a). Both processes belong to the emerging platform technology known as engineered osmosis (EO) that has the potential to sustainably produce clean drinking water and electric power (Huang, Bui, Meyering, Hamlin, & Mccutcheon, 2013). Unlike the pressure-driven membrane processes (PDMPs), EO offers the possibility to use osmotic pressure gradients in a wide range of applications. These include FO for water desalination, PRO for electric power generation, and direct osmotic concentration for dewatering (Arena, Mc Closkey, Freeman, & Mc Cutcheon, 2011).

9.2 Electric potential gradient driven membrane processes: ED/RED

A typical ED system includes a membrane stack with a number of cell pairs, each consisting of cation and anion exchange membranes (CEM and AEM, respectively) stacked in an alternating pattern between a cathode and an anode (see Figure 9.1(a)). The compartments between the membranes are alternately filled with a concentrated salt aqueous solution and a diluted salt aqueous solution. The electrodes are continually flushed to reduce fouling or scaling. Some of the advantages of ED compared with other membrane processes such as reverse osmosis (RO) and nanofiltration (NF) include the high water recovery, the long useful life of the membranes due to their high chemical/mechanical stability, the possibility to operate at temperatures up to 50 °C, and the achievement of higher brine concentrations. ED technology is also used for the treatment of industrial effluents and the removal of fluoride, nitrate, and heavy metals from water sources (Mulyati, Takagi, Fujii, Ohmukai, & Matsuyama, 2013). When the polarity of the electrodes is regularly reversed, the process is called electrodialysis reversal (EDR). This variation on the ED process uses electrode polarity reversal to clean automatically the membrane surfaces, increasing membrane life. This process minimizes the effect of inorganic scaling and fouling by converting product streams into waste streams and allows running at higher recovery rates. (Valero & Arbós, 2010). However, EDR requires additional plumbing and electrical controls.

A typical RED membrane unit consists of an alternating series of CEM and AEM situated between two electrodes (see Figure 9.1(b)). The salinity gradient between both solutions induces an electrochemical potential difference through each membrane. This electrochemical potential difference causes the transport of ions through the membranes from the concentrated solution to the diluted solution. At the electrodes, the ionic species accumulate and induce electron current via red-ox reactions, which can be used to power on an external device (Hong et al., 2013). To optimize both ED and RED processes, various research studies were focused on the improvement of the IEMs' performance, including their physicochemical (e.g., thickness and swelling degree) and electrochemical (e.g., area resistance, i.e., electrical membrane resistance (Ω cm^2), permselectivity, and charge density) characteristics (Güler, Elizen, Vermaas, Saakes, & Nijmeijer, 2013).

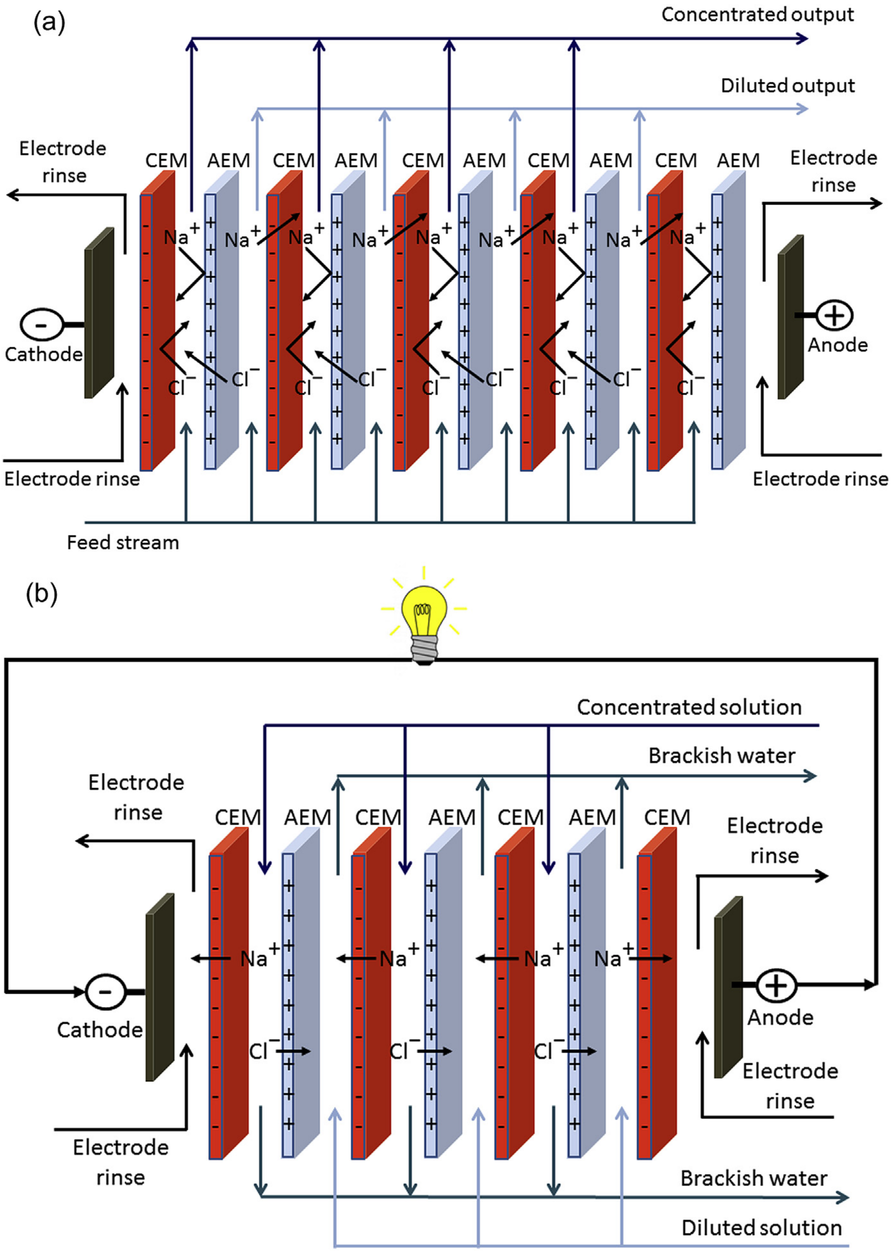

Figure 9.1 Schematic diagrams: (a) Electrodialysis unit with five cell pairs and (b) Reverse electrodialysis unit.

When the ED process is used to produce NaCl (table salt) from high-salinity brine, the salt rejection factor (or membrane selectivity) to monovalent and multivalent ions is important to avoid the possible salt precipitation taking placing in the concentrating compartments (Wang, Jia, Yao, & Wang, 2013). It is worth noting that high process cost and low selectivity, efficiency, and durability of IEMs are still important issues in ED technology (Kumar, Khan, Alothman, & Siddiqui, 2013). Many researchers are investigating to develop specific selective membranes/materials to overcome these problems.

Chakrabarty et al. (2011) developed thermally and chemically cross linked stable IEMs in an aqueous medium for water desalination by ED. CEM was prepared by sulfonation of poly (ether sulfone) (SPES), while AEM was fabricated by using polyvinyl alcohol (PVA) and 4-vinylpyridine (4-VP) in three steps: (1) sol–gel process, (2) chemical cross linking, and (3) quaternization. The membrane electrochemical properties and stabilities could be controlled by either the degree of sulfonation of SPES (in the case of CEM) or chemical cross linking (in the case of AEM). Both CEM and AEM showed excellent electro-transport properties and a good ED performance and energy consumption (4.29 kWh/kg of NaCl removed) for water desalination.

Zendehnam, Robatmili, Hosseini, Arabzadegan, and Madaenic (2013) prepared acrylonitrile/butadiene/styrene heterogeneous AEMs using anion exchange resin powder as functional group agents and tetrahydrofuran as a solvent. In addition, a silver (Ag) nanolayer was deposited on the prepared membrane surface using the magnetron sputtering method. Activated carbon (AC) was also used as an inorganic filler additive to create adsorptive active sites in the membrane matrix. The results showed a maximum of the membrane permselectivity for 2 wt.% AC concentration in the casting solution. Both the ionic permeability and permeate flux were enhanced by increasing the AC amount up to 0.5 wt.%, and then they declined with further increase of AC concentration from 0.5 to 4 wt.%. The modified membranes showed good ability in *Escherichia coli* removal due to the increase of the coating thickness of Ag nanolayer, which reduced the growth rate of *E. coli*.

To improve the ED membrane monovalent selectivity, Wang et al. (2013) performed a promising modification method consisting on a photo-induced covalent immobilization and self-crosslinking of a chitosan (CS) layer on a conventional CEM surface. This modification resulted in both chemical and morphological membrane surface changes, such as the formation of chemical bonds between the base membrane and the covalently immobilized and self-crosslinked CS layer. The ED experimental results with respect to Na^+/Mg^{2+} and H^+/Zn^{2+} systems showed that the modified CEMs achieved a superior monovalent selectivity after the immobilization of CS layer. The Zn^{2+} and Mg^{2+} leakage of the modified membrane were reduced by 27.4% and 62.4%, respectively, whereas the diffusion coefficient of Na^+, electrical resistance, and limiting current density were not declined remarkably after the modification by CS immobilization.

Other research studies have demonstrated that the modification of CEMs with polyaniline (PANI) is an efficient approach for improving the stability and selectivity of IEMs toward monovalent ions. For example, Kumar et al. (2013) developed PANI chemically modified organic–inorganic hybrid CEMs by in situ polymerization of aniline in an HCl aqueous solution using ferric chloride ($FeCl_3$) as an oxidizing agent. The PANI modified membranes were thermally stable in ED separation of Na^+ from binary mixtures of (Na^+/Zn^{2+} and Na^+/Al^{3+}) in aqueous solutions. The water uptake, ion exchange capacity, cation transport number in the membrane phase, and equivalent membrane conductivity of the modified membranes were improved for a 0.01 M NaCl aqueous solution. The cation transport number value for Zn^{2+} and Al^{3+} (0.40 and 0.34, respectively) of the PANI modified membranes were lower than the cation transport number value for Na^{+} (0.92), which indicated that the modified membranes were more selective for Na^{+} in comparison to Zn^{2+} and Al^{3+} ions.

Mulyati et al. (2012) improved the ED anti fouling properties of the commercial AEM (NEOSEPTA AMX, Astom Corp., Tokyo, Japan) by surface modification with poly(sodium 4-styrene sulfonate) (PSS). Antifouling potential of the AEM was evaluated based on the elapsed time before fouling took place, using sodium dodecylbenzene sulfonate (SDBS) as a model organic foulant. It was observed an enhanced antifouling property of the modified membrane attributed to the increase of the negative charge density and hydrophilicity of the membrane surface. However, the monovalent anion selectivity was not improved by the deposition of a single layer of PSS. A year later, the same research group developed a new approach to simultaneously improve the monovalent anion selectivity and antifouling properties of commercial AEMs (Mulyati et al., 2013). The method was based on the generation of a high negative charge on the membrane surface using layer-by-layer (LbL) deposition of different polyelectrolyte solutions in which PSS was used as a polyanion, while poly(allylamine hydrochloride) (PAH) was used as a polycation. A commercial AEM (NEOSEPTA AMX membrane, Astom Corp., Tokyo, Japan) was modified via alternating contact with the PSS and PAH solutions for 30 min. The results showed that the increase of the number of layers resulted in better monovalent anion selectivity and anti fouling character.

Cross-linked zirconium tri-ethylene tetra-amine (ZrT) chelating membranes were prepared by sol—gel method for Cu^{2+} removal in the presence of other bivalent metal ions (Chakrabarty, Shah, Srivastava, Shahi, & Chudasamab, 2013). The incorporation of ZrT in the PVA polymer matrix ensures the formation of homogeneous and interconnected polymer network. The developed ZrT membrane exhibited good thermal, mechanical, and chemical stabilities with a controlled pore size. ED studies revealed high Cu^{2+} permeate flux ($5.5 \cdot 10^{-7}$ mol/m^2 s at 10 mA/cm^2 applied current density) of ZrT membranes in comparison with other bivalent metal cations ($1.5-2 \cdot 10^{-7}$ mol/m^2 s for Ni^{2+}, Zn^{2+}, and Mn^{2+}). The selective recovery of Cu^{2+} was attributed to the hydrophilic structural membrane morphology having many amino groups and highly cross linked. The separation factor was estimated from the ratio of Cu^{2+} permeate flux ($J_{Cu^{2+}}$) and other bivalent cation permeate flux ($J_{Cu^{2+}}/J_{M^{2+}}$) in equimolar solution metal ion mixtures. The obtained high separation factor (3.0—4.0) for separating Cu^{2+}/Ni^{2+}, Cu^{2+}/Zn^{2+}, and Cu^{2+}/Mn^{2+} suggested the application of ZrT chelating membranes for Cu^{2+} recovery from industrial wastewaters.

Hosseini, Askari, Koranian, Madaeni, and Moghadassia (2014) and Hosseini et al. (2013) investigated the effects of the concentration of different additives, iron oxide (Fe_3O_4) nanoparticles (NPs), and multiwalled carbon nanotubes (MWCNTs) on the physicochemical and electrochemical properties of polyvinylchloride (PVC)-based ED CEM. An increase of the water content (from 22% to 25.9%) and the ion exchange capacity (from 1.43 to 1.72 meq/g) of the CEM with the increase of Fe_3O_4 NPs from

0 to 2 wt.% followed by a decline of both parameters for high NPs concentrations was observed. The same behavior was observed for the ionic permeability for sodium and barium ions, achieving high values of $35.5 \cdot 10^7$ and $33.7 \cdot 10^7$ m/s, respectively, at 2 wt.% Fe_3O_4 content. The membrane permselectivity was enhanced with the increase of the additive content from 0 to 4 wt.% in sodium (79.0−86.0%) and barium chloride (36.4−42.5%) ionic solutions. These results suggested that the prepared membranes were less selective to bivalent ions (Ba^{2+}) compared to monovalent ions (Na^+). For MWCNTs, the prepared membrane water content also showed a maximum of 28.3% for 4 wt.% MWCNT concentration in the casting solution. The increase of MWCNTs' loading ratio also resulted in an increase of the permeability for monovalent ions (Na^+) from $23.98 \cdot 10^7$ to $24.20 \cdot 10^7$ m/s, while the permeability for bivalent ions (Ba^{2+}) did not show a straightforward relationship with MWCNTs' loading ratio.

ED was also carried out using bipolar membranes (BPMs), which are composite IEMs consisting of a layered ion exchange structure composed of a cation exchange layer (CEL) and an anion exchange layer (AEL) with a hydrophilic intermediate layer in between (Venugopal & Dharmalingam, 2012; Xu, 2005). This composition of anionic and cationic exchange layers exhibits various advantages in ED, such as the separation of monovalent and divalent ions, antideposition, antifouling, water dissociation into OH^- and H^+ ions, increase of reusability and recyclability of waste through chemical production (acidic and alkaline solutions), low initial cost, and no electrochemical reactions (oxidation and/or reduction species) that may produce undesirable products, etc. (Kariduraganavar, Nagarale, Kittur, & Kulkarni, 2006). Today, synthetic BPMs are receiving much attention because of their potential for application in different industries, such as chemical production and separation industry, biochemical engineering (i.e., producing inorganic acid/base from the corresponding salts, recovery/produce organic from fermentation broth, etc.), environmental conservation, purification or separation in food industries (i.e., inhabitation of polyphenol oxidase in apple juice), etc. When applied to treat salt-containing wastewater, BPM ED can produce acids and bases due to its ability to split water into OH^- and H^+ ions and overcome salt pollution and be discharged without treatment (see Figure 9.2). Venugopal and Dharmalingam (2012) developed a novel functionalized polysulfone (PS)-based BPM with an intermediate layer of PVA and investigated its ED performance for seawater desalination and recovery of acid and alkali. The prepared BPM possessed excellent mechanical and chemical stabilities due to its unique ply structures in both AEL and CEL forms. The PS-based BPM showed higher current efficiency (i.e., 18%), lower power consumption (i.e., 8%), greater salt rejection factor, and higher process efficiency for the production of acid and alkali than those of the commercial BPM made of gel polystyrene crosslinked with divinylbenzene (PSDVB) (Arun Electro chemicals, Chennai).

Wang, Peng, et al. (2010) developed a hybrid BPM for high temperature applications. The CEL was prepared by hybridizing sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) with (3-aminopropyl) triethoxysilane (A1100), while the AEL was prepared from a hybrid anion exchange material, poly(VBC-co-γ-MPS) (vinylbenzyl chloride (VBC) and γ-methacryloxypropyl trimethoxy silane (γ-MPS)), and PVA. Palygorskite (a silicate mineral) and $FeCl_3$ were added in the intermediate layer

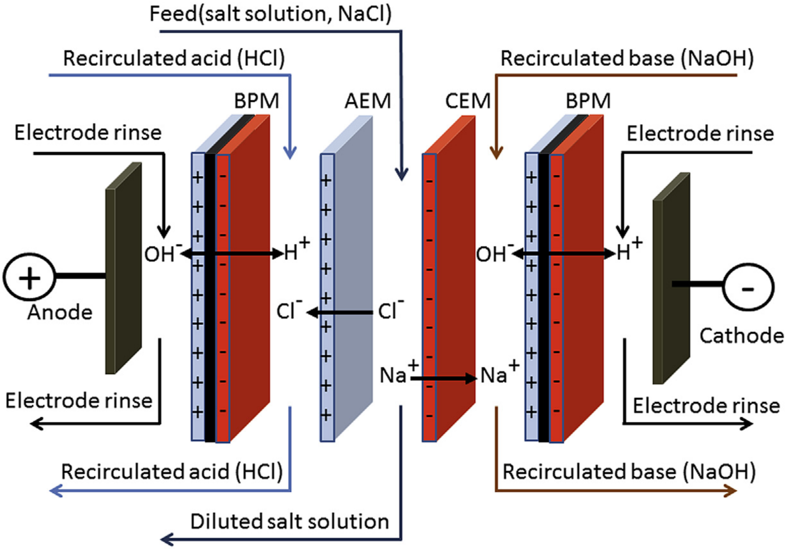

Figure 9.2 Schematic diagram of electrodialysis with bipolar membranes cell to treat salt-containing wastewater.

as catalysts to further enhance water dissociation, improving the generation of H^+ and OH^-, although the voltage drop across the BPM was detected. By incorporating inorganic silane (A1100 and γ-MPS) in both the AEL/CEL, the BPM showed higher thermal stability, dimensional stability, and catalytic effect on water dissociation in the range 25−80 °C.

Not only the improvement of the membrane properties is necessary to achieve high ED and RED performances, but it is also important to consider the scale-up and design of the ED/RED unit and the optimization of the electrode systems. Güler et al. (2013) successfully constructed a RED unit completely built with tailor-made IEMs, in which CEMs were fabricated by sulfonated polyetheretherketone (SPEEK) and AEMs with polyepichlorohydrin (PECH). The bulk membrane properties (i.e., area resistance, permselectivity, and charge density) of both series of commercially available membranes and tailor-made ones were investigated and correlated to the obtained RED performance. Experimental and theoretical statistical results showed that increasing the area resistance resulted in an increase of the power density in RED, whereas permselectivity did not show any straightforward relationship with the power density. Furthermore, the performance of the tailor-made RED unit exhibited a higher power density (1.28 W/m^2) than other RED units based on the commercially considered membranes Fumatech FKS/FAS (1.11 W/m^2), Tukuyama CMX/AMX (1.07 W/m^2), Qianqui CEM/AEM (0.83 W/m^2), or Ralex CMH/AMH (0.60 W/m^2).

For the design of a typical system of both RED and ED processes, metal oxide catalysts are commonly used to convert the electronic current to ionic current. This conversion results from the red-ox reaction that occurs in the electrodes of the system. Burheim et al. (2012) studied the performance of electrode systems for RED and ED separation processes by testing two different electrode materials and red-ox salts, demonstrating that these electrochemical reactions were controlled by mass transfer in the electrolyte rather than by the electro-catalytic properties of the electrode material. It was concluded that relatively cheap carbon materials (graphite and glassy carbon) with $FeCl_2$/$FeCl_3$ could act as good electrodes in a red-ox system with lower electrode concentration overpotential. The power losses (i.e., dissipated energy) in the electrode compartments were reduced by increasing the concentration of the electroactive species. Vermaas, Saakes, and Nijmeijer (2011) developed a RED unit using membranes with a specific laboratory-made profile (profiled membranes) and evaluated its performance, comparing it to that of RED unit of commercial IEMs (Ralex CMH and AMH, Mega a.s., Czech Republic) separated by non-conductive spacers. This new morphology resulted in a slight reduction in permselectivity (from 89% to 87%), a significant decrease in area resistance (from 7.3 to 2.7 $\Omega\ cm^2$), a large increase in conductivity (from 9.1 to 17.7 mS/cm), and a slightly higher maximum power density (from 0.69 to 0.80 W/m^2).

9.3 Concentration gradient driven membrane processes: FO and PRO

In the case of FO, a high-concentration solution (i.e., draw solution) is separated from a low-concentration solution by a water-selective semipermeable membrane. As it is shown in Figure 9.3, the concentration gradient between both the feed and draw solutions results in a transmembrane osmotic pressure. Consequently, water flows spontaneously through the membrane from the low-concentration side to the draw-solution side. PRO and FO are similar separation processes, except for the additional back pressure applied on the draw solution for PRO. In both processes, water flows from the low-concentration side of the membrane to the high-concentration side as long as the applied pressure is lower than the transmembrane osmotic pressure. When the applied pressure is greater than the osmotic pressure difference, the direction of the water flux is reversed, leading to the well-known RO separation process (Figure 9.4). Unlike RO, in which mechanical energy is used for pumping the feed saline aqueous solution through a water-selective membrane to overcome the transmembrane osmotic pressure, PRO converts the chemical potential (osmotic energy) of a salt-concentrated aqueous solution into mechanical energy (Xu, Peng, Tang, Fu, & Nie, 2010).

It must be pointed out that the membranes used in FO and PRO are not ideal, and reverse solute(s) permeate fluxes also occur through the membrane opposite to the direction of water permeate flux. This causes solute(s) concentration polarization inside the membrane, known as internal concentration polarization (ICP) phenomenon (Xu et al., 2010). ICP is one of the most severe drawbacks in the osmotic membrane processes, because it significantly reduces the membrane water permeability (Achilli & Childress, 2010; Chou et al., 2012). Therefore, preparation of specific membranes is essential for the development of FO and PRO technologies. In this case, three main

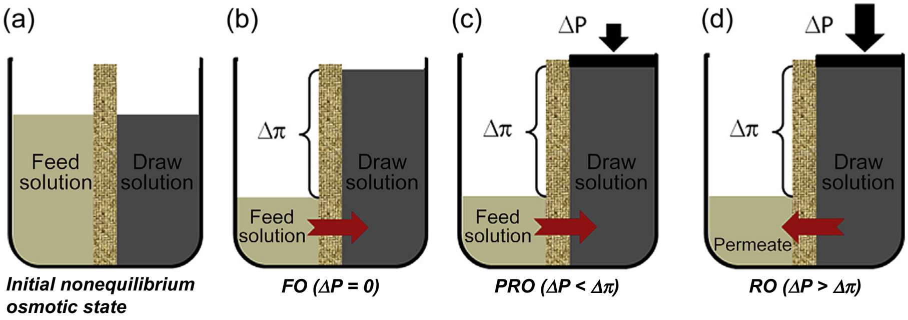

Figure 9.3 Illustration of forward osmosis (FO), reverse osmosis (RO), and pressure retarded osmosis (PRO) processes: (a) Initial non-equilibrium osmotic state; (b) FO process in which no pressure is applied on the draw solution; (c) PRO process in which a hydrostatic pressure lower than the transmembrane osmotic pressure is applied on the draw solution; (d) RO process used for desalination of a saline feed solution by applying a hydrostatic pressure greater than the transmembrane osmotic pressure.

challenges must be addressed, ICP, weak mechanical strength of the membranes, and membrane fouling propensity (Chou et al., 2012).

An ideal FO/PRO membrane should be a semipermeable membrane with a high water permeability and a high solute rejection factor, a small resistance toward solute diffusion, high chemical stability, low ICP using thin and highly porous supports with low mass transfer resistance, high mechanical strength to support high hydraulic pressure when used in PRO applications, low susceptibility to fouling (i.e., hydrophilic membrane to get high permeate fluxes and reduce membrane fouling), and low structural parameter (S), defined as the ratio of the pore tortuosity and porosity multiplied by the thickness of the membrane ($S =$ thickness $\times$ tortuosity/porosity) (Cath, Childress, & Elimelech, 2006; Chou et al., 2010; Han, Zhang, et al., 2013; Sivertsen, Holt, Thelin, & Brekke, 2013; Zhang et al., 2010). In addition, the surface structure of the FO membrane facing the feed aqueous solution is critical because it is directly associated with fouling tendency, while a relatively dense substrate surface is desirable for a membrane with an active layer facing draw solution (AL-DS).

For the preparation of FO and PRO membranes, different polymers are used, including cellulose acetate (CA) (Herron, 2008), cellulose triacetate (CTA) (H.T.I., 2013), PS (Yip, Tiraferri, Phillip, Schiffman, & Elimelech, 2010), polyethersulfone (PES) (Yu, Seo, Kim, & Lee, 2011), polybenzimidazole (PBI) (Wang, Chung, & Qin, 2007), polyamide (PA) (Alsvik & Hägg, 2013b), and poly(amide-imide) (PAI) (Setiawan, Wang, Li, & Fane, 2011). These FO and PRO membranes were designed as thin-film composite (TFC) flat sheet membranes using different types of supports and hollow fiber membranes.

Until now, three methods have been adopted to prepare polymeric FO membranes: the non-solvent phase inversion method developed by Loeb and Sourirajan (Loeb & Sourirajan, 1963); the interfacial polymerization (IP) on porous substrates invented by Cadotte (Cadotte, 1981) to prepare TFC membranes; and the LbL deposition of nanometer thick polycations and polyanions on porous charged substrates (Qi, Qiu,

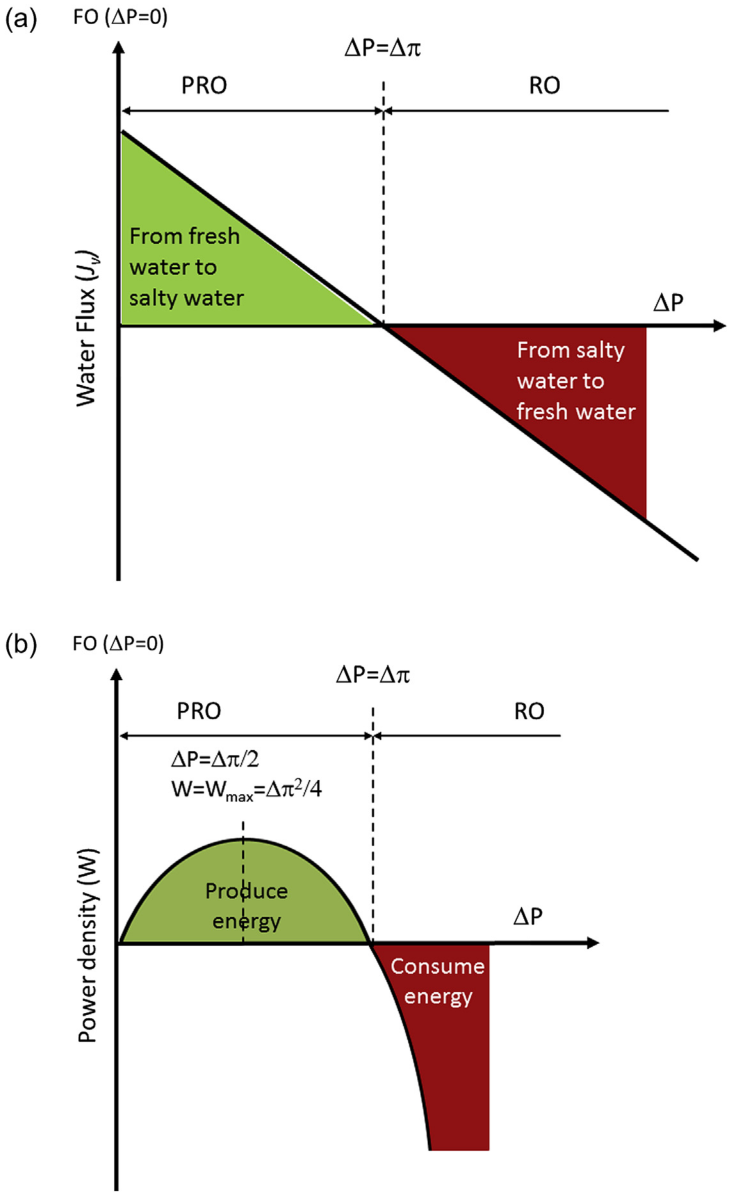

Figure 9.4 (a) Water flux direction and (b) energy consumption/production in forward osmosis (FO), pressure retarded osmosis (PRO), and reverse osmosis (RO) using a selective semipermeable membrane.

& Tang, 2011). Fully integrated asymmetric FO membranes made of CTA (Herron, 2008), PBI (Wang et al., 2007; Wang, Goh, et al., 2009; Yang, Wang, & Chung, 2009), CA (Su & Chung, 2011; Su, Yang, Teo, & Chung, 2010), and PES (Yu et al., 2011) are typical examples of the first method, while FO membranes made of

PA via IP on PS-based substrates (Wang, Shi, et al., 2010; Yip et al., 2010), sulfonated substrates (Wang, Chung, & Amy, 2012; Widjojo, Chung, Weber, Maletzko, & Warzelhan, 2011), cellulose acetate propionate substrates (Li, Wang, Helmer, & Chung, 2012), and nanofibrous supports (Bui, Lind, Hoek, & Mc Cutcheon, 2011) belong to the second method. A comparison of the performance of membranes applied in FO/PRO process is listed in Table 9.1.

It is worth noting that CA has been widely used to prepare FO membranes via phase inversion because of its relatively high hydrophilicity that favors high water permeability and low fouling propensity, good mechanical strength, wide availability, and good resistance to degradation by various compounds including chlorine (Zhao, Zou, Tang, & Mulcahy, 2012). The company Hydration Technology Innovations (HTI, Albany, OR, USA) has provided asymmetric cellulose-based membranes for FO for nearly 25 years. This company developed flat sheet membranes using cellulose esters exclusively for FO applications. In 2008, HTI patented commercial asymmetric CA/CTA FO membranes composed of a thin skin layer for salt separation (10–20 μm) and a thicker porous scaffold layer (about 100 μm thick) with a woven or non-woven mesh embedded within it (Herron, 2008). These membranes exhibit high permeate flux and salt rejection factors, low resistance to water diffusion, lack of defects, and good structural integrity. It was claimed that these membranes have far superior permeate fluxes than other commercially available composite membranes such as cellulose ester blend RO membrane (Osmonics, now GE Water Systems) used in FO.

Recently, Nguyen, Yun, Kim, and Kwon (2013) prepared CTA/CA flat sheet membranes with enhanced FO performance by immersion precipitation using different casting compositions and support layers (Figure 9.5). The optimized membrane (WF1, Figure 9.5(a)) was prepared by casting 6.3 wt.% CTA, 12.6 wt.% CA, 49.9 wt.% 1,4-dioxane, 17.2 wt.% acetone, 3.7 wt.% maleic acid, and 10.3 wt.% methanol to a thickness of 250 μm on a porous woven support layer with a subsequent evaporation for 30 s at 25 °C and 70% relative humidity, and then annealing at 85 °C. The optimized membrane showed a more hydrophilic and smoother surface than the commercial CTA FO membrane (090128-NW-1, HTI) with lower fouling, the highest water permeate flux (9.270 L/m^2 h for a draw solution of 1 M NaCl), 99.533% NaCl rejection factor, and a reverse salt permeate flux of 0.248 mol Br^-/m^2 h.

To develop FO membranes with a high salt rejection factor, Su et al. (2010) fabricated a CA-based NF hollow fiber membrane modified by heat treatment. The heat-treated hollow fiber membrane at 95 °C resulted in a significant shrinkage of pores at the membrane surface with a denser outer skin layer, but a low FO performance with increasing saline concentration in the feed solution due to the more severe ICP effect. One year later, Su and Chung (2011) carried out both experimental and theoretical studies using different CA hollow fiber membranes prepared with different bore fluid compositions via a dry/jet wet spinning technique. It was observed that the internal membrane structure did not exert any apparent influence on the membrane performance used in PRO mode, whereas it affected significantly the concentration polymerization and the FO performance. It was also claimed that the preferred internal sublayer of a hollow fiber for FO should have a high porosity, low tortuosity, and small thickness to enhance the water permeate flux.

Table 9. 1 Overview of recent researches on forward osmosis/pressure retarted osmosis (FO/PRO) process with different membranes

Membrane (material-support-shape (commercial name))	Water permeability (L/m^2 h bar)	Salt rejection (%)	FO performance			Testing conditions			References
			Water flux (L/m^2 h)	Salt flux (g/m^2 h)	Membrane orientation	Feed solution	Draw solution	Temperature (°C)	
CA NF HF	0.47	96.7	7.3/5.0	0.52/—	PRO/FO	DI water	2 M $MgCl_2$	22—25	Su et al. (2010)
CA HF	0.97	74.16	36.3/8.3	1.0/1.0	PRO/FO	DI water	2 M $MgCl_2$	—	Su and Chung (2011)
CA double dense layer FS	0.17	99.0	17.3/10.3	1.2/0.8	PRO/FO*	DI water	2 M $MgCl_2$	22	Zhang et al. (2010)
		92.0	11.3/7.8	4.4/3.8	PRO/FO*	DI water	2 M NaCl	22	
CA double-skinned FS	0.78	79.0	25.5/16.8	4.6/2.5	PRO/FO*	DI water	2 M $MgCl_2$	22	Wang, Ong, et al (2010)
CA HTI[c] FS	—	—	4.5	2.7	FO	DI water	1.5 M $MgSO_4$	20	Cornelissen et al. (2008)
CA HTI[c] FS	—	—	43.2/18.1	—	PRO/FO	DI water	1.5 M NaCl	20	Mc Cutcheon and Elimelech (2008)
CTA HTI[c] FS	0.68	—	19.6/12.4	8.8/6.2	PRO/FO	DI water	1.5 M NaCl	25	Bui and Mc Cutcheon (2013)
CTA HTI[c] FS	—	91.0	11.9	5.5	FO	DI water	2 M NaCl	20—25	You et al. (2013)
CTA HTI[c] FS (CTA-W)	0.33	81.9	6.55/5.0	4.8/2.9	PRO/FO	10 mM NaCl	0.5 M NaCl	23	Wei, Qiu, Tang, Wang, and Fane (2011)
			22.9/12.1	—	PRO/FO	10 mM NaCl	2 M NaCl	23	

Asymmetric PBI NF HF	0.5	48.1	3.8	–	PRO	DI water	2 M NaCl	22.5	Wang et al. (2007)
		86.5	9.0/5.3	–	PRO/FO	DI water	2 M $MgCl_2$	22.5	
PBI NF HF (original)	2.43	76.2	25.0/12.6	–	PRO/FO	DI water	2 M $MgCl_2$	23.0	Wang, Yang, et al. (2009)
PBI NF HF (2h modified)	1.53	85.6	22.1/11.2	–	PRO/FO	DI water	2 M $MgCl_2$	23.0	Wang, Yang, et al. (2009)
PBI-PES/PVP dual-layer NF HF	1.74	87.2	19.5/14.8	–	PRO/FO	DI water	2 M $MgCl_2$	23.0	Yang et al. (2009)
Positively charged PAI single-layer HF	2.25	92.7	13.2/8.4	9.9/2.6	PRO/FO	DI water	0.5 M $MgCl_2$	23.0	Setiawan et al. (2011)
			17.9/13.2	17.5/4.9	PRO/FO	DI water	2 M $MgCl_2$	23.0	
PAI/PES dual-layer HF	15.9	89.0	15.5/27.5	83.7/5.5	PRO/FO	DI water	0.5 M $MgCl_2$	23.0	Setiawan, Wang, Shi, Li, and Fane (2012)
Positively charged PAI with PET substrate FS	7.56	87.5	23.9/19.2	36.6/9.2	PRO/FO	DI water	0.5 M $MgCl_2$	22–25	Qiu, Setiawan, Wang, Tang, and Fane (2012)
			32.5/27.5	107/33.3	PRO/FO	DI water	2 M $MgCl_2$	22–25	
PES with PET substrate FS	–	–	31.4	8.2	FO	DI water	3 M NaCl	20.0	Yu et al. (2011)

Continued

Table 9. 1 Continued

Membrane (material-support-shape (commercial name))	Water permeability (L/m^2 h bar)	Salt rejection (%)	FO performance			Testing conditions			References
			Water flux (L/m^2 h)	Salt flux (g/m^2 h)	Membrane orientation	Feed solution	Draw solution	Temperature (°C)	
Cellulosic RO^c without PET FS, GE Osmonics	–	–	36.0/18.6	–	PRO/FO	DI water	1.5 M NaCl	20.0	Mc Cutcheon and Elimelech (2008)
TFC-PA-PES HF (#A-FO)	0.95	78.0	12.9/5.0	5.0/2.1	PRO/FO	DI water	0.5 M NaCl	23.0	Wang et al. (2010)
			25.9/8.6	–	PRO/FO	DI water	2 M NaCl	23.0	
TFC-PA-PES HF (#B-FO)	2.22	91.0	32.2/14	3.5/1.8	PRO/FO	DI water	0.5 M NaCl	23.0	Wang et al. (2010)
			45.0/22.5	4.4/2.5	PRO/FO	DI water	2M NaCl	23.0	
TFC-PA-PES HF (#C-FO)	3.5	90.0	42.6/18.7	4.0/1.6	PRO/FO	DI water	0.5 M NaCl	23.0	Chou et al. (2010)
			68.0/29.5	5.8/2.6	PRO/FO	DI water	2 M NaCl	23.0	
TFC-PA- PES$_{water}$ HF	1.18	87.95	25.6/22.5	3.2/2.8	PRO/FO	DI water	0.5 M NaCl	20-25	Sukitpaneenit and Chung (2012)
			57.1/32.1	6.9/6.1	PRO/FO	DI water	2 M NaCl	20-25	
TFC-PA-PES$_{water/NMP/PEG}$ HF	1.83	81.52	65.1/34.5	12.3/9.9	PRO/FO	DI water	2 M NaCl	20-25	Sukitpaneenit and Chung (2012)

TFC-PA-PES HF	1.9	87.8	38.3	10.6	PRO	DI water	1 M NaCl	—	Han, Wang, et al. (2013)
TFC-PA-sPPSU HF	1.99	90.9	49.4/22.5	11.0/5.5	PRO/FO	DI water	0.5 M NaCl	23	Zhong, Fu, Chung, Weber, and Maletzko (2013)
TFC-PA-PS FS	1.78	93.4	20.5/12.0	5.9/4.9	PRO/FO	10 mM NaCl	0.5 M NaCl	23	Wei et al. (2011)
			54.3/22.2	—	PRO/FO	10 mM NaCl	2 M NaCl	23	
TFC-PA-PS FS	3.1	70.0	37.6/24.9	7.5/3.2	PRO/FO	10 mM NaCl	2 M NaCl	23	Amini, Jahanshahi, and Rahimpour (2013)
TFC-PA-PS FS	—	—	32.5/14.1	14.4/5.3	PRO/FO	DI water	2 M NaCl	—	Emadzadeh, Lau, Matsuura, Ismail, and Rahbari-Sisakht (2014)
TFC-PA-PS with PET substrate FS	1.9	98.6	25.0	—	FO	DI water	1 M NaCl	23	Tiraferri, Yip, Phillip, Schiffman, and Elimelech (2011)
TFC-PA-PS with PET substrate FS	1.44	98.4	16.7	—	FO	DI water	1 M NaCl	25	Hoover, Schiffman, and Elimelech (2013)
TFC-PA-PS/SPEK FS	0.75	89.5	20.1/16.1	4.5/3.3	PRO/FO	DI water	0.5 M NaCl	23	Han, Chung, Toriida, and Tamai (2012)
			50.0/35.0	9.0/7.0	PRO/FO	DI water	2 M NaCl	23	

Continued

Table 9. 1 **Continued**

Membrane (material-support-shape (commercial name))	Water permeability (L/m^2 h bar)	Salt rejection (%)	FO performance			Testing conditions			References
			Water flux (L/m^2 h)	Salt flux (g/m^2 h)	Membrane orientation	Feed solution	Draw solution	Temperature (°C)	
TFC-PA-SPPSU FS	3.23	84.1	32.2/30.0	4.7/5.2	PRO/FO	DI water	0.5 M NaCl	–	Widjojo, Chung, Weber, Maletzko, and Warzelhan (2013)
			54.0/48.0	8.8/7.6	PRO/FO	DI water	2 M NaCl	–	
TFC-PA-CPSF FS	–	–	27.5/17.9	7.3/4.8	PRO/FO	DI water	1 M $MgCl_2$	25	Cho, Han, Han, Guiver, and Park (2013)
TFC-PA-PES/ sulfonated polymer substrate FS	0.73	91.0	16.2/15.3	2.7/3.0	PRO/FO	DI water	0.5 M NaCl	20–25	Widjojo et al. (2011)
			33.0/21.0	2.8/2.2	PRO/FO	DI water	2 M NaCl	20–25	
TFC-PA-PES/ SPSf FS	0.77	93.5	24.1/13.0	4.5/3.6	PRO/FO	DI water	0.5 M NaCl	20–25	Wang et al. (2012)
			47.5/26.0	12.4/8.3	PRO/FO	DI water	2 M NaCl	20–25	
TFC-PA-PVDF FS	0.82	–	21.7/15.0	10.2/7.8	PRO/FO	DI water	0.5 M NaCl	20-25	Wang et al. (2012)
			36.0/23.3	18.3/ 11.2	PRO/FO	DI water	2 M NaCl	20–25	
TFC-PA-CAP FS	1.82	89.2	15.5/7.8	0.8/0.9	PRO/FO	DI water	0.5 M NaCl	20–25	Li et al. (2012)
			35/17.5	1.95/1.8	PRO/FO	DI water	2 M NaCl	20–25	

TFC-PA-nylon 6.6 MF FS	0.92	95.8	21.9/6.2	0.8/0.7	PRO/FO	DI water	1.5 M NaCl	20	Huang et al. (2013)
TFC-PA-Matrimid FS	10.0	–	89.1	15.4	PRO	DI water	1 M NaCl	25	Han, Zhang, et al. (2013)
TFC-PA PS nanofiber with PET substrate FS	1.74	–	26.0	2.3	FO	DI water	1.5 M NaCl	23	Bui et al. (2011)
TFC-PA-PES nanofiber FS	1.7	97.0	63.7/57.6	–	PRO/FO	DI water	1.5 M NaCl	23	Song, Liu, and Sun (2011)
TFC-PA-PVDF nanofiber FS	3.15	84.4	62.1/36.5	28.1/16.9	PRO/FO	DI water	1.5 M NaCl	23	Tian, Qiu, Liao, Chou, and Wang (2013)
TFC-PA-PAN nanofiber FS	2.04	–	61.9/35.0	5.2/8.4	PRO/FO	DI water	1.5 M NaCl	25	Bui and Mc Cutcheon (2013)
TFC-PA-PAN/CA nanofiber FS	1.8	–	54.8/30.1	4.2/10.6	PRO/FO	DI water	1.5 M NaCl	25	Bui and Mc Cutcheon (2013)
TFC NF FS(TS80), Trisep	–	–	1.1	0.04	FO	DI water	1.5 M $MgSO_4$	20.0	Cornelissen et al. (2008)
TFC RO FS (SWC1), Hydranautics	–	–	0.4	0.01	FO	DI water	1.5 M $MgSO_4$	20.0	Cornelissen et al. (2008)
TFC-PA RO PS with PET FS (SW30 XLE), Dow FilmTec	–	–	8.1/3.6	–	PRO/FO	DI water	1.5 M NaCl	20.0	Mc Cutcheon and Elimelech (2008)

Continued

Table 9. 1 **Continued**

Membrane (material-support-shape (commercial name))	Water permeability (L/m^2 h bar)	Salt rejection (%)	FO performance			Testing conditions			References
			Water flux (L/m^2 h)	Salt flux (g/m^2 h)	Membrane orientation	Feed solution	Draw solution	Temperature (°C)	
TFC-PA HTI[c] FS	–	–	49.0/20.0	–	PRO/FO	DI water	1 M NaCl	23	H.T.I. (2013)
TFN-PA/F-MWCNT-PS FS	4.47	73.0	95.1/39.0	5.2/2.9	PRO/FO	10 mM NaCl	2 M NaCl	23	Amini et al. (2013)
TFN-PA/TiO$_2$–PS FS	2.99	77.4	39.1/22.5	20.8/10.2	PRO/FO	DI water	0.5 M NaCl	–	Emadzadeh et al. (2014)
			75.1/37.4	43.8/23.3	PRO/FO	DI water	2 M NaCl	–	
LbL nanocomposite PVA/MMt-TA/LiCl FS	–	–	18.9/10.0	0.1/0.03	PRO/FO	DI water	0.5M NaCl	23.0	Pardeshi and Mungray (2014)
			37.7/25.5	0.28/0.05	PRO/FO	DI water	2 M NaCl	23.0	

LbL nanocomposite NF-PAN/PSS/Ag FS	–	95.0	42.2/17.8	3.0/2.8	PRO/FO	10 mM NaCl	0.5 M $MgCl_2$	26.0	Liu et al. (2013)
LbLTFI-SSM/silica xerogels/TEOS FS	–	92.0	60.3/59.8	10.6/10.5	PRO/FO	DI water	2 M NaCl	20–25	You et al. (2013)
LbL double-skinned PAN/PAH-PSS FS	1.6	95.5	35.4/76.6	11.9/21.4	PRO/FO*	DI water	0.5 M $MgCl_2$	22–23	Qi, Qiu, Zhao, and Tang (2012)
			50.1/106.1	20.3/51.6	PRO/FO*	DI water	2 M $MgCl_2$	22–23	

Note: HF, Hollow fiber; FS, flat sheet. The superscript “c” refers to commercial and PRO/FO* refers to such membrane that the bottom layer faces the draw solution in the PRO mode and the top layer faces draw solution in the FO mode.

Recently, Alsvik and Hägg (2013b) coated hydrolyzed commercial CA/CTA (CA from Alfa Laval; and CTA from HTI) support membranes with a PA layer by a modified IP method, forming a covalent bond between the active layer and the support. The prepared membranes displayed salt rejection factors up to 97% and water permeate fluxes varying from 0.76 to 4.7 L/m^2 s at transmembrane pressure of $1.3 \cdot 10^6$ Pa (RO mode).

During the last eight years, several studies have been published on the formation of hollow fiber membranes specially designed for osmotically driven processes (Alsvik & Hägg, 2013a). Wang, Yang, et al. (2009) fabricated hollow fiber membranes for FO applications by the dry/jet phase inversion method using PBI and modified via cross-linking using *p*-xylylene dichloride. To improve the FO performance, Yang et al.

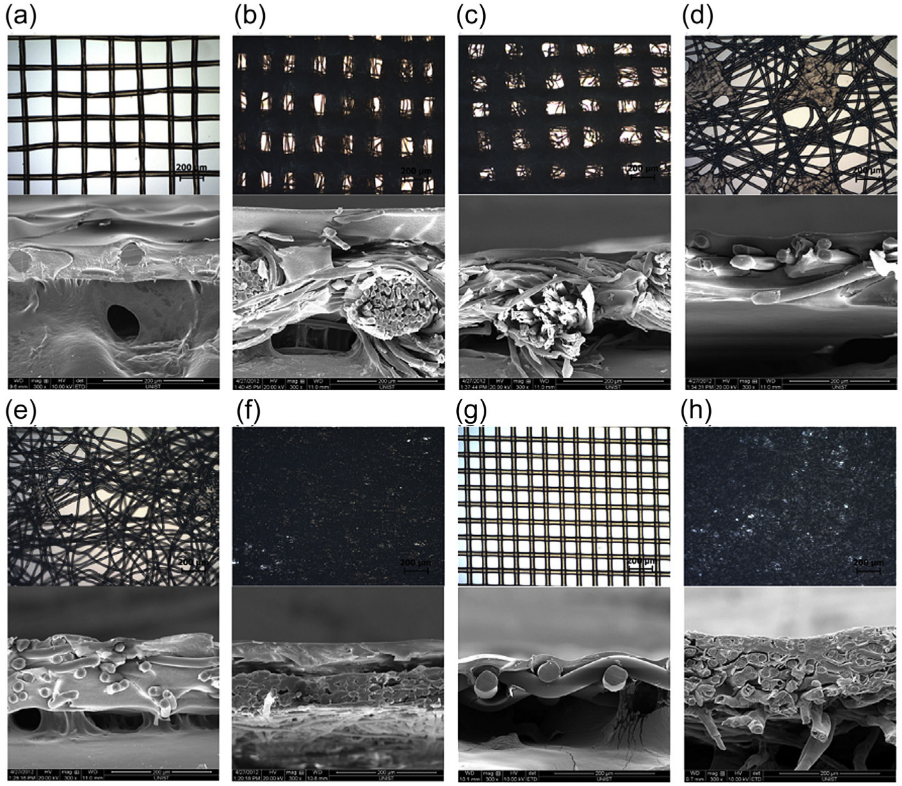

Figure 9.5 Images of supports (first row) and SEM cross-sectional images of forward osmosis membranes (second row) fabricated on the corresponding support layers. Three woven fabrics, labeled WF1 (a), WF2 (b), and WF3 (c), and three non-woven fabrics, labeled NWF1 (d), NWF2 (e), and NWF3 (f), were used as support layers for the cellulose triacetate/cellulose acetate (CTA/CA)-based membranes. Two commercial membranes were used to compare: a cartridge CTA-based membrane (090128-NW-1, HTI1 (g)) and a pouch CTA-based membrane (081118-SS-2, HTI2 (h)).
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(2009) developed a dual-layer PBI—PES hollow fiber membrane via a co-extrusion technique. This membrane consisted on an ultrathin selective skin layer, fully porous water channels underneath, and a microporous sponge-like support structure. The prepared PBI—PES/polyvinylpyrrolidone (PVP) dual-layer membrane achieved a pure water permeability (*PWP*) of 1.74 L/m^2 h bar and an $MgCl_2$ rejection factor of 87.2%. The obtained water permeate fluxes in FO and PRO mode using 2 M $MgCl_2$ as a draw solution at 23 °C (14.8 and 19.5 kg/m^2 h, respectively) were higher than those of the commercial RO membranes (AG, GE Osmonics, 2.5 kg/m^2 h and AD, GE Osmonics, 1.1 kg/m^2 h) (Miller & Evans, 2006), but comparable to most commercial HTI FO flat sheet membranes (i.e., 12.9 kg/m^2 h for FO experiment and 8.5 kg/m^2 h for PRO experiment (Cornelissen et al., 2008)).

Setiawan et al. (2011) fabricated hollow fiber membranes with a positively charged layer (i.e., NF-like skin layer) using asymmetric microporous hollow fibers made of Torlon® PAI material as substrates followed by chemical crosslinking using polyethyleneimine (PEI). The PAI hollow fiber membranes exhibited a *PWP* of 2.19—2.25 L/m^2 h bar and a high $MgCl_2$ rejection factor more than 91.1% under a pressure of 1 bar. By using 1 M $MgCl_2$ draw solution, better FO water permeate fluxes (10.4—11.0 kg/m^2 h) than those of previously reported PBI NF modified hollow fibers (Wang, Yang, et al., 2009) prepared with 4 and 9 h of crosslinking time (5.0 and 1.7 kg/m^2 h, respectively) and CA-based NF hollow fiber (3.1 kg/m^2 h) (Su et al., 2010). However, it was noted that the chemical crosslinking of the PAI hollow fiber membranes resulted in a denser substrate, which adversely affected the water permeate flux. To overcome this problem, Setiawan et al. (2012) developed asymmetric microporous PAI/PES dual-layer hollow fiber membranes that consisted of an external layer made from PAI polymer and an internal layer made of PES. Subsequently, PEI polyelectrolyte modification was carried out on the outer PAI layer to produce an NF-like thin layer, while the PES porous inner layer remained intact because PES is inert to PEI. The developed PAI/PES dual-layer hollow fiber membranes achieved a *PWP* of 15.9 L/m^2 h bar and high $MgCl_2$ rejection factors up to 89%. In FO process, the dual-layer hollow fiber exhibited a water permeate flux of 27.5 L/m^2 h by using 0.5 M $MgCl_2$ as draw solution and deionized water as feed at room temperature.

Fang, Wang, Chou, Setiawan, and Fane (2012) also fabricated novel composite double-skinned PAI hollow fiber membranes for FO. In this case, two selective skin layers were integrated in each side of an ultrafiltration (UF) hollow fiber substrate via IP and chemical modification to yield a PA RO-like inner skin layer and a positively charged NF-like outer skin layer. The hydrophilic nature of the two skin layers reduced the contact angle of the membrane from 80° for PAI hollow fiber substrate to 46° for the composite FO membrane. The prepared double-skinned composite hollow fiber membrane exhibited a high *PWP* of 2.05 L/m^2 h bar and 85% NaCl rejection at 1 bar pressure. Furthermore, compared to commercial HTI FO flat sheet membranes (water flux of 18.6 kg/m^2 h (Mc Cutcheon, Mc Ginnis, & Elimelech, 2006)) and other double-selective layer membranes reported in the literature (19.5 kg/m^2 h for dual-layer PBI—PES hollow fiber membrane (Yang et al., 2009)), the prepared double-skinned composite hollow fiber membrane presented higher water permeate flux of 41.3 kg/m^2 h and a low salt flux/water flux (J_s/J_w) ratio of 0.126 when using distilled water and 2 M NaCl as feed and draw solution, respectively; the active layer faced the AL-DS orientation (PRO mode).

Compared to the conventional asymmetric membranes (i.e., CA-based membranes) made by the non-solvent induced phase inversion, TFC membranes made by IP on porous support layers have several advantages, such as a higher *PWP*, greater solute rejection factors, higher chemical stability, and mechanical strength (Han et al., 2012). In addition, TFC membranes have more design flexibility by separately tuning selective skins and sub-layers with the aid of using specific designed substrates. TFC membranes are widely used in RO process separation with high performance, especially in desalination and high energy efficiency. However, these RO TFC membranes have poor permeate water fluxes when used in FO, mainly due to the thick and denser support layer that results in high ICP effect (Yip et al., 2010). In fact, the porous support layer acts as a diffusive boundary layer, which severely reduces the osmotic pressure difference across the active layer (Mc Cutcheon & Elimelech, 2006). Therefore, an enhancement of this support layer is essential to minimize the ICP effect. It was demonstrated that the additional resistance to mass transfer of this boundary layer is proportional to the thickness of the support layer, and it is inversely proportional to its porosity (Mc Cutcheon & Elimelech, 2007; Yip et al., 2010). Consequently, the support layer for FO membranes must be as thin as possible, with a high porosity and a minimal resistance for osmotically driven water transport across the membrane (Widjojo et al., 2011).

It is also believed that the membrane performance limiting effects can be reduced by modifying the support layer of the FO membranes (Alsvik & Hägg, 2013a). Wei et al. (2011) synthesized flat sheet TFC-FO membranes based on a PS substrate with a straight finger-like structure under a thin sponge-like skin layer. The PA selective layers were prepared by IP of trimesoyl chloride (TMC) and *N*-methyl-2-pyrrolidone (NMP). The obtained FO membranes had relatively small structural parameters (*S*: 670—710 μm) as a result of the thin cross-section (72.8—76.1 μm), low tortuosity, and high porosity (77—82%) of the membrane substrates. In addition, these membranes had high *PWP* (1.15—1.78 L/m^2 h bar) and NaCl rejection factors (93.4—94.5%) in the RO testing mode. Compared to the commercial CTA-based asymmetric FO membranes (HTI, Albany) and the brackish water RO membrane (BW30, Dow FilmTec, Minneapolis, MN), both prepared TFC membranes exhibited superior FO performance, achieving FO water permeate flux from 18.1 to 20.5 L/m^2 h in the AL-DS orientation and water permeate flux from 9.53 to 12.0 L/m^2 h in the active layer facing feed solution (AL-FS) orientation, when using 0.5 M NaCl draw solution. Moreover, the TFC-FO membranes achieved high water permeate flux maintaining relatively low J_s/J_w ($2.9 \cdot 10^{-4}$—$3.5 \cdot 10^{-4}$) as a result of their excellent rejection layer selectivity (i.e., their low salt permeability/water permeability ratio).

Tiraferri et al. (2011) prepared PA TFC flat sheet membrane with PS support layer by casting different polymer solution concentrations and confirmed that the optimal FO membrane consisted of a mixed structure support layer, in which a thin sponge-like layer was formed on top of a highly porous macrovoids structure. The authors concluded that both the active layer transport properties and the support layer structural characteristics needed to be optimized to fabricate a high-performance FO membrane.

Water permeate fluxes of 25 L/m^2 h with a consistently high salt rejection factor (>95.5%) were produced using 1 M NaCl aqeous solution as a draw solution and deionized water as feed.

To improve the FO membrane performance by reducing and delaying the fouling effect, Tiraferri, Kang, Giannelis, and Elimelech (2012) fabricated a highly hydrophilic PA TFC-FO flat sheet membrane by surface functionalization with tailored silica (SiO_2) NPs. The surface of SiO_2 NPs was functionalized by coating with two different super-hydrophilic cationic ligands ((3-aminopropyl)trimethoxysilane and *N*-trimethoxysilylpropyl-*N*,*N*,*N*-trimethylammonium chloride) to produce either quaternary ammonium or amine functional groups, which were used to irreversibly bind the NPs to the native carboxylic groups of PA FO membranes. Lower adhesion forces were obtained when using 2000 mg/L model organic foulant solution, bovine serum albumin, and the hydrophilic surfaces, compared to the unmodified PA membranes, indicating an increase of membrane fouling resistance.

With the purpose to prepare high hydrophilic flat sheet TFC membranes for desalination by FO with a reduced thickness and a sponge-like structure instead of a finger-like structure, Han et al. (2012) prepared a super-hydrophilic support using sulfonated poly(ether ketone) (SPEK) polymer. It was observed that the TFC-FO membranes with the most hydrophilic support exhibited the lowest membrane thickness, a fully sponge-like structure morphology, and the highest water permeate fluxes, 50 L/m^2 h and 35 L/m^2 h tested under PRO and FO modes, respectively, when using distilled water as feed and 2 M NaCl as draw solution. The highest water permeate flux of this type of membranes was 22 L/m^2 h when tested under PRO mode with a model seawater solution (3.5 wt.% NaCl) used as feed and 2 M NaCl as draw solution. Moreover, a reduced S value of the membrane and ICP effects were observed when blending a hydrophilic material in the membrane support.

The FO performance of TFC-FO membranes was found to be further enhanced if the hydrophilicity of the substrates was increased, as reported by Wang et al. (2012). By blending 3 wt.% of hydrophilic sulfonated PS and PES into the membrane substrates, the resultant TFC-FO flat sheet membranes showed a water permeate flux as high as 47.5 L/m^2 h in the PRO mode, with a salt permeate flux up to 12.4 g/m^2 h using 2 M NaCl as draw solution. An enhancement of FO performance can be realized by either increasing the hydrophilicity of the membrane substrate or fabricating membrane substrates with finger-like structures to enhance water transport through the membranes.

Widjojo et al. (2013) also used a sulfonated polyphenylenesulfone (SPPS) membrane as a support to prepare FO membranes. Compared to TFC-FO membranes made of hydrophobic non-sulfonated PPS supports, those prepared with the hydrophilic SPPS supports comprising 2.5 mol% of sulfonated monomer 3,3′-di-sodiumdisulfate-4,4′-dichlorodiphenyl sulfone achieved 4.4-fold increment of water permeate flux, up to 54 L/m^2 h, with 8.8 g/m^2 h salt reverse permeate flux in PRO mode using 2 M NaCl as draw solution. Surprisingly, the newly developed TFC-FO membranes showed a much smaller difference in water permeate flux between PRO and FO modes compared to previous studies, indicating much lower ICP effects particularly at low draw solution concentrations (i.e., 0.5−2 M NaCl). When tested for seawater desalination using 3.5 wt.% NaCl as feed and 2 M NaCl as a draw solution, these membranes showed the highest water permeate flux ever reported for PRO process (i.e., 22 L/m^2 h).

Zhong et al. (2013) also developed TFC-FO hollow fiber membranes using SPPS supports. The obtained water permeate fluxes were 30.6 and 82.0 L/m^2 h for FO and PRO modes, respectively, using distilled water as feed and 2 M NaCl as a draw solution, while the salt reverse fluxes were maintained below 12.7 g/m^2 h. The S of these membranes was reduced 4.5 times when the membrane support was changed from a non-sulfonated to a sulfonated one.

Sukitpaneenit and Chung (2012) assumed that the existing macrovoids in the membrane support were undesirable because of their mechanically weak points, which could cause membrane failure under continuous vibration and backwashing operations. In addition, a macrovoid-free hollow fiber with a highly sponge-like structure could reduce the ICP effects and enhance the water permeate flux. In this sense, novel high performance TFC-FO hollow fiber membranes with a high porous structure and macrovoid-free were prepared. As expected, this structure enhanced the mechanical properties of the membranes, which had an S value in the range 219−261 μm and a higher permeate flux than the membrane prepared using a support containing macrovoids (Chou et al., 2010).

Wang et al. (2010) prepared two types of TFC-FO hollow fibers with an ultrathin layer PA-based RO-like skin layer on either the outer surface (#A-FO, with a skin layer thickness of 300 nm) or inner surface (#B-FO, 600 nm) of a porous PES hollow fiber substrate. It was observed that the #B-FO hollow fiber membrane had an S parameter comparable to that of pouch-type HTI or cartridge-type HTI FO flat sheet membranes (Figure 9.6). The #A-FO membrane had less water permeate flux and salt rejection factor than the #B-FO membrane, which showed a water permeate flux of 32.2 L/m^2 h for a draw solution of 0.5 M NaCl at 23 °C. Wang et al. (2010) finally suggested that the optimal FO membrane structure should exhibit a small portion of sponge-like layer in a thin and a highly porous substrate.

Last year, the company HTI announced the production of a new highly durable and dimensionally stable TFC flat sheet membrane (the OsMem™ FO membrane line) designed by H.T.I. (2013). The new TFC membrane has a high permeability and a high rejection factor, and it is pH tolerant in the range 2.0−12.0 with a permeate flux of 20 L/m^2 h in FO mode and 49 L/m^2 h in PRO mode when tested using 1 M NaCl draw solution and distilled water as feed solution at 23 °C. The salt rejection factor was 99.3%. Comparatively, HTI's CTA FO membrane (HTI-CTA) has a permeate flux of 9 L/m^2 h. The tested new membrane has a power rate of 3.5 W/m^2 for PRO at 10 °C and 10 bar.

Various research studies were performed to improve the characteristics of the support of PRO membranes. PA-based TFC membranes over a polyacrylonitrile (PAN) support were studied by Zhang, Fu, and Chung (2013). It was revealed that the mechanical strength, pore structure, and hydrophilicity of the support could be tailored by increasing PAN concentration, pre-compressing the substrate, and coating with polydopamine (PDA). By increasing the PAN polymer concentration in the support, better mechanical strength, smaller and more uniform pore sizes, and increased

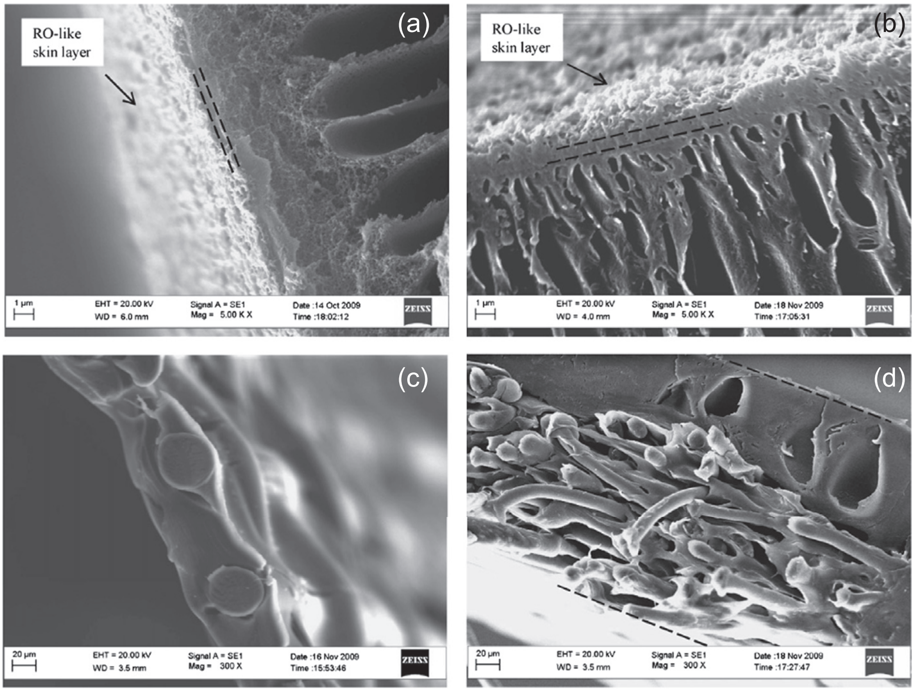

Figure 9.6 Cross-section SEM images of forward osmosis (FO) membranes. (a) #A-FO hollow fiber at X5000; (b) #B-FO hollow fiber at X5000; (c) Cartridge-type HTI flat sheet at X300; (d) Pouch-type HTI flat sheet at X300.
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hydrophilicity were obtained. The resultant TFC membranes in PRO tests showed an increased burst pressure from 0.5 to 8 bar and a power density from almost 0 to 1.3 W/m^2. Much higher water permeate flux and mechanical stability were achieved after immersing the TFC membranes in methanol and ethanol. It was proved that the ethanol-treated TFC membrane could support a hydraulic pressure of 10 bar and exhibited a power density of 2.6 W/m^2.

High-performance TFC PRO membranes with excellent mechanical strength and power density were designed for osmotic power generation by Han, Zhang, et al. (2013). These PRO membranes consisted of an aromatic PA selective layer formed by IP on the top of a porous polyimide (Matrimid® 5218) microporous membrane support. The support layer showed a fully sponge-like structure with a small *S* and excellent mechanical properties, while the PA selective layer was chemically modified using post-fabrication procedures. The membranes not only exhibited an excellent *PWP* of about 10 L/m^2 h bar and an outstanding power density of 7−12 W/m^2 depending on the feed and water salinity, but they also could withstand a hydraulic pressure of 15 bar. The obtained superior PRO performance is a combinative result of the robust support layer with small *S* and highly permeable PA active layer with a moderate salt permeability.

Thin-film nanocomposite (TFN) membranes were also prepared by incorporating different amounts of titanium dioxide (TiO_2) NPs (ranging from 0 to 0.90 wt.%) in a PS substrate to reduce the ICP effect (Emadzadeh et al., 2014). The results revealed that both the hydrophilicity and porosity of the substrate were increased, and a large number of finger-like macrovoids were formed, leading to an enhancement of the membrane *PWP*. The TFN membrane prepared with 0.60 wt.% TiO_2 NPs (designated as TFN 0.60) exhibited the best FO performance tested at AL-FS orientation with distilled water as feed and 0.5 M NaCl as a draw solution, with no significant change in reverse solute flux (i.e., a water permeate flux of 18.81 L/m^2 h, which is 97% higher than that of the TFC membrane prepared without TiO_2). The enhancement of the water permeate flux was attributed to the decrease of the *S* (0.39 mm), mainly due to the formation of the finger-like macrovoids throughout the substrate and the reduced tortuosity. It was also observed that a further increase of TiO_2 NPs content to 0.90 wt.% increased the membrane *PWP*; but the FO performance of these membranes was compromised by the significant increase in the reverse solute permeate flux.

Amini et al. (2013) used functionalized MWCNTs (F-MWCNTs) to synthesize novel TFN FO flat sheet membranes. Amine F-MWCNTs were used as additive in an aqueous solution of 1,3-phenylendiamine (MPD) to enhance the FO membrane performance. Different concentrations of F-MWCNTs (0.01, 0.05, and 0.1 wt.%) were added and dispersed in the MPD aqueous solution via sonication for 4 h at 30 °C (Figure 9.7). The PA active layer was formed by IP on the top of a cast PS substrate. The obtained water permeate flux of these membranes (in both AL-FS and AL-DS modes) and their salt rejection factors were simultaneously improved. The highest water permeate flux was 95.7 L/m^2 h, which is nearly 160% greater than that of TFC membranes. These improvements were in accordance with the increase of the roughness and hydrophilicity of the TFN membranes when F-MWCNTs were incorporated in the PA selective layer.

Electrospun nanofibrous supports were also used to prepare FO and PRO membranes because of their superior void volume fraction (i.e., porosity) and pore interconnectivity, which results in reduced ICP effects. A novel flat sheet PA composite membrane supported by a non-woven web of electrospun nanofibers was prepared by Bui et al. (2011). This TFC membrane comprises an electrospun polymeric nanofiber support layer and a PA skin layer formed by in situ polymerization. It was observed that these membranes exhibited greater water permeate fluxes, two to five times higher than those of the commercial HTI-CTA membrane. Recently, Bui and Mc Cutcheon (2013) used different materials to develop hydrophilic nanofibrous supports by electrospinning different blends of CA at different ratios and PAN (Figure 9.8). In this study, PA selective layer was formed on the PAN/CA nanofibrous supports by IP between MPD and TMC. The prepared membranes exhibited excellent permselectivity, a reduced resistance to mass transfer, low *S*, and high water permeabilities, two to three times greater than HTI-CA membranes (2.036 L/m^2 h bar for PAN nanofibrous supports and 0.683 L/m^2 h bar for HTI-CA membranes).

Hoover et al. (2013) prepared TFC membranes composed of an electrospun terephthalate (PET) nanofibrous support, a PS phase inversion microporous layer, and a PA selective layer formed by IP. The obtained *PWP* was 1.13 L/m^2 h bar, the salt

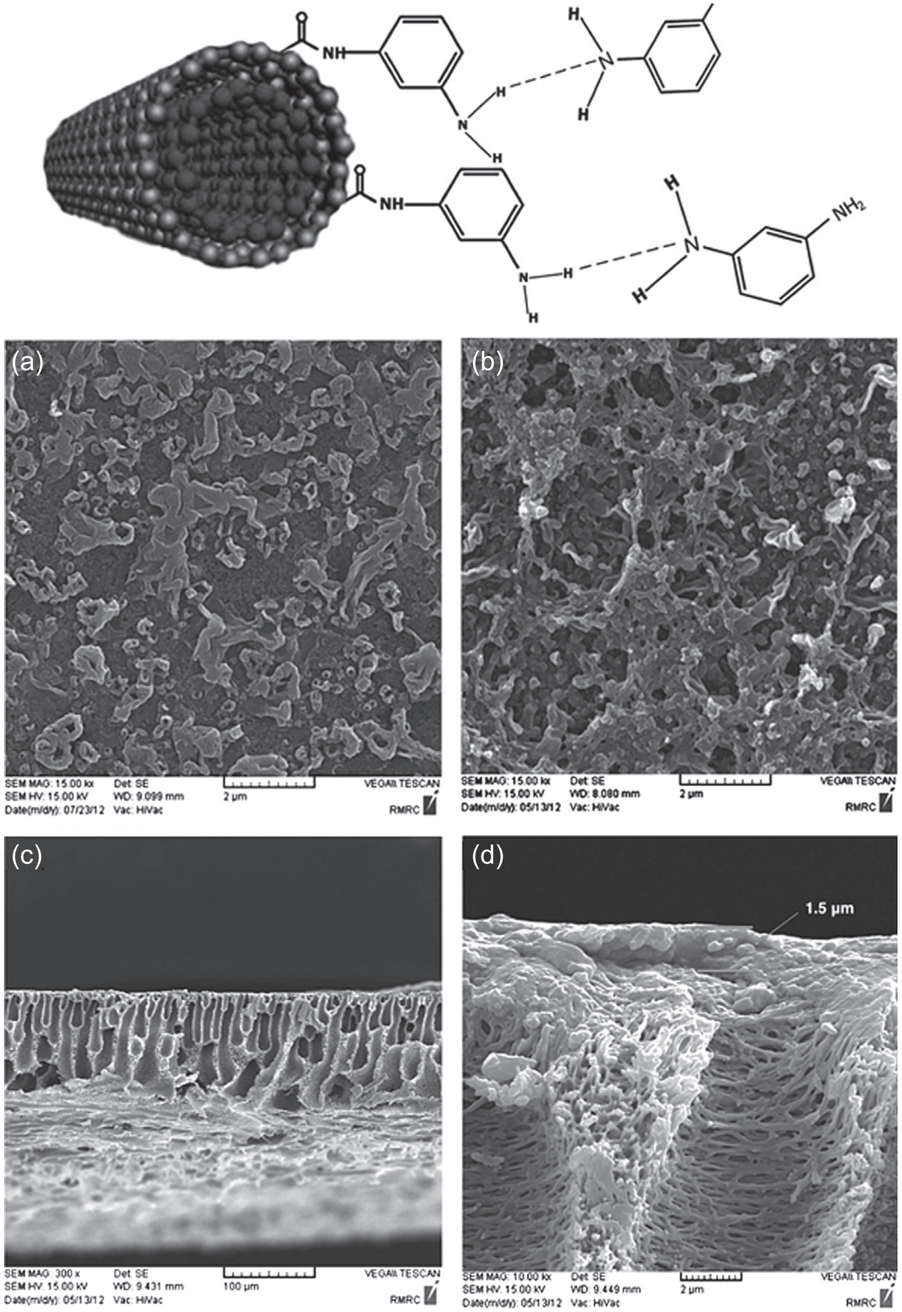

Figure 9.7 Conceptual model of amine functionalized MWCNTs in 1,3-phenylendiamine (MPD) solution used to prepare novel thin-film nanocomposite (TFN) membranes for forward osmosis process. SEM micrographs displaying the top surface and cross-section of conventional thin-film composite (TFC) membranes (a and c) and TFN membranes with 0.01 wt./vol.% (b and d), respectively.

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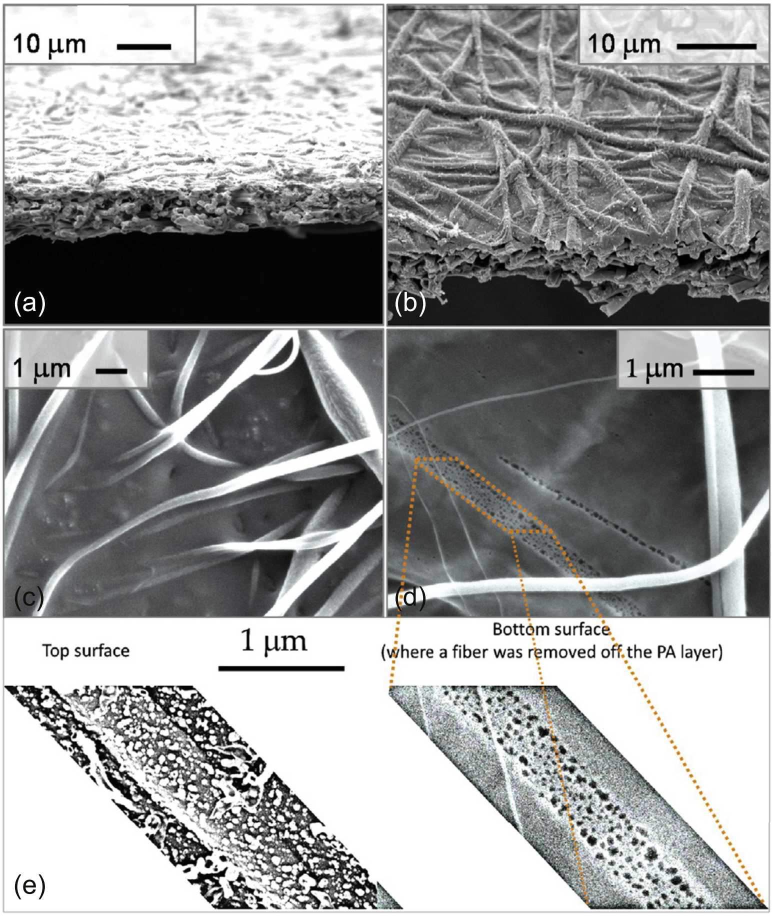

Figure 9.8 SEM images of thin-film composite membranes supported on a polyacrylonitrile (PAN) nanofibrous support: Cross-sectional (a) X1500 and (b) X2500. Top surface: (c) X10 000 and (e) X40 000. Bottom surface: (d) X20 000 and zoom-in image showing the pores that were formed on the bottom side of the polyamide (PA) selective layer when a fiber was removed from this layer.
Reprinted with permission from Bui and Mc Cutcheon (2013). Copyright 2012 American Chemical Society.

permeability was 0.23 L/m^2 h, and the *S* value was 0.651 mm. It was detected that the use of electrospun fibers in the support layer enhanced the membrane resistance to delamination at high cross-flow velocities.

It is worth noting that most supports used for the fabrication of FO membranes are hydrophilic, mainly because of the concerns of higher fouling tendency of the more hydrophobic supports. However, hydrophobic materials such as polyvinylidene fluoride (PVDF) normally possess strong chemical resistance, which could extend the use of FO process to some harsh environments with chemical wastes such as aromatic hydrocarbons, ketones, ethers, and esters. Tian et al. (2013) used electrospun PVDF nanofibrous supports followed by IP to prepare high-performance TFC-FO membranes. The *S* value of the TFC membrane was found to be as low as 0.315 mm, which is better than most of the FO membranes reported in the literature. As a result, a water permeate flux of 30.4 L/m^2 h was obtained when using 1 M NaCl as a draw solution and distilled water as feed in AL—DS orientation.

LbL assembly method was used for the fabrication of high-FO-performance membranes because of the formed ultrathin layers. For instance, LbL method was used to produce ultrathin barrier layers assembled by oppositely charged polyelectrolytes (Pardeshi & Mungray, 2014). NaOH treated PAN membrane substrate (PAN-OH) is immersed in a polycation solution (1 g/L PAH/0.5 M NaCl solution) and a polyanion solution (1 g/L PSS/0.5 M NaCl solution) following an alternative sequence. This type of membranes exhibits high *PWP* and good retention against divalent ions, which makes them suitable candidates for FO membranes. In addition, LbL polyelectrolyte layers generally have high solvent resistance (except in some ternary solvent mixtures) and high thermal stability (e.g., no deterioration under 200 °C annealing temperature) (Qi et al., 2011).

By using the LbL assembly method, Qi et al. (2011) synthesized a novel NF-like FO membrane with good magnesium chloride retention factors. The membrane substrate was tailored (high porosity, finger-like pores, thin cross-section, and high hydrophilicity) to achieve a small *S* of 0.5 mm. It was observed that the increased number of polyelectrolyte layers, from one to six, improved the selectivity but reduced the *PWP*. Severe solute reverse transport was also detected for the AL—DS orientation. In contrast, the AL—FS orientation showed remarkable FO performance (water permeate fluxes of 15, 20, and 28 L/m^2 h at 0.1, 0.5, and 1.0 M $MgCl_2$, respectively, for the membrane 3#LbL using distilled water as feed solution), superior to other NF-like FO membranes reported in the literature (Setiawan et al., 2011; Su et al., 2010; Wang et al., 2007, Wang, Yang, et al., 2009; Yang et al., 2009) (see Table 9.1).

With the aim to investigate and compare the FO performance and fouling behavior of double-skinned and single-skinned FO membranes, Qi et al. (2012) synthesized novel membranes following the LbL assembly method as shown in Figure 9.9. The LbL rejection skin on the top surface was formed by soaking only the top substrate in PAH solution and then in PSS solution. Three polyelectrolyte layers were deposited for the top rejection skin. The bottom LbL rejection skin was similarly prepared by exposing only the bottom surface of the substrate during the soaking steps, and the effects of the number of polyelectrolyte layers (from 0 to 3) on the FO membrane performance were studied. The results revealed that both the top and bottom skins contributed to the overall water resistance of the double-skinned LbL membranes. However, the overall salt rejection factor was mainly determined by the top skin layer. The double-skinned LbL FO membranes achieved excellent FO water permeate fluxes up to 50.1 and 106.1 L/m^2 h when the bottom skin layer was faced the draw solution (DS-PRO mode) or the feed solution (FS—FO mode), respectively, and low J_s/J_w ratios (0.405 and 0.487 g/L for PRO and FO mode, respectively) when using 2 M $MgCl_2$ as draw solution at 23 °C and distilled water as feed. Furthermore, the double-skinned LbL membranes demonstrated much better antifouling performance compared to the single-skinned counterpart.

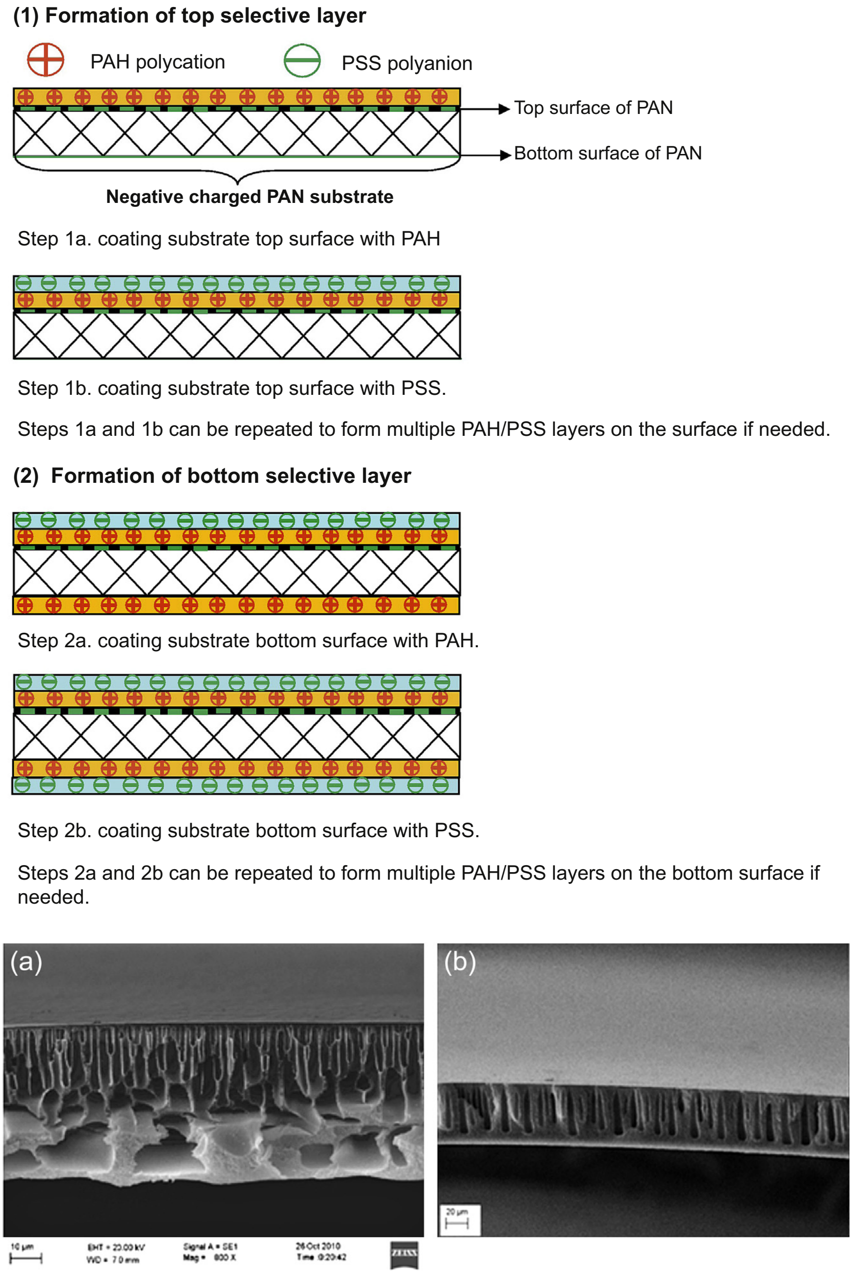

Figure 9.9 Conceptual illustrations of double-skinned LbL membrane fabrication and SEM cross-section of the PAN-OH supports of a single-skinned forward osmosis (FO) membrane (1, a) and a double-skinned FO membrane (2, b).
Figure 9.9a reprinted with permission from Qi et al. (2011). Copyright 2011 American Chemical Society and Figure 9.9b reprinted from Qi et al. (2012), with permission from Elsevier.

To reduce biological fouling and enhance the performance of the membranes in FO applications, Liu et al. (2013) added Ag NPs to the top surface of the membrane supports. The LbL assembly method was used to fabricate novel Ag nanocomposite (LbL-Ag) NF and FO membranes. It was observed that the surface roughness increased with the amount of Ag NPs. The incorporation of Ag NPs also increased the hydrophilicity of the membrane surface (i.e., the contact angle decreased from 69.1° to 51.3°). The experimental results indicated that the small amount of Ag NPs incorporated in the LbL-Ag FO membranes had little effect on the membrane structure and thus maintaining their original separation properties. Around 0.01 wt.% was chosen as the optimal Ag NPs concentration to obtain LbL-Ag membranes with good FO performance ($MgCl_2$ rejection factor of 95% and water permeate fluxes of 42.2 and 17.8 L/m^2 h in PRO and FO mode, respectively, using 10 mM NaCl as feed and 0.5 M $MgCl_2$ as draw solution at 23 °C). Moreover, LbL-Ag membranes exhibited excellent antibacterial properties against Gram-positive (*Bacillus subtilis*) and Gram-negative bacteria (*E. coli*).

Pardeshi and Mungray (2014) used polymer nanocomposites to tailor membrane support and develop FO LbL self-assembled membranes with appropriate transport characteristics. Nanocomposite of PVA, lithium chloride (LiCl), and montmorillonite clay (surface modified with 25–30 wt.% methyl dihydroxyethyl hydrogenated tallow ammonium, MMt-TA) were used to synthesize the substrate of the FO membrane (PVA/MMt-TA/LiCl nanocomposite substrate). This type of substrates showed a spongy structure, a high porosity (81%), an average thickness of about 26.43 μm, and a high hydrophilicity. The active layer of the membrane was prepared by LbL assembly of polyelectrolytes (CS as a polycation and polyacrylic acid as a polyanion). Three layers of polyelectrolyte were applied on PVA/MMt-TA/LiCl substrate. The resultant membranes (PVA/MMt-TA/LiCl 3LbL) had a thin sponge-like skin layer (about 3 μm), which was responsible for the observed low reverse salt diffusion (0.281 and 0.051 g/m^2 h for PRO and FO mode, respectively). The high hydrophilic nature of the PVA/MMt-TA/LiCl support enhanced the water permeate flux up to 37.65 L/m^2 h (PRO mode) and 25.5 L/m^2 h (FO mode) when distilled water was used as feed and 2 M NaCl solution as draw solution at 26 °C.

You et al. (2013) developed a thin-film inorganic (TFI) membrane by LbL deposition of microporous SiO_2 xerogels immobilized onto a stainless steel mesh support. It was observed that the quasi-symmetry TFI microporous structure of the SiO_2 membrane was responsible for the low ICP effect enhancing the water permeate flux during the FO process. The TFI membrane showed a good NaCl rejection factor of 92% and high water permeate fluxes of 60.3 L/m^2 h and 59.8 L/m^2 h for PRO and FO mode, respectively, when using distilled water as feed and 2 M NaCl solution as draw solution at ambient temperature. Particularly, by increasing the temperature to 70 °C, the water permeate flux was increased to 85.02 L/m^2 h at pH 6. It was claimed that the ability of the TFI membrane to sustain FO process without any curling, wrinkling, cracking, deformation, or dissolution under harsh conditions also suggested a superior mechanical strength, and thermal and chemical stability of these membranes over polymeric FO membranes.

9.4 Conclusions

This chapter focuses on water treatment by ED and FO, with special attention to the alternative technologies of emerging interests RED and PRO used for energy generation through a salinity-gradient difference. Although membranes typically used for ED and RED processes are IEMs (AEMs and CEMs), BPMs are also reviewed due to their advantages (e.g., separation of monovalent and divalent ions, antideposition, antifouling, water dissociation into OH^-— and H^+—ions, increase of reusability and recyclability of waste through chemical production, low initial cost, etc.). Most of the research studies have been focused on the improvement of the performance of these membranes, including their physicochemical and electrochemical properties to optimize both ED and RED processes. Various membrane-based polymers (SPES, PS, PVC, PVA, SPEEK, PECH, etc.) have been used, and different membrane modification techniques have been applied, such as thermal and chemical crosslinking, quaternization, sulfonation, photo-induced covalent immobilization, in situ polymerization, addition of NPs or inorganic fillers as functional groups or additives, etc. Not only is the improvement of the membrane properties necessary to achieve high ED and RED performances, but it is also important to consider the scale-up and design of the ED/RED unit and the optimization of the electrode systems.

For the preparation of FO and PRO membranes different polymers were used including CA, CTA, PS, PES, PBI, PA, PAI, PVP, PAN, and PET. Three different methods have been adopted to prepare polymeric FO/PRO membranes (non-solvent phase inversion, IP on porous substrates, and the LbL deposition). IP is the most-used technique. TFC membrane structure either in flat sheet or hollow fiber configuration exhibits high water permeability, solute rejection factor, chemical stability and mechanical strength, and good design flexibility by separately tuning the selective skins and sub-layers.

Improved membrane characteristics and performance were achieved using different modification techniques, such as chemical or thermal post-treatment, chemical cross-linking, surface functionalization via coating, pre-compressing and coating the substrate, incorporating different amounts of additives or fillers, etc.

9.5 Future trends

Membrane technologies experienced significant development during the last decades, driven by available advanced materials, novel technologies, changes of environmental regulations, increasing demand of water supply and sanitation, etc. The availability of novel tailored membranes with specific properties and new membrane processes offers important tools for the design of alternative production systems appropriate for a sustainable growth.

Researchers have made sufficient progress in the development of new membrane materials, modifying the membrane surface to improve their performance, detecting new application fields and emerging membrane technologies, etc. Furthermore, the integration of different membrane processes was also explored, because it potentially allows the possibility to redesign important industrial processes with enhanced benefits in terms of product quality, quantity, energy efficiency, and cost.

Some technologies, especially the emerging ones, are still far from fulfilling all the deposited expectations on them. However, they are still in continuous improvement, trying to overcome the many challenges and barriers to extend their field of industrial applications.

List of acronyms

γ-MPS	γ-methacryloxypropyl trimethoxy silane
4-VP	4-vinylpyridine
A1100	(3-aminopropyl) triethoxysilane
AC	Activated carbon
AEL	Anion exchange layer
AEM	Anion exchange membrane
Ag	Silver
AL-DS	Active layer facing draw solution
AL-FS	Active layer facing feed solution
BPM	Bipolar membrane
CA	Cellulose acetate
CEL	Cation exchange layer
CEM	Cation exchange membrane
CS	Chitosan
CTA	Cellulose triacetate
ED	Electrodialysis
EDR	Electrodialysis reversal
EO	Engineered Osmosis
Fe_3O_4	Iron oxide
$FeCl_3$	Ferric chloride
F-MWCNTs	Functionalized MWCNTs
FO	Forward osmosis
HTI	Hydration Technology Innovations
ICP	Internal concentration polarization
IEMs	Ion-exchange membranes
IP	Interfacial polymerization
LbL	Layer-by-layer
LiCl	Lithium chloride
MMt-TA	Methyl dihydroxyethyl hydrogenated tallow ammonium
MPD	1,3-phenylendiamine
MWCNTs	Multiwalled carbon nanotubes
NF	Nanofiltration
NMP	*N*-methyl-2-pyrrolidone
NPs	Nanoparticles
PA	Polyamide
PAH	Poly(allylamine hydrochloride)
PAI	Poly(amide-imide)
PAN	Polyacrylonitrile
PANI	Polyaniline

PBI	Polybenzimidazole
PDA	Polydopamine
PECH	Polyepichlorohydrin
PEI	Polyethyleneimine
PES	Polyethersulfone
PET	Terephthalate
PRO	Pressure retarded osmosis
PS	Polysulfone
PSS	Poly(sodium 4-styrene sulfonate)
PVA	Polyvinyl alcohol
PVC	Polyvinylchloride
PVDF	Polyvinylidene fluoride
PVP	Polyvinylpyrrolidone
RED	Reverse electrodialysis
RO	Reverse osmosis
SDBS	Sodium dodecylbenzene sulfonate
SGP	Salinity gradient power
SiO_2	Silica
SPEEK	Sulfonated polyetheretherketone
SPEK	Sulfonated poly(ether ketone)
SPES	Sulfonated poly(ether sulfone)
SPPS	Sulfonated polyphenylenesulfone
TFC	Thin-film composite
TFI	Thin-film inorganic
TFN	Thin-film nanocomposite
TiO_2	Titanium dioxide
TMC	Trimesoyl chloride
UF	Ultrafiltration
VBC	Vinylbenzyl chloride
ZrT	Zirconium tri-ethylene tetra-amine

List of symbols

$J_{M^{2+}}$	Bivalent cation permeate flux
$J_{Cu^{2+}}$	Cu^{2+} permeate flux
J_S	Salt/solute permeate flux
J_W	Water permeate flux
PWP	Pure water permeability
S	Structural parameter

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Part Two

Improving membrane performance

Planning and design of membrane systems for water treatment

10

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10.1 Introduction

Population and industry growth and limits to the current water supply are driving the need to find new sources of water, develop the more sustainable use of current water sources, and improve water reuse. Membrane technologies are playing a vital role in all these areas in increasing the available water supply portfolio for communities, industry, or agricultural users. As a confirmation, membrane projects are demonstrating significant growth of membrane technology applications by increasing capacities of new membrane projects and upgrading existing facilities with membranes. Membrane technologies have entered every corner of water and wastewater treatment, such as municipal and industrial water, advanced wastewater treatment and reuse, and sea and brackish water desalination. The major reasons are the unique features that membrane technologies can provide for solving water shortages, which is in close association with global climate change. This trend accelerated the growth of the membrane market in past years and fuels the expected growth for the future.

Because membrane technologies are separation technologies, the simplified schematic of the membrane separation process is shown, using the example of the reverse osmosis (RO) membrane process, in Figure 10.1.

The membrane process comprises three major streams:

- Feed
- Permeate (product water)
- Concentrate (reject or brine).

The mass balance for the entire system can be represented as follows:

$$Q_f \times C_f = Q_c \times C_c + Q_p \times C_p,$$

in which:

- Q_f - feed flow (gpm or m^3/hr)
- C_f - salt concentration in feed water (mg/L or ppm)
- Q_c - concentrate flow (gpm or m^3/hr)
- C_c - salt concentration in concetrate (mg/L or ppm)
- Q_p - product flow (gpm or m^3/hr)
- C_p - salt concentration in product water (mg/L or ppm).

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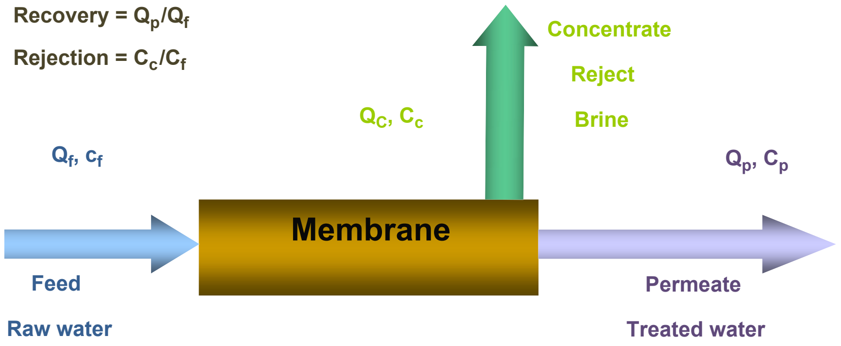


Figure 10.1 Simplified diagram of reverse osmosis (RO) process: major RO streams.

The membrane technology mass and hydraulic balance is a cross-check that allows one to perform validation of the process integrity.

10.2 Membrane types and configurations for water treatment

Membranes are represented by four major membrane types, categorized by the rate of treatment, and are in commercial use at present (Design of Municipal Waste, 2009; Frenkel, 2011):

- **Microfiltration (MF)** - screens particles from 0.1 to 0.5 μm,
- **Ultrafiltration (UF)** - screens particles from 0.005 to 0.05 μm,
- **Nanofiltration (NF)** - screens particles from 0.0005 to 0.001 μm,
- **RO** - ranging molecular size down to 10 MWCO.

Figure 10.2 demonstrates the relative size of different membrane types compared to the conventional treatment processes and constituents of concern when treating water.

MF and UF membranes were commercialized for drinking water treatment just about 15 years ago. Because they provide significant technical benefits and have become cost-competitive, membrane technologies are rapidly replacing traditional processes verified by the centuries.

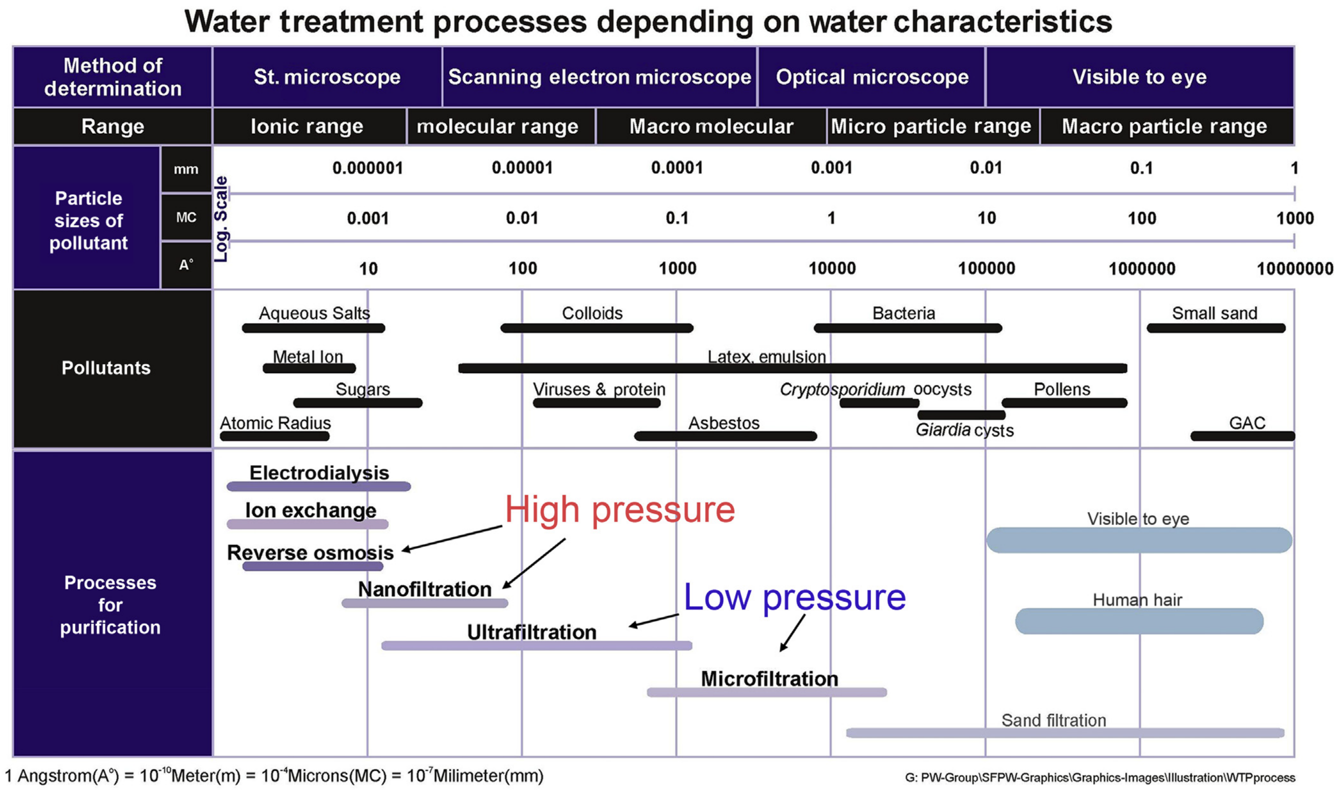
The differences in membrane shape and the type of membrane process driving forces can be categorized as shown in Figure 10.3.

Membrane shape type: Spiral wound, hollow fiber, flat sheet.

Membrane type depending on driven pressure:

- Pressure-driven (low-pressure MF, UF, and high-pressure NF and RO)
- Immersed, vacuum driven (low-pressure MF, UF only).

The electrical current can drive membrane treatment as well, and it is used in electrodialysis (ED), electrodialysis reversal (EDR), and electrodeionization (EDI) membrane treatment processes.

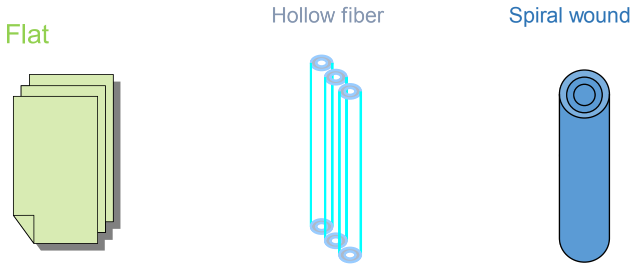


Water treatment processes depending on water characteristics

1 Angstrom(A°) = 10^{-10}Meter(m) = 10^{-4}Microns(MC) = 10^{-7}Milimeter(mm)

G: PW-Group\SFPW-Graphics\Graphics-Images\Illustration\WTPprocess

Figure 10.2 Membranes and water treatment processes.
Courtesy of Val S. Frenkel.



Membrane type depending on driven power:

1. Pressure driven (MF, UF, NF, and RO)
2. Vacuum driven (MF and UF only)
3. High voltage current (EDR and EDI)
4. Osmotic power (FO and PRO)

Figure 10.3 Membranes shape, type, configuration, and driven forces.

10.3 Low- and high-pressure membranes

As shown in Figure 10.2, membranes are broken down to two major categories:

- Low-pressure membranes, represented by MF and UF membranes, and
- High-pressure membranes represented by NF and RO membranes.

One of the key difference between high- and low-pressure membranes is that the high-pressure membranes were developed to remove dissolved matter from the water, while they are not tolerant of suspended and colloidal matter. The low-pressure membranes are opposite, having high tolerance and high efficiency in the removal of suspended and organic matter, while dissolved matter passes through the membranes. A number of techniques were developed for numerous applications to convert certain dissolved ions to the solid phase, followed by removal using low-pressure membranes. Due to the different treatment properties between low- and high-pressure membranes, the integrated membrane systems (IMS) found a niche in numerous applications when high-pressure membranes are following low-pressure membranes in the treatment train, using low-pressure membranes as a pretreatment for high-pressure membranes.

10.4 Low-pressure membrane applications

Low-pressure membranes are represented by MF and UF membranes.

10.4.1 Microfiltration and ultrafiltration

Membrane technologies include MF and UF membranes. These membranes can remove particles and colloidal matter and are often selected over conventional granular-media filters based on their high removal efficiencies for *Giardia* cysts, *Cryptosporidium* oocysts, bacteria, and viruses and the consistently high-quality water produced by membranes, independent from the source water quality variation and operator skill (Frenkel & Mourato, 1998).

Membrane separation is a well-developed technology that is becoming a standard practice in water treatment. Membrane separation provides a physical barrier to pathogens and can produce high-quality, safe drinking water at a reasonable cost.

10.4.2 Microfiltration

MF is the "loosest" membrane, and it screens particles in the range 0.1−0.5 μm, removing bacteria, protozoan pathogens (*Cryptosporidium* oocysts, *Giardia* cysts, and some viruses), silt, colloids, and precipitates.

MF is a pressure-driven or vacuum-driven (immersed type) membrane separation process that separates particulate matter from a fluid (water, wastewater, or industrial process fluid) by physical straining. MF membranes have demonstrated more than 6-log removal of particles and are credited by regulatory agencies up to 4-log removal for *Giardia* and *Cryptosporidium*. MF membranes remove some viruses and are credited by regulatory agencies up to 0.5−2.5-log removal for viruses, depending on the brand and model.

The MF membrane filtration surface is a thin synthetic polymer manufactured into a hollow fiber. It can be supported or not supported. The membrane surface can be on the outside of the fiber ("outside-in" flow path) or on the inside of the fiber ("inside-out" flow path). Most MF membranes have an outside-in flow configuration in which the feed water is on the outside surface of the fiber, and treated water is collected in the inside of the fiber. This outside-in configuration typically permits treating water with greater solids loading. MF membranes can be also operated either in a cross-flow or in a dead-end flow mode. In the dead-end mode, all the source water passes through the membrane and periodically by batches is discharged on solid concentration around membranes. In the cross-flow mode, a portion of the source water is discharged or recycled back to the inlet of the system continuously. The cross-flow mode can accommodate higher solids loading, but it may require more energy.

Most MF membranes are manufactured from the polymers that are hydrophilic in nature, such as polyvinylidene fluoride (PVDF), polysulfone (PSF), polytetrafluoroethylene (PTFE), polypropylene (PP), and nylon. The newer version of Teflon membranes were introduced to the market within last few years. Most of the membranes are resistant to oxidants such as chlorine, with the exception of PP. Special agents are often added to the membranes during the fabrication process to reduce fouling of the membranes by dissolved organics.

The MF filtration system typically consists of membrane modules, cassettes, units, and trains, as shown in Figure 10.4.

Membrane fibers are grouped together and secured into a single common module. The membrane module is repairable and replaceable. Multiple membrane modules are supported and manifolded together with common piping, valves, and instrumentation to form a complete integrated unit: pressure MF skids or immersed MF units in basins. The membrane unit has independent flow control and is backwashed, cleaned, and integrity-tested as a complete unit. Multiple membrane units are manifolded together

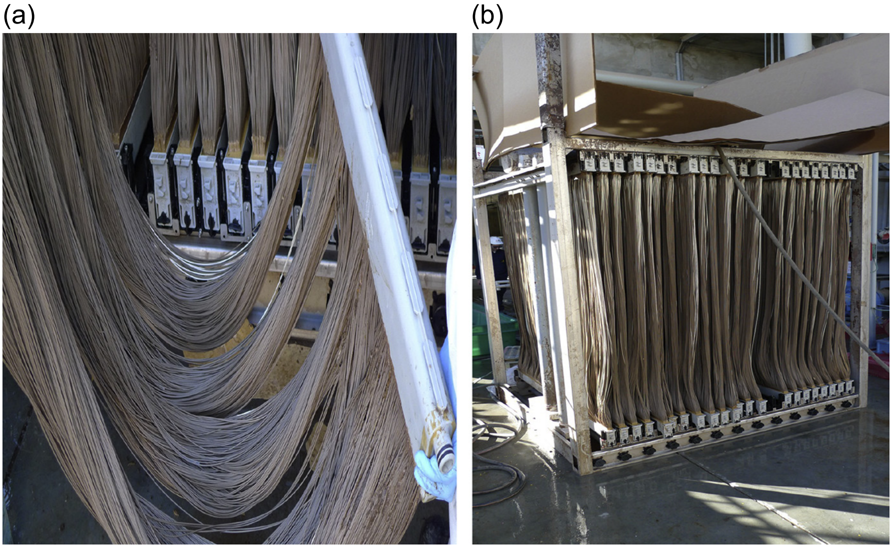


Figure 10.4 Hollow fiber microfiltration/ultrafiltration membrane fibers (a) and cassette with modules (b).

into trains or banks to meet the overall capacity requirements for a system, as shown in Figure 10.5.

MF systems consistently provide high-quality, low-turbidity filtered water (typically below 0.1 NTU) independently of the source water turbidity fluctuations and operator skills. Depending on the source water characteristics, most MF membrane applications do not require pretreatment. In some applications, coagulant can be added to the water to form flocs increasing the membrane treatment efficiency, reduce membrane fouling, and/or to adsorb and to allow increasing removal efficiency of dissolved total organic carbon (TOC) from the water. In applications with high source water solids, a clarification process, or dissolved air flotation (DAF) ahead of the MF system

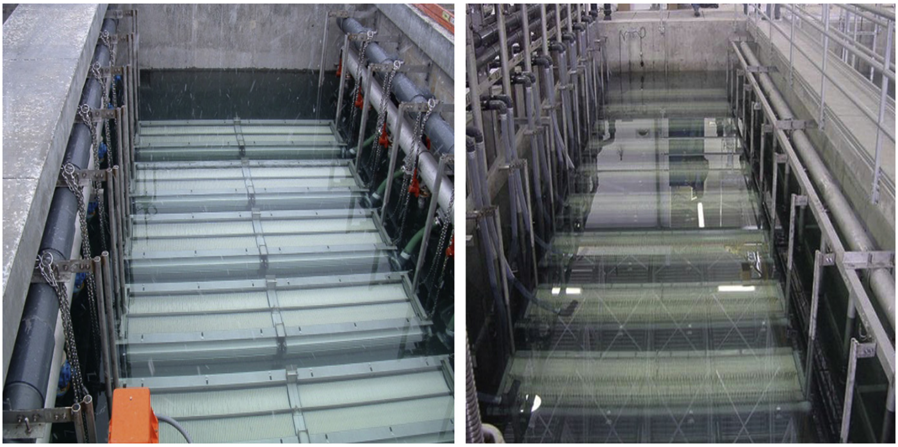


Figure 10.5 Flat plate microfiltration/ultrafiltration immersed membrane train/bank/basin.

may help reduce the membrane system capital and operating costs. Depending on the water chemistry and operational parameters, the average MF recovery range is 90–95%. When coagulant is used, the higher recovery of 95–98% can be achieved. MF systems typically operate with feed pressures of 25–40 psi.

10.4.3 Ultrafiltration

UF screens particles from 0.005 to 0.05 μm and removes most viruses and pathogens in addition to the particles removed by an MF system.

Similarly to MF, the UF is a pressure-driven or vacuum-driven (immersed type) membrane separation process that separates particulate matter from a fluid (water, wastewater, or industrial process fluid) by physical straining. UF membranes have a high removal efficiency for particles greater than approximately 0.05 μm, including bacteria, pathogens (*Cryptosporidium* oocysts, *Giardia* cysts), and viruses. UF membranes have demonstrated removal of more than 6-log for particles and are credited by regulatory agencies with 4-log removal for *Giardia* and *Cryptosporidium*. UF membrane systems also remove most viruses and are credited by regulatory agencies with 2- to 4-log removal of viruses.

Similarly to MF, the UF membrane filtration surface is a thin synthetic polymer manufactured into a hollow fiber. Many pressure UF membranes have an inside-out flow configuration, in which the source water is on the inside surface of the fiber and filtered water is collected on the outside of the fiber. This inside-out configuration permits improved hydrodynamics at the membrane surface to minimize membrane fouling and also permits higher pressure across the membrane for greater flux rates. However, the inside-out configuration requires more energy and cannot handle as high a solid loading as the outside-in configuration. The inside-out configuration can be operated in the pressurized mode only, not allowing the use of the immersed/vacuum concept. The pressurized UF membranes can be also operated either in a cross-flow or in a dead-end flow mode. In the dead-end mode, all the source water passes through the membrane. In the dead-end mode, all the source water passes through the membrane and periodically by batches is discharged on solid concentration around the membranes. In the cross-flow mode, a portion of the source water is discharged or recycled back to the inlet of the system continuously. The cross-flow mode can accommodate higher solids loading, but may require more energy. UF membranes typically operate in a cross-flow mode on the high solid water.

Similarly to MF, most UF membranes are manufactured from the polymers that are hydrophilic in nature, such as PVDF, PSF, polyethersulfone (PES), and PTFE. Most UF membranes are resistant to oxidants such as chlorine. Specific agents are often added to the membranes during the fabrication process to reduce fouling of the membranes by dissolved organics.

Like MF, the UF filtration system typically consists of membrane modules, units, and trains. Hollow fiber membranes are grouped together and secured into a single common module. This membrane module is repairable and replaceable. Multiple membrane modules are supported and manifolded together with common piping, valves, and instrumentation to form a complete integrated unit: pressure UF skids or immersed UF units in basins. The membrane unit has independent flow control and is backwashed, cleaned, and integrity-tested as a complete unit. Multiple membrane units are manifolded together into trains or banks to meet the overall capacity requirements for a system.

UF systems provide consistent high-quality, low-turbidity filtered water (typically below 0.1 NTU) independent of the source water turbidity variations and operator skills. Depending on the source water characteristics, UF membrane applications may not require pretreatment. In some applications, coagulant can be added to the water to form floc particles to increase the membrane's filtration efficiency and/or to adsorb and reduce dissolved TOC in the water. In applications with high source water solids, a clarification process ahead of the UF system may help reduce the capital and operating costs of the membrane system. Depending on the water chemistry and operational parameters, the average UF recovery range is 85–95%. When coagulant is used, the higher recovery of 95–98% can be achieved. UF systems typically operate with feed pressures of 35–50 psi.

10.5 Applications of low-pressure membranes for water treatment, surface water, and groundwater

When introduced to the market, the low-pressure membranes, MF and UF, were an alternative technology to the media filtration, as illustrated schematically in Figure 10.6 (Frenkel & Mourato, 1998).

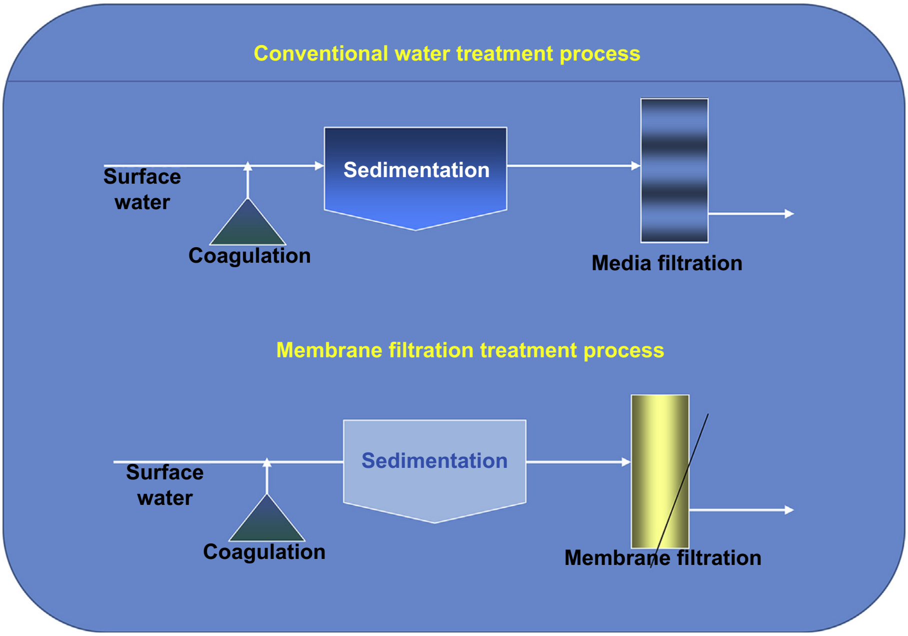


Figure 10.6 Example of one of the technological process using low-pressure membranes.

In applications in which the solid—liquid separation is required, the low-pressure membranes performed, providing treated water with the quality superior compared to the media filtration in most cases.

Most applications were related to the surface water treatment replacing media filtration. Due to the low-pressure membranes' relatively high tolerance to the suspended solids, applications of MF/UF membranes allowed the removal of the clarification step in the treatment process for many projects, providing significant reduction in the project cost and overall footprint of the plant. This concept has been called direct membrane filtration. MF/UF membranes were successfully applied for iron and manganese removal from the groundwater, similarly to greensand filters. Because low-pressure membranes are tolerant to suspended solids, they are used as a pretreatment for the high-pressure membranes, NF/RO, as highlighted in clause two above, compiling the IMS process. Low-pressure membranes attracted significant interest by the wastewater industry and were successfully applied as a tertiary treatment technology and as a basic technology for MBRs (Cui, Muralidhara, & Frenkel, 2010; Frenkel, Reardon, Shlater, Gharagozian, & Kondo, 2011; Using Reclaimed Water, 2008).

10.6 Planning and designing low-pressure membrane treatment

Similarly to any water-treatment technology planning, the low-pressure membrane project needs careful planning and administration. The major differences in the low-pressure membrane project compared to the basic conventional technology, such as media filtration, are:

- Membranes can tolerate higher solids load;
- Membranes can produce higher quality water compared to the conventional processes;
- Most of the membrane plants are designed for continuous reject flow rather than batch filtration, compared to the batch operation of the medial filters. In this case, the overall recovery of the membrane plant may be lower. To improve membrane plant recovery, the secondary stage of the membrane treatment train concentrating reject from the major treatment train can be applied;
- When water is coagulated, membranes may need smaller size flocs and less flocculation time to achieve similar or better performance compared to the conventional processes;
- Because membranes provide higher-quality product water, fewer UV doses and/or a lower chlorine injection rate are required.

Because low-pressure membranes are still not standardized across the industry, they are manufacturer specific and not replaceable widely by the other suppliers. This situation complicates the membrane planning process, and most of the membrane plants that were using the design-bid-build conventional procurement process are using the two-step procurement process. During the first step, the membrane suppliers are prequalified and preselected or membranes are prepurchased; during the second step, the general contractor is selected. This concept extends the overall project schedule, requiring more time for the project procurement. Because low-pressure membranes are showing signs of standardization, this situation may change in the future.

The design of low-pressure membranes depends on the source water quality, local conditions, project size, project preferences, and requirements for the treated water quality. Depending on the solid load in the source water, the low-pressure membranes can be designed to be operated in the dead-end filtration mode or cross-flow filtration mode. The dead-end filtration mode is limited by the solid content in the source water, while it provides higher overall system recovery and lower reject flow rate as a result. The cross-flow mode is the opposite. The system design needs to account the following major plant components and parameters:

- Pretreatment requirements, including fine screens, chemical injection, and clarification if required;
- System recovery rate, the ratio of the product flow to the feed flow expressed in percent;
- Membrane active filtration area, which is a function of the flow load on the membranes per membrane area, which is called membrane flux and expressed in gallons/square feet/day (GFD) or liter/hour/meter square (LHM);
- Energy requirements;
- Posttreatment requirements;
- Solids treatment.

Good design practice accommodates the maximum system recovery at the lowest energy consumption and the best possible project economics, both capital and operational.

10.7 High-pressure membrane applications

High-pressure membranes are represented by NF and RO membranes.

10.7.1 Nanofiltration and reverse osmosis

Membrane technology for groundwater treatment to remove color and/or total dissolved solids (TDS) includes NF and RO membranes. These membrane-separation processes have a tighter membrane than MF and UF membranes, which allows them to remove dissolved matter from the water, organic and inorganic in nature.

NF and RO also have been used as finishing processes in recycled water projects, removing salt and constituents of concern, being an integrated part of any indirect potable reuse (IPR) or direct potable reuse (DPR) project.

10.7.2 Nanofiltration

NF separates particles in the range of 0.0005–0.001 μm and is effective in removing hardness, some TDS, and TOC.

NF is a pressure-driven membrane separation process that separates sparingly soluble salts and large organic molecules from a fluid (water, wastewater, or industrial process fluid). NF membranes have a high removal efficiency for multivalent ions such as calcium and magnesium (hardness), but will also remove partially monovalent salts such as sodium and chloride depending on the size cutoff of the NF membrane.

The NF membrane separation surface is a thin synthetic polymer manufactured into a flat sheet and then spiral wound to form a membrane element. The source water is pressurized and passed through the membrane module. As the pressurized source water passes along the membrane surface, water molecules pass through the NF membrane, and the larger salt ions and organic molecules are rejected and concentrated in the water passing along the membrane.

The NF system produces a high-quality (low TDS) permeate and a concentrated high salinity reject.

The first generation of the NF membranes were manufactured from cellulose acetate (CA); the newer generation of NF membranes are manufactured from polyamide thin film composites (TFC). The CA material is resistant to strong oxidants, while having lower permeability and needing higher operational pressure as a result, compared to the TFC membranes. The TFC material operates at lower pressures, while it has relatively low tolerance to the oxidizing agents in the water, and it can be damaged by oxidants. Hydrophilic agents are often added to the membranes during the fabrication process to reduce fouling of the membranes by dissolved organics.

An NF separation system typically consists of membrane elements, pressure vessels (PVs), units, and trains. The membrane element is repairable and replaceable. NF membrane elements are loaded into PVs that are fabricated mainly from fiberglass reinforced plastic (FRP) or stainless steel. The PVs can be different sizes and lengths to accommodate from one to eight membrane elements. While MF and UF membrane elements are not standardized across the industry, NF membrane elements have standard diameters of 2.5, 4, and 8 inches and standard element lengths of 40 and 60 inches. This standardization permits flexibility in designing and operation of the NF system. Currently, the large-diameter RO elements in the range of 16−18.5 inches were used for numerous RO facilities, while they are not standardized across the industry at this time. Groups of parallel PVs are supported and manifolded together with common piping, valves, and instrumentation to form a complete integrated NF unit or skids.

The NF unit has independent flow control and is chemically cleaned and operated as a complete unit. Multiple NF units are manifolded together into trains or banks to meet the overall capacity requirements for a system, as shown in Figure 10.7.

Because NF membranes do not tolerate suspended and colloidal matter in the water, they require pretreatment ahead of the membranes to protect them from solids and to prevent fouling of the membrane surface. Because the spiral-wound NF membranes cannot be backwashed, the suspended solids must be removed from the NF feed water. Depending on the source water quality, MF and/or other filtration technologies are typically used to protect membranes from the large particles. Acids and/or antiscalents also can be added to the feed water to reduce scale formation on the membrane surface. Depending on the water chemistry and system operational parameters, the average NF recovery range is 75−85%. Depending on the source water TDS, NF systems typically operate with feed pressures in the range 70−150 psi (5−10 Bar-g).

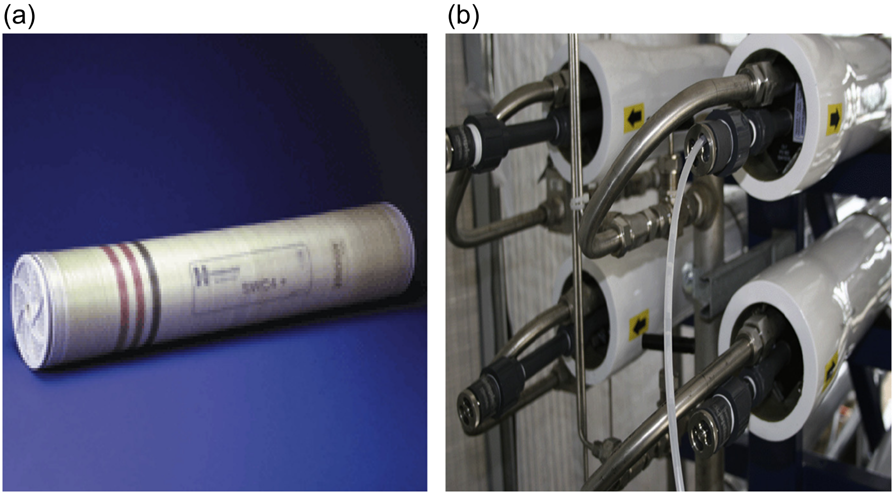


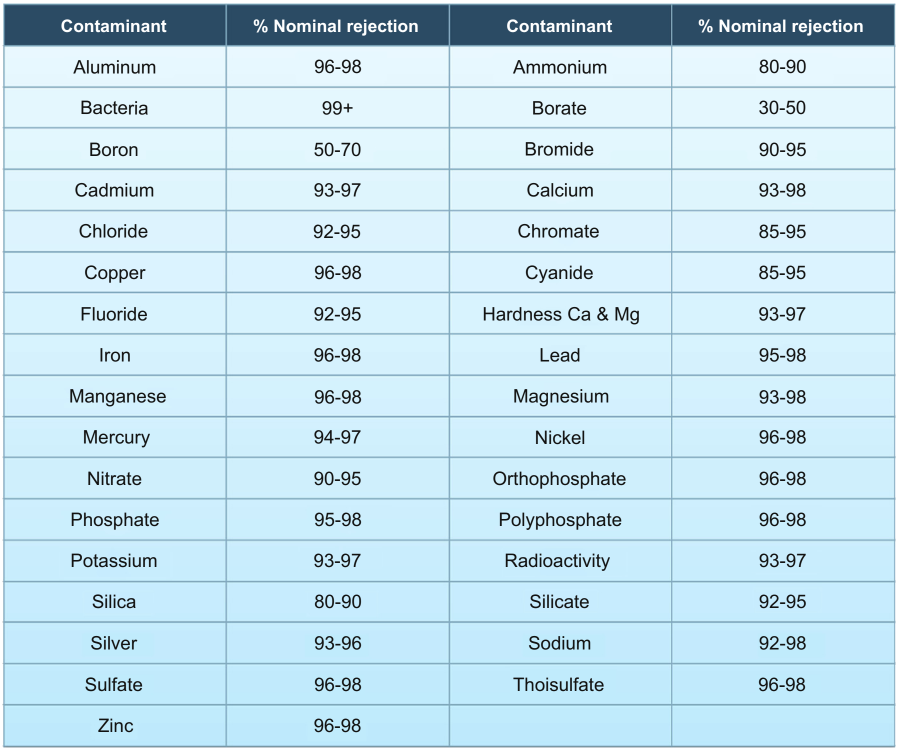
Figure 10.7 High-pressure membrane nanofiltration/reverse osmosis element (a) and system (b).

10.7.3 Reverse osmosis

RO separates ions and molecules down to less than 10 molecular weight units and is effective in removing TDS, hardness, TOC, constituents of concern such as endocrine disruptors, pharmaceutically active compounds, and personal care products (Frenkel, 2009).

Similarly to NF, RO is a pressure-driven membrane separation process that separates soluble salts and organic molecules from a fluid (water, wastewater, or industrial process fluid). Osmosis is a natural process in which water passes through a semipermeable membrane from low TDS concentration to high TDS concentration (Bartels, Franks, Rybar, Schierach, & Wilf, 2005). The RO process is a reverse of the natural osmosis process, which is the pressure-driven process in which the high TDS source water is pressurized, and water then passes through the semipermeable membrane. RO membranes have high removal efficiency for monovalent ions such as sodium and chloride and will also remove organic molecules depending on the size and charge of the molecule. Typical RO salt rejection is up to 99.8% by one single element at standard conditions. However, the overall RO system rejection rate is lower because RO elements are operated in series within the PVs, which results in the increased salt concentration in the feed to each element as water moves along the PV. Some rejections rates by one RO single membrane element at the standard conditions are shown in Figure 10.8.

Similarly to NF, the RO membrane separation surface is a thin synthetic polymer manufactured into a flat sheet and then spiral wound to form a membrane element. The source water is pressurized and passed through the membrane module. As the pressurized source water passes along the membrane surface, water molecules pass through the RO membrane, and the salt ions and organic molecules are rejected and concentrated in the water passing along the membrane. The RO system produces a high-quality (low TDS) permeate and a concentrated (high TDS) reject.



Contaminant	% Nominal rejection	Contaminant	% Nominal rejection
Aluminum	96-98	Ammonium	80-90
Bacteria	99+	Borate	30-50
Boron	50-70	Bromide	90-95
Cadmium	93-97	Calcium	93-98
Chloride	92-95	Chromate	85-95
Copper	96-98	Cyanide	85-95
Fluoride	92-95	Hardness Ca & Mg	93-97
Iron	96-98	Lead	95-98
Manganese	96-98	Magnesium	93-98
Mercury	94-97	Nickel	96-98
Nitrate	90-95	Orthophosphate	96-98
Phosphate	95-98	Polyphosphate	96-98
Potassium	93-97	Radioactivity	93-97
Silica	80-90	Silicate	92-95
Silver	93-96	Sodium	92-98
Sulfate	96-98	Thoisulfate	96-98
Zinc	96-98		

Figure 10.8 Typical contaminants removal rates from the water by reverse osmosis system.

The first generation of the RO membranes were manufactured from CA; the newer generation of NF membranes are manufactured from polyamide TFCs. The CA material is resistant to strong oxidants, while having lower permeability and needing higher operational pressure as a result compared to the TFC membranes. The TFC material operates at lower pressures, while it has relatively low tolerance to the oxidizing agents in the water, and it can be damaged by oxidants. Hydrophilic agents are often added to the membranes during the fabrication process to reduce fouling of the membranes by dissolved organics.

An RO separation system typically consists of membrane elements, PVs, units, and trains. The membrane element is repairable and replaceable. RO membrane elements are loaded into the PVs fabricated mainly from the FRP or stainless steel. The PVs can be different sizes and lengths to accommodate from one to eight membrane elements (Frenkel, 2011; Liberman & Wilf, 2005). While MF and UF membrane elements are not standardized across the industry, RO membrane elements have standard diameters of 2.5, 4, and 8 inches and standard element lengths of 40 and 60 inches. This standardization permits flexibility in designing and operation of the RO system. Currently, the large-diameter RO elements in the range of 16–18.5 inches were used for numerous RO facilities, while they are not standardized across the industry at this time. Groups of parallel PVs are supported and manifolded together with common piping, valves, and instrumentation to form a complete integrated RO unit or skids. The RO unit has independent flow control and is chemically cleaned and operated as a complete unit. Multiple RO units are manifolded together into trains or banks to meet the overall capacity requirements for a system.

RO membranes require pretreatment ahead of the membranes to protect them from solids and to prevent fouling of the membrane surface. Because the spiral-wound RO membranes cannot be backwashed, suspended solids must be removed from the RO feed water. Depending on the source water quality, MF and/or other filtration technologies are typically used to protect membranes from the large particles. Acids and/or antiscalants are also added to the feed water to reduce scale formation on the membrane surface. Depending on the water chemistry and system operational parameters, the average brackish water RO recovery range is 75–85%. Seawater RO (SWRO) usually operates with a recovery of 40–60%. Depending on the source water TDS, RO systems typically operate with feed pressures in the 150–1200 psi (10–83 Bar-g) range.

10.7.4 Seawater reverse osmosis

Membrane technology to remove salt from seawater to provide an alternative drinking water source can be designed with MF or UF pretreatment ahead of SWRO membranes. This process currently represents a small segment of the US market, but is expected to see future growth in Florida, Texas, California, and numerous other costal places where there is no other drinking water source (Desalination of Seawater, 2011; Stevens, Kowal, Herd, Wilf, & Bates, 2003; Wilf et al., 2006).

10.8 Applications of high-pressure membranes for water treatment, brackish water, seawater/ocean water

High-pressure membranes are widely applied to treat groundwater to reduce salt content, nitrates, and specific contaminants of concerns. RO membranes became the dominant technology for seawater desalination, providing beneficial process economics compared to thermal desalination processes. RO membranes are becoming the integrated part of the process in the water reuse, and in IPR and DPR, which are attracting attention lately, and in light of the global warming and climate changes particularly. Another niche for the high-pressure membranes is preparation of the deionized (DI) water and ultrapure water (UPW) of which many industries are in need.

10.9 Planning and designing high-pressure membrane treatment

Similarly to low-pressure membrane planning, the high-pressure membrane projects need careful planning and administration. The major differences in the high-pressure membrane projects compared to the low-pressure membrane projects and conventional technologies are:

- Membranes cannot tolerate high suspended and colloidal solids load, while being efficient in removing dissolved matter from the water to be treated;
- Reliable pretreatment is required to reduce particular matter and colloids load prior to treating water by high-pressure membranes;
- As membranes provide higher-quality product water, the fewer ultraviolet doses and/or lower chlorine injection rate are required compared to the conventional processes.

Because high-pressure membranes are well standardized across the industry, they are not manufacturer-specific and are replaceable by other suppliers (Frenkel & Wilf, 2009). The current status in the industry simplifies the high-pressure membrane planning process, and most of the conventionally procured membrane plants are using a one-step procurement process, the opposite of the low-pressure membrane procurement process. The one-step procurement process reduces the project schedule compared to the low-pressure membrane procurement process.

Similarly to low-pressure membranes, the design of high-pressure membranes depends on the source water quality, local conditions, project preferences, and requirements of the treated water quality. Because high-pressure membranes do not tolerate suspended and colloidal matter in the water, design, and performance of the high-pressure membranes depend on design and performance of pretreatment, either conventional or low-pressure membranes. Since development, most of the engineering and design efforts were directed to design high-pressure membranes in the continuous operation. The continuous operation has certain benefits and negatives, as highlighted below.

Benefits of RO operation in continuous mode:

- All membranes are operated continuously, allowing a relatively simple system, fittings, and piping arrangements;
- Equipment, fittings, and components are not cycling periodically, increasing the lifetime of equipment;
- Energy recovery devices can be easily added, reducing overall energy demand by the system;
- There are number of techniques developed, allowing system operation to be flexible, such as concentrate recycling and hybrid design.

Within the last few years, RO operation in a semibatch mode was proposed, which brings the following benefits compared to the continuous RO operation:

- Flux can be better balanced between RO membrane elements within the PV;
- Higher overall system recovery can be achieved at the same conditions compared to the continuous RO operation;
- Less potential membrane fouling may be achieved due to the change in the salt load within each cycle.

The high-pressure membrane system design needs to account for the following major plant components and parameters:

- Pretreatment requirements, including chemical injection, clarification when required, filtration using conventional processes, or low-pressure membranes;
- System recovery rate, the ratio of the product flow to the feed flow expressed in percent;
- Membrane active filtration area, which is a function of the flow load on the membranes per membrane area, which is called membrane flux and is expressed in GFD or LHM;
- Energy requirements;
- Posttreatment requirements due to the low alkalinity of the product water and water aggressiveness as a result;
- Concentrate discharge/management;
- Treatment/management solids from pretreatment.

Good design practice accommodates the maximum system recovery at the lowest energy consumption and the best possible project economics, both capital and operational (Desalination of Seawater, 2011).

10.10 Integrated membrane systems

As described above, low-pressure mmbranes were designed to remove suspended matter from the water, similarly to media filtration or other solids-water separation technology. High-pressure membranes are not tolerant of suspended and colloidal matter, while being designed to remove dissolved matter from the water similarly to the ion exchange resins or water evaporators. IMS found their application in a number of industries and in municipal applications.

A number of seawater desalination plants were designed by applying the IMS concept when low-pressure membranes are followed by high-pressure membranes. Surface water treatment adopted the IMS concept in which dissolved matter, inorganic or organic in nature, needs to be removed from the water. Many industries adopted IMS design when preparing to make up DI or UPW or when treating industrial effluent for reuse. As IPR is gaining popularity and DPR is knocking on the door, the IMS concept is becoming the gold standard for these applications.

10.11 Combination of membrane treatment with other technological processes

Membrane technologies have number of beneficial features allowing for rapidly expanding market shares, such as:

- Absolute barrier for treatment/removal;
- Smaller footprint/layout;
- Product water is not affected by the feed water hydraulic and contaminant overloads, spikes, and fluctuations;
- Less or no chemicals required;
- Minimal or no pretreatment required;
- Single-step process;
- Modular expandability (for future expansion);

- Less volume of discharged wastes (including sludge and chemicals);
- Simplicity of operation with remote monitoring;
- Lower postdisinfection demand in chlorine, UV intensity.

Also, membrane technologies have certain limitations such as:

- Prompt to foul;
- Needs pretreatment;
- Have low rejection rate of non-ionized ions;
- Have low rejection rate of dissolved gases.

Depending on the application, feed water quality, and criteria of the treated water, membrane technologies can be successfully combined with conventional processes. Good examples could be:

- Using clarification upstream of low-pressure membranes to reduce suspended matter load to the membranes;
- Using DAF to minimize low-pressure membrane fouling caused by the colloidal matter, fine organics, and algae;
- Applying chemicals similarly to the conventional processes to form flocs, coagulate water, and change water pH;
- Polish permeate from high-pressure membranes by activated carbon;
- Add decarbonators to remove CO_2 and balance pH in the product from high-pressure membranes;
- Use advanced oxidation concept to destruct constituents of concert and low molecular weight organics that may pass through the high-pressure membranes.

10.12 Conclusions: future trends in membrane treatment development for water treatment

Membranes are gaining popularity and market growth. While traditionally membrane technologies started to develop in the United States, Europe, and Japan, the latest trends are that more membranes companies are being established in different parts of the world, including Korea and China. Besides traditional membrane technology suppliers, there is a good number of players showing up on the market. Competition drives improvements in membrane technology developments, finding newer applications, improving technical features of membranes, and reducing cost.

Several trends in membrane technology developments can be identified:

- Improvements of membrane properties such as increase of permeability, e.g., higher flux at lower pressure;
- Fouling minimization;
- Overall system energy reduction;
- Minimization of the treatment plant footprint by applying larger-size treatment trains, common headers, and large-diameter membrane elements (RO);
- Newer membrane technology developments, such as forward osmosis, pressure retarded osmosis, membrane distillation, and combinations of the newer processes with the established technologies.

As the membrane market grows, sooner or later membrane technology will be one of the preferred choices for projects.

List of acronyms

BWRO	Brackish water reverse osmosis
C	Concentration, ppm or mg/L
CA	Cellulose acetate
DPR	Direct potable reuse
FRP	Fiberglass reinforced plastic
gpm	Gallons per minute (US units of flow)
IMS	Integrated membrane system
IPR	Indirect potable reuse
m^3/hr	Cubic meter per hour (metric units of flow)
mg/L	Milligram per liter (metric units of concentration)
MBR	Membrane bioreactor
MF	Microfiltration
MWCO	Molecular weight cut off
NF	Nanofiltration
NTU	Nephelometric turbidity units
ppm	Part per million (fractional units of concentration, equal to mg/L)
PV	Pressure vessel
Q	Flow, gpm, or m^3/hr
RO	Reverse osmosis
SWRO	Seawater reverse osmosis
TDS	Total dissolved solids
TFC	Thin film composite
TOC	Total organic carbon
UCLA	University of California at Los Angeles
UF	Ultrafiltration
UPW	Ultrapure water

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Membrane ageing during water treatment: mechanisms, monitoring, and control

11

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11.1 Introduction

Microporous and semipermeable membrane filtration processes are used to efficiently and reliably achieve consistent product water quality and quantity on a range of water sources (see Figure 11.1). In general, membrane processes are less complex compared to conventional water treatment processes that use chemical flocculation, clarification, and chlorination. Product water quality can be easily monitored using a range of techniques that check for membrane integrity. Similarly, the capacity to maintain product quantity can be assessed by online monitoring of membrane permeability. One challenge unique to drinking water plants using membrane technology is anticipating and scheduling activities to renew the inventory of membranes in service.

The prorated warranty provided by membrane manufacturers can range from 3 to 10 years. However, experience teaches that some plants' effective membrane life can either exceed or fall short of the manufacturer's expectations. Moreover, it is not uncommon to have significant variability in the integrity and productivity of

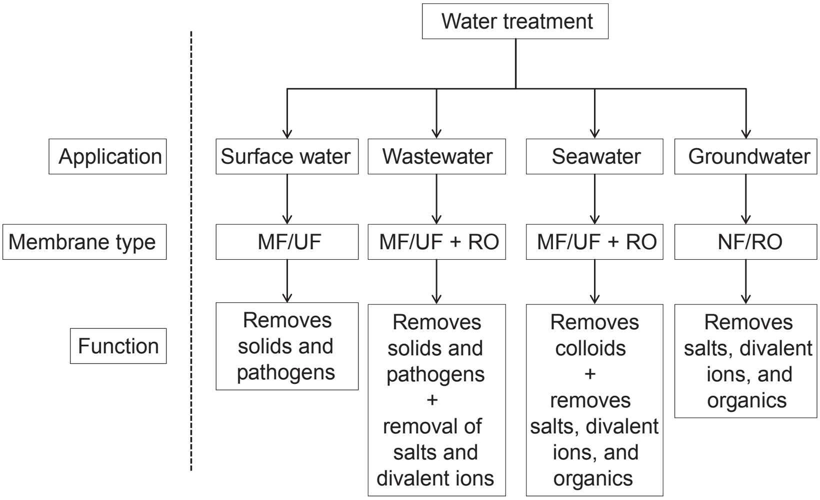

Figure 11.1 Typical membrane filtration applications in the water treatment industry.

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membrane modules on site at any given time. The capacity of an individual membrane element or module can range from 42,000 L per day for a microporous MF/UF membrane to 21,600 L per day for a semipermeable reverse osmosis (RO) membrane. Consequently, operators of plants with a treatment capacity of 50 MLD would need to manage a membrane inventory of several thousand membranes.

The paramount operating objective is to avoid any failure that could compromise quality and restrict capacity. Developing a strategy that relies exclusively on manufacturer's warranty to estimate membrane lifespan and replacement schedules is fraught with uncertainty.

Membrane ageing and failure occurs throughout the membrane's operational lifetime. The literature has been silent with regard to the understanding and prediction of membrane failure and has largely been focused on ageing due to exposure to strong oxidants such as sodium hypochlorite. This chapter reviews the mechanisms and modes of membrane failure, approaches and methods used to monitor, and the control membrane ageing and integrity in the water treatment industry.

11.1.1 Membrane ageing and failure

Membrane ageing is usually the main cause behind overall membrane failure as a membrane reaches the end of its lifespan (Prulho, Therias, Rivaton, & Gardette, 2013). This section would make a clear distinction between ageing and failure and further discuss how membrane ageing can lead to a membrane that is more susceptible to failure.

11.1.1.1 Membrane ageing

Membrane ageing is defined as the deterioration of the surface layer and sublayers of composite membranes due to irreversible deposition of foulants or by frequent exposure to chemical cleaning agents (Antony, Fudianto, Cox, & Leslie, 2010; Benavente & Vázquez, 2004; Thominette, Farnault, Gaudichet-Maurin, Machinal, & Schrotter, 2006). Membrane productivity and removal efficiency are undermined by the retention of dissolved salts, organics, microorganisms, and suspended solids after extended operation, also known as fouling (see Figure 11.2(a), (b), and (d)). Membrane fouling is the central bottleneck for all membrane filtration processes; therefore, the industry uses routine chemical cleaning protocols. In some cases, strong oxidants, such as sodium hypochlorite, are used to control fouling. Regrettably, repeated chemical cleaning exacerbates membrane aging.

During the cleaning in place (CIP) process, chemicals are intermittently applied to the fouled membranes at specific concentrations, temperatures, and extended times. The combination of these factors can lead to ageing of the membrane, with membranes becoming discoloured over time (see Figure 11.2(c)). Prolonged filtration and cleaning cycles not only have an adverse effect on membrane integrity, but can also lead to internal fouling of membranes, which is irreversible and detrimental to membrane performance (see Figure 11.2(b)). This also reduces the lifespan of the membrane, leading to a higher likelihood of failure.

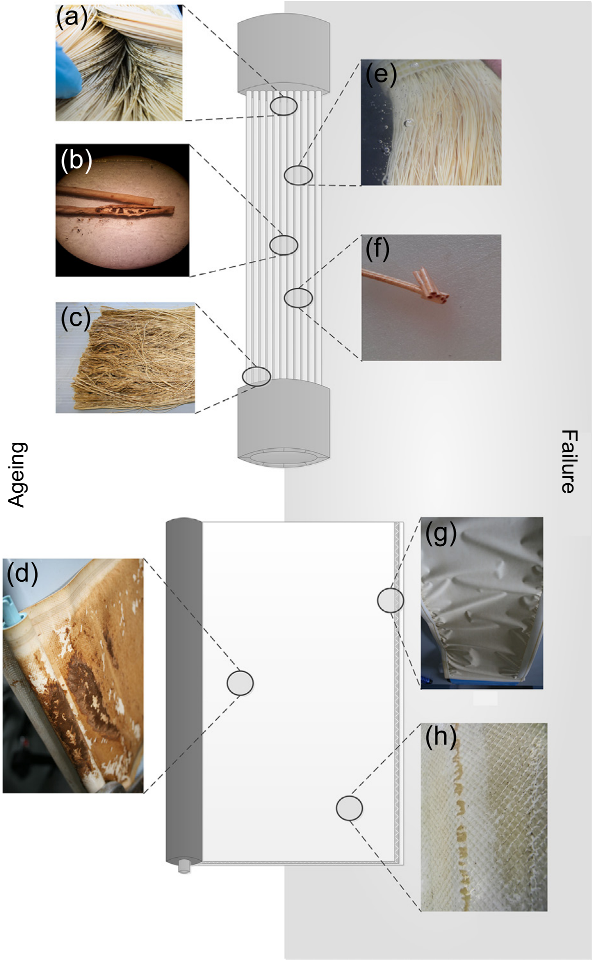


Figure 11.2 Effects of membrane ageing and failure. (a) Foulant accumulation; (b) Membrane internal fouling; (c) Membrane fibre discolouration; (d) Membrane surface fouling; (e) Surface punctures; (f) Fibre embrittlement; (g) Surface delamination; (h) Surface scratches and scores.

11.1.1.2 Membrane failure

Membrane failure can be defined as the loss of membrane mechanical integrity leading to the inability to achieve rated log removal values (LRV) (Childress, Le-Clech, Daugherty, Chen, & Leslie, 2005; Gijsbertsen-Abrahamse, Cornelissen, & Hofman, 2006; Mallevialle et al., 1996). Membrane failure can occur during two phases of the membrane's operational lifespan. Membrane fibres can be damaged before and during installation, and also during membrane filtration. Failure before and during installation is often caused by inconsistent manufacturing and fabrication techniques and installation. This issue is kept in check via implementation of more rigorous quality control methods and integrity testing of membrane modules before commissioning.

Membrane failure during the filtration process can largely be attributed to operating parameters and maintenance protocols (Johnson & Maccormick, 2003). During operation, the likelihood of damage to the membrane is high given the astringent nature of operating protocols, such as vigorous mechanical cleaning, chemical cleaning using strong oxidants, and high-pressure backwashes. Although this ensures that the membrane's performance is maintained, it indirectly puts a strain on the membrane's integrity, leading to accelerated membrane aging and subsequent failure. According to Childress et al. (2005), failure results from physical damage to the membrane module structure. The damage maybe caused as a result of a suite of factors: actions by chemicals, excessive external forces, scores, scratches, and punctures due to the presence of foreign bodies (see Figure 11.2(h)), all of which are exacerbated by faulty membrane module structures and designs. Membrane fibre breakage due to chemical attack leads to embrittlement of membrane fibres, leading to both discolouration and breakage of membrane fibres (see Figure 11.2(f)). Membrane damage and integrity compromise can also be caused by unexpected water quality fluctuations or failure of pretreatment processes leading to inadequate removal of material (Gijsbertsen-Abrahamse et al., 2006). These foreign bodies coupled with the effects of strong aeration can puncture the membrane, resulting in a rapid pressure loss and detection of bubbles in a pressure decay test (PDT) (Cui, Chang, & Fane, 2003) (see Figure 11.2(e)).

Although membrane ageing and failure are closely related, a distinction should be made between these two aspects. Ageing results in membrane degradation, and the onset of these adverse effects, in turn, leads to membrane failure. Subsequently, membrane failure results in loss of process removal efficiency, reduction in product water throughput, and product water noncompliancy.

11.2 Reliability, maintainability, and resilience

Many communities rely on hollow-fibre membranes to remove pathogens from drinking water. The resilience of water treatment plants using hollow-fibre membranes is defined as the ability to meet a specified log reduction in pathogen concentration in routine, as well as in unexpected, circumstances. The reliability of a membrane filtration system is therefore critical to ensuring that treated water meets regulatory requirements. Maintainability of the system is also important because that would determine the system's downtime before being put back into service once the failure has been rectified. Therefore, the reliability and maintainability of an asset are two factors that are crucial in evaluation of the asset's resilience.

11.2.1 Reliability

The reliability of a membrane filtration process unit is an essential factor in maintaining the continuous compliance with specific performance criteria, such as environmental discharge consent requirements and water quality parameters. The evaluation of the reliability of such process units is an important part of its design and operation.

However, this has always been difficult to assess and quantify and often has been based on the number of redundancies and/or backup facilities (Eisenberg, Soller, Sakaji, & Olivieri, 2001).

11.2.1.1 Mean time to failure and mean time between failure

Process equipment is said to be completely reliable if there is no failure in the process performance and it meets the required effluent discharge standards and targets. Equipment reliability can be measured in terms of mean time to failure (MTTF) and mean time between failure (MTBF) (Stanley, 2011). Although MTTF and MTBF can be used to quantify equipment reliability, there is a distinct difference between these two terms. MTTF can only be applied to nonrepairable components and equipment, while MTBF is applied to repairable equipment (Kagan, 2004). MTTF is the average time equipment remains functional until its failure and can be calculated by dividing the total operation time of equipment by the number of units of equipment. For mean time to repair (MTTR) to be accurate, this statistical value should be measured for a long period and over a large number of units (Stanley, 2011).

$$\text{MTTF} = \frac{\text{Cumulative operational time of equipment (hours)}}{\text{Number of equipment}} \tag{11.1}$$

In the case of repairable components, MTBF is used instead of MTTF. MTBF is the average time equipment remains in service until it fails and can be calculated by the following equation (Smith & Mobley, 2008):

$$\text{MTBF} = \frac{\text{Cumulative time in service (hours)}}{\text{Number of failures}} \tag{11.2}$$

For example, MTTF could be applied to irreparable failure events of RO membranes in which delamination or damage to the membrane housing had occurred due to excessive backwash pressure, whereas MTBF would apply to repairable faults such as sealing of detected leaks in compromised hollow-fibre membranes before being returned to service.

11.2.1.2 Failure rates

Equipment failure rates (events/time) also can be used to quantify reliability. A higher failure rate or a greater number of failure incidences will directly translate to less-reliable equipment. The failure rate of any given piece of equipment can be described by a “bathtub” curve (see Figure 11.3). The bathtub curve is divided into three sections. The first section is known as the “wearing in period.” During this period, the failure rates are high due to infant mortality failures caused by defective components and improper quality control measures prior to operation. An example in a membrane system would be a failure that occurs during the commissioning stages, when poor installation, manufacturing defects, and incorrect membrane preconditioning protocols can result in an early failure of the membrane units (Johnson & Maccormick, 2003). The failure rate then decreases rapidly as the equipment and its components are worn in, until it reaches the second section, the "intrinsic failure period." This period is when most of the equipment's lifespan remains, and throughout this long period the equipment has a constant failure rate due to random failures. Failure events that occur during this period could be a result of a pretreatment process' ineffective removal of gross particles or unintentional operator error leading to damage and failure of the membranes (Yang, Cicek, & Ilg, 2006). The last section is the "wearing out period." In this period, the failure rate increases again because of cumulative damage caused by wear and mechanical fatigue over time (Klutke, Kiessler, & Wortman, 2003). This period occurs toward the end of the membrane's lifespan and would be replaced when it eventually fails to maintain removal efficiency and process integrity. The typical lifespan of a membrane usually ranges from 5 to 10 years and varies with material type and manufacturers (Lesjean, Rosenberger, Schrotter, & Recherche, 2004).

11.2.1.3 Availability

The availability of an equipment or component is defined as the proportion of time that it is functioning properly and is available for operation. Availability is the ratio of the total operational time to the sum of operational time and repair times. Repair times are quantified via the equipment's MTTR. This is the average time required for repairs to be made to restore the equipment back to its operational state. The equipment's availability can be calculated via the equation below:

$$\text{Availability} = \frac{\text{MTBF}}{\text{MTBF} + \text{MTTR}} \tag{11.3}$$

To maximise availability, a balance between component reliability and maintenance has to be achieved. Downtime is inevitable, because both scheduled preventative maintenance and repairs require time and cause disruptions to the system's operation (Marshall & Chapman, 2002). Implementation of different design

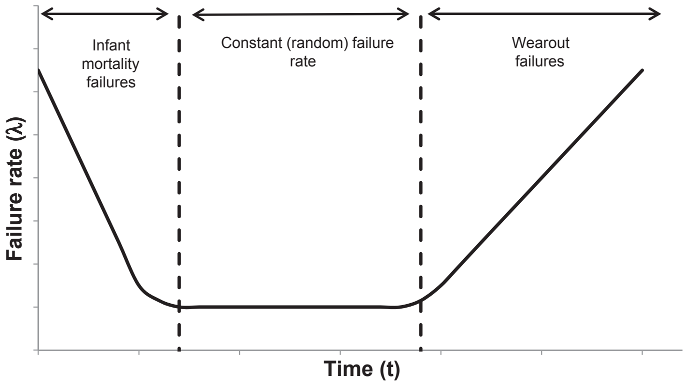


Figure 11.3 Bathtub curve describing equipment's failure rates with time.

approaches, for example, having multiple smaller systems integrated to form a larger, complete system working with an optimised maintenance protocol can result in a higher system reliability and availability.

11.2.2 Maintainability

Maintainability of a membrane filtration system is defined as the probability of the failed system returning back to an operable condition using the recommended procedures in a specific period (Sutton, 2010a).

Conventional maintenance can be divided into three categories: repair, condition-based maintenance, and scheduled maintenance. Repair and condition-based maintenance are performed when the process equipment has either failed or starts showing signs of imminent failure, with the only difference being repairs are usually done without equipment shutdown, and condition-based are done with a shutdown. In a membrane system, an example of repair and condition-based maintenance would be isolating and replacing membrane modules on detection of a compromise in membrane integrity. Scheduled maintenance is regular maintenance performed regardless of condition or performance during operation. Routine chemical backwashing is an example of scheduled maintenance that is used to restore membrane flux and control fouling during membrane filtration. To reduce process equipment downtime and labour costs, reliability centred maintenance (RCM) was developed. RCM uses a risk-based approach to prioritise process equipment so that equipment that is critical to process integrity is inspected and maintained more frequently (Sutton, 2010b).

11.2.3 Resilience

A system's resilience is defined as the ability for the system to tolerate the disturbance and return back to its steady-state following the perturbation (Gunderson & Pritchard, 2002). In the case of membrane filtration systems, the resilience is described as how robust the system is in recovering from a failure event and can be defined by the duration of the failure occurrence (Zhang, Achari, Sadiq, Langford, & Dore, 2012). For example, having only one operator responsible for an entire treatment system would result in the operator requiring a longer time to isolate and remediate the failing process, leading to a longer downtime and deeming the process to be less resilient. Therefore, the resilience of the membrane system plays a critical role in ensuring that continuous process throughput is maintained while the treated water still remains compliant with strict water discharge guidelines upholding public health and safety.

11.3 Membrane failure modes

There are two categories of membrane failure, failure during installation and failure during operation (see Table 11.1). Of the two aspects, failure during operation is more critical because it could lead to product water noncompliancy, which is a threat

Table 11.1 Common failure modes of membranes and modules

Failure mode	Failure location	Cause	Incidence of failure	Consequences	Membrane types
Manufacturing defects	Module or membrane	Accidental	Installation or operation	Poor removal efficiency; abnormal differential pressures	All
Cracks and ruptures	Module	Hydraulic shock, accidental high pressure or shear stress, abrasion or backwash pressure	Operation, start-ups, shutdowns	Abnormal differential pressures	All
O-ring and seal failures	Module	Accidental	Operation	Poor removal efficiency; abnormal differential pressures	All
Mechanical damage	Module	Accidental	Installation or operation	Abnormal differential pressures	All
Damage of active layer	Membrane	Pretreatment failure, presence of crystalline or abrasive particles	Operation	Poor removal efficiency; abnormally high permeate flux	All
Oxidative damage of membrane	Membrane	Use of strong oxidants	Prolonged operation	Poor removal efficiency; abnormally high permeate flux	All

Colloidal or inorganic fouling	Membrane	Pretreatment failure	Prolonged operation	Permeate flux decline; high TMP	All
Organic fouling	Membrane	High organic loading of feed water	Prolonged operation	Permeate flux decline; high TMP	All
Internal fouling (lumen-side)	Membrane	Prolonged operation	Prolonged operation	Permeate flux decline; high TMP	Hollow fibre
Fractures and cleavages	Membrane	Hydraulic shock, accidental high pressure or shear stress	Operation, start-ups, shutdowns	Poor removal efficiency; abnormally high permeate flux	Hollow fibre
Delamination of active layer	Membrane	High backwash pressure	Operation, shutdowns	Poor removal efficiency	Flat sheet
Compaction	Membrane	High operation pressure and sudden pressure surges	Operation	Low permeate flux	Flat sheet

to public health. Failure during installation is less critical, given that it can be easily overcome by having more rigorous inspections prior to commissioning. Therefore, this section will focus on failure modes of membrane systems during operation.

Hollow-fibre membranes are widely used in municipal and industrial wastewater treatment (Chang, 2011; Cheryan, 1998; Oschmann, Nghiem, & Schäfer, 2005). Large bundles of hollow-fibre membranes are often either encapsulated in a pressure vessel forming a module or potted into large curtains for submerged filtration in wastewater (Gijsbertsen-Abrahamse et al., 2006). Fibre failure can occur via four different mechanisms; however, only three are related to membrane ageing that leads to its subsequent failure: chemical attack, excessive fibre movement, and improper membrane module design. The fourth aspect, presence of foreign bodies, can be attributed to poor removal efficiency of pretreatment processes and thus does not directly contribute to membrane ageing.

11.3.1 Failure due to chemical attack

The removal efficiency of both microporous and semiporous membranes is optimal only when membrane fouling is kept to the minimum while maintaining overall integrity. Therefore, to control the fouling on the membrane surface, frequent in-situ backwash regimens using strong oxidants are implemented. Oxidative damages are largely caused by the chemical incompatibility of the chemicals used and the membrane material itself (Childress et al., 2005). Due to this exposure to harsh chemicals, the membrane properties would be altered, resulting in membrane degradation (Antony & Leslie, 2011). Oxidants are the main causes behind membrane integrity deterioration, with sodium hypochlorite being the most common cleaning agent used and studied. However, it should be noted that sodium hypochlorite is not universally used given the health and environmental impacts of the chlorinated organic by-products and the low chlorine tolerance of certain membrane types (Kang et al., 2007; Kwon & Leckie, 2006). From the equilibria equations below, sodium hypochlorite dissociates into hypochlorous acid, HClO, when it comes in contact with water and further dissociates into hypochlorite ions, ClO^-. The pH largely affects the stoichiometric ratio of hypochlorous acid dissociated with a low pH favouring a higher dissociation of the stronger oxidant HClO (Rouaix, Causserand, & Aimar, 2006).

$$NaClO + H_2O \leftrightarrow HClO + NaOH \tag{11.4}$$

$$HClO \leftrightarrow H^+ + ClO^- \tag{11.5}$$

An example of the chemical incompatibility between cleaning reagents and membranes is the unexpected internal fouling of membranes in the presence of iron species. In Australia, iron salts are dosed in wastewater treatment plants with the aim to aid phosphorous removal and odour control. The presence of iron salts coupled with the oxidative nature of hypochlorite can lead to formation of amorphous ferric oxides (AFO) that could accumulate in the lumen side of the hollow-fibre membranes, causing internal fouling and sudden, unexpected fibre failure (Tng, Wang, Waite, & Leslie, 2013).

11.3.2 Failure due to faulty membrane module structure

Membrane module design is usually correlated to the efficiency of membrane fouling prevention. Current membrane modules consist of up to 20,000 hollow fibres held together with either an epoxy or urethane resin. Depending on the manufacturing process, the resin can be cured under static or dynamic conditions. In static conditions, the resin is allowed to cure without heat or external forces acting on it. This method is slower than the dynamic curing method that uses centrifugal forces under elevated temperatures. Each method would produce varying results, and thus would have different mechanical tensile strengths.

Membranes that are potted statically would have the resin wick up the fibre's edge due to the effects of capillary forces. This leads to a development of a sharp edge that can cause fibre breakage (Figure 11.4(a)). Application of an elastomer overlay is added to minimise the sharp edges (Figure 11.4(b)). However, only the dynamic cured resins can almost negate the development of these sharp edges (Figure 11.4(c)) (Childress et al., 2005). With the addition of air scouring, the probability of fibre breakage due to the type of potting method increases.

Membrane filtration and routine backwashes carried out at pressures higher than the manufacturer's recommendations can lead to membrane failure via delamination of membrane sheets (see Table 11.2(f)), damage to membrane module housing (see Table 11.2(a)), and degradation of membrane module seals (see Table 11.2(c)). Consequently, the tolerable stress load on a membrane module will depend on the type of membranes, the way the membrane is packed into the module, and the method used to cure the resin that holds the membrane in place.

The optimal membrane module design would have to find a balance between stress imposed on the membrane fibre and the amount of force required to hold the membrane fibres firmly in place. Presently, there is a lack of fundamental data on stresses experienced by fibres during the filtration and cleaning cycles in the presence of air scouring (Regula et al., 2014). This, coupled with the difficulty in accurately measuring/calculating stresses in multiple fibre systems, has significantly limited the development of better-designed membrane modules. This underlines the need for both a better understanding in membrane potting methods and stress–strain forces acting on the membrane fibres for better membrane module design.

11.3.3 Failure due to excessive movement

The advantage of submerged membranes is that the hydrostatic pressure generated does away with the need for the membrane modules to be pressurised. For such configurations, air scouring or bubbling is used to provide a shear force along the membrane surface to help alleviate the fouling phenomena (Cui, Chang, & Fane, 2003). The higher the shear force on the membrane surface, the more efficient the removal of foulants; however, the excessive membrane movement due to the higher shear force can

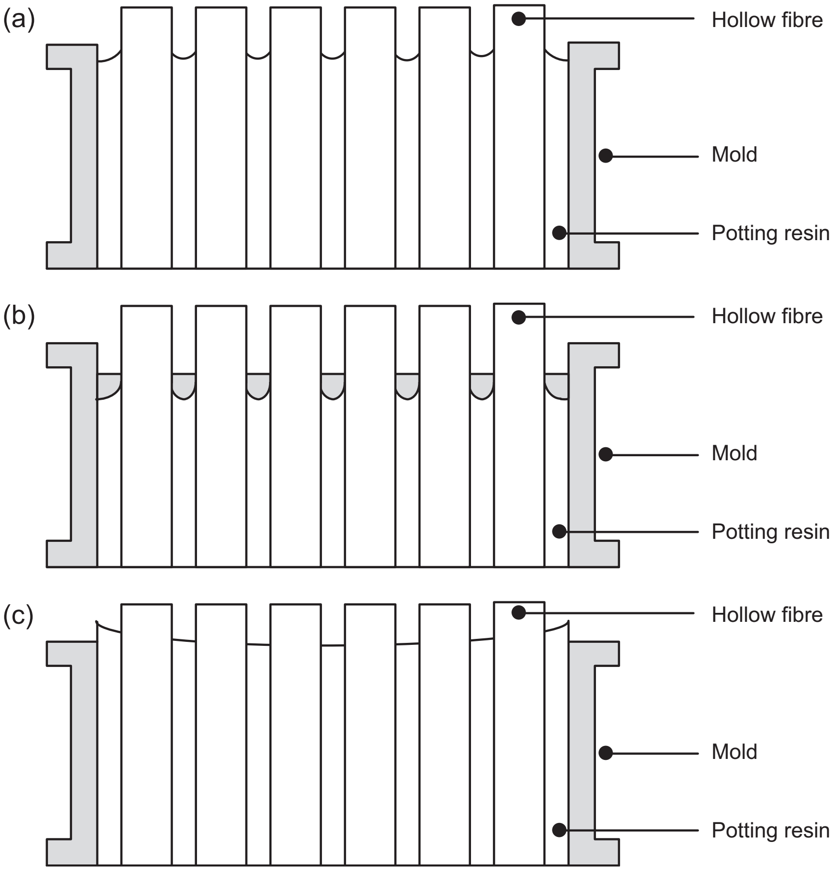
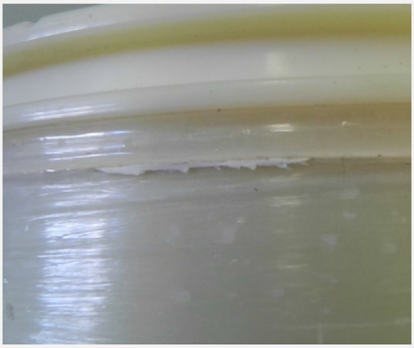
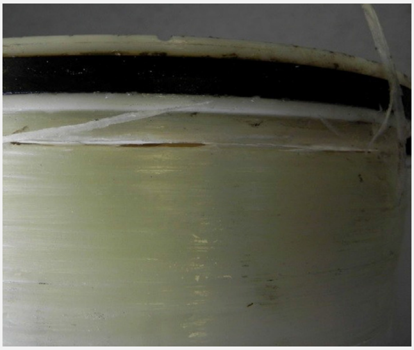
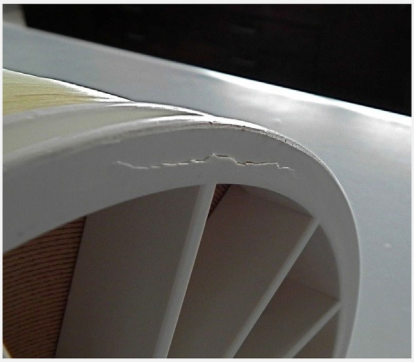


Figure 11.4 (a) Static conditions, (b) static with elastomer overlay, and (c) dynamic conditions. Adapted from Childress et al. (2005).

also lead to fibre breakage (Wicaksana, 2006). This phenomenon, coupled with degradation of membrane fibres due to ageing, could lead to a higher occurrence of fibre failure.

Flat sheet, thin film composite (TFC) membranes are widely used in desalination and water recycling applications via an RO process (Cadotte John, 1985; Cadotte John & Petersen Robert, 1981; Prakash Rao, Desai, & Rangarajan, 1997). TFC membranes consist of a polyamide active top layer on top of a polysulfone microporous substrate support layer on a woven or nonwoven polyester reinforcing backing to provide additional mechanical strength (Antony & Leslie, 2011). These membranes are usually used in submerged or tubular module configurations. TFC membranes with a polyamide active layer are able to operate at high recovery rates and wide pH ranges; however, similar to hollow-fibre membranes, they are highly susceptible to chemical attack by chlorine (Antony et al., 2010; Glater, Hong, & Elimelech, 1994). To mitigate biofouling, chlorine disinfection is often introduced through upstream dosing, before

Table 11.2 **Failure of membrane modules**

2(a) Cracks in module housing	
	
2(b) Cracks in module end caps	
	
2(c) Module seal failure	2(d) Improper seal installation
	

the RO membrane system, and excess residual chlorine is removed via the dosing of sodium bisulfate. However, due to unexpected changes in the quality of the feed water, a higher than tolerable amount of free chlorine is present in the RO system, thus leading to the degradation of membrane integrity by chemical attack.

Flat sheet membranes are also more prone to delamination during routine backwashing. When cake layer fouling occurs on the membrane surface, the hydraulic resistance increases, resulting in a decrease in membrane flux. As a way to restore the flux, a backwash is used. The backwash entails pumping either permeate water or compressed air in the reverse direction from the permeate side to the feed side. This would dislodge caked particles from the membrane surface back into the bulk feed water (Ratnayaka, Brandt, & Johnson, 2009). Conventional backwash frequencies range from once every 30–90 min, with a backwash duration of 30–90 s (Howe, Hand, Crittenden, Trussell, & Tchobanoglous, 2012). Backwash pressures should be performed according to the membrane manufacturer's specifications and should also take into account site-specific considerations to prevent delamination of membrane sheets, formation of hairline cracks in the membrane module, and membrane module seal failure, all of which can result in membrane failure and subsequent contamination of product water.

11.4 Membrane ageing monitoring methods

Membrane ageing affects the performance of membranes via three different aspects. As the membrane ages, the permeate quality, flux restoration after cleaning, and the mechanical strength are all adversely affected. Membrane ageing also presents itself as degradation in the membrane's functional properties and characteristics. Because membranes are extensively used in the production of drinking water, integrity breaches can result in an increase in microbial contamination of the permeate (Antony, Blackbeard, & Leslie, 2012) and can also lead to a public health compromise should the pathogens and viruses not be removed prior to distribution (Gitis, Haught, Clark, Gun, & Lev, 2006). Therefore, to monitor the effects of membrane ageing, monitoring methods are used to detect and assess the impacts of membrane ageing.

11.4.1 Membrane ageing assessment tools

Multiple analytical techniques are used to assess membrane ageing and are categorised based on five different membrane aspects. They range from filtration characteristics to morphological characteristics (see Figure 11.5). These techniques are well established and have been used by many researchers in the field of membrane characterisation. The principles behind these techniques will be briefly covered in the sections below.

11.4.1.1 Filtration characteristics

Permeability, membrane resistance, and solute rejection are filtration characteristics that can provide useful, real-time information regarding the membrane's filtration

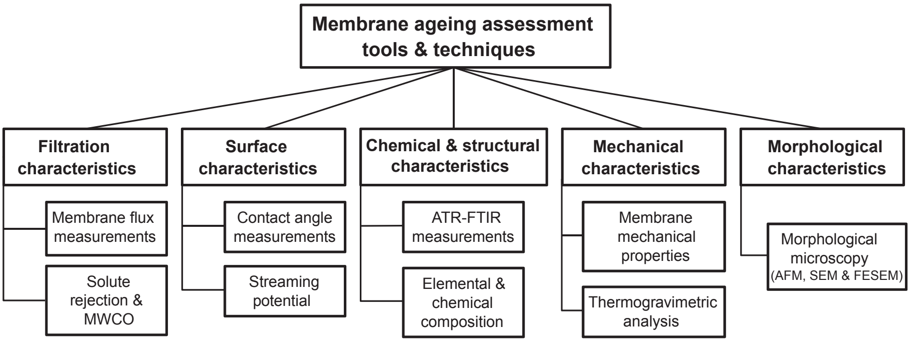


Figure 11.5 Membrane ageing assessment tools and techniques.

properties. These methods are also nondestructive and are fundamental in principle, thus are usually the first tools used to monitor membrane ageing.

Membrane permeability and resistance provides a direct measurement of the membrane flux restoration after a cleaning cycle. The membrane is said to have undergone degradation if the flux restored is greater than the initial membrane flux (Yadav & Morison, 2010). Although membrane permeability is a clear and distinctive way to detect membrane degradation, it is often too late, because it only occurs when a gross integrity loss has happened and thus is not a reliable tool for real-time monitoring of membrane ageing.

Solute rejection is determined by the molecular weight cut-off (MWCO) of the membrane. Changes in the membrane's pore size and subsequent rejection can be detected via solute rejection tests. Molecular weight markers or molecules with specific, known molecular weights are used to test the membrane's rejection capabilities (Arkhangelsky, Kuzmenko, & Gitis, 2007). This method is superseded by other more accurate analytical techniques, such as pore size distribution measurements based on bubble point and gas permeation methods. Despite the limitations of these filtration characteristic assessment tools, they still provide the most distinct and fundamental information about membrane aging and degradation in real time.

11.4.1.2 Surface characteristics

Two critical parameters that affect fouling on the membrane surface are membrane hydrophilicity and surface charge. After multiple cleaning cycles, the membrane surface properties are altered due to the exposure to harsh cleaning chemicals. Therefore, two analytical techniques are used to measure changes of these two parameters.

For surface hydrophilicity, contact angle measurements are conducted via the sessile drop technique, and the angle obtained determines the nature of the membrane surface. Streaming potential is an electrokinetic measurement used to characterise the membrane surface's zeta potential (see Figure 11.6). Membranes that were exposed to chlorine became more hydrophilic due to leaching of polymeric additives resulting in formation of larger pores. With chain scission, the membrane's surface charge was also

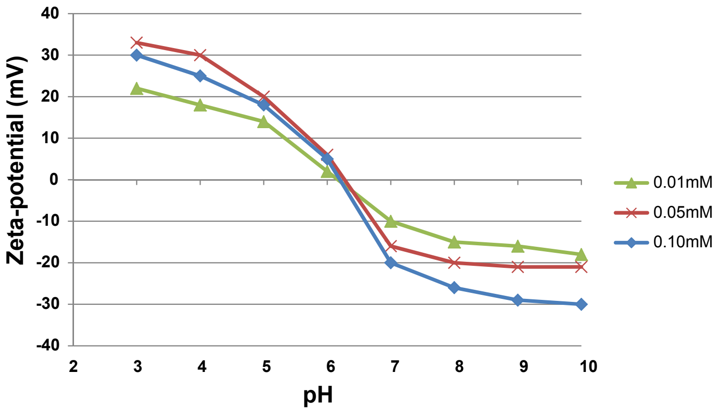


Figure 11.6 Streaming potential graph of membranes with varying additive concentrations.

altered, resulting in a more hydrophilic membrane surface (Arkhangelsky et al., 2007; Wang, Wang, Wu, Zhou, & Yang, 2010).

11.4.1.3 Chemical and structural characteristics

To assess the membrane's chemical and structural properties, two techniques are widely used. Attenuated total reflectance—Fourier transform infrared (ATR—FTIR) is used to identify the membrane's functional groups, and shifts in transmission peaks would mean that the membrane chemical structure was altered (see Figure 11.7). X-ray photoelectron spectroscopy (XPS) measures the elemental composition and chemical binding of the membrane surface. For both techniques, comparison of the results obtained from the virgin and aged membranes would provide a definitive conclusion as to whether the membrane was missing certain functional groups or there were chemical depositions on the membrane surface (Antony et al., 2010; Arkhangelsky et al., 2007; Puspitasari, Granville, Le-Clech, & Chen, 2010; Rouaix et al., 2006). ATR—FTIR is a qualitative measure of change, while XPS is quantitative, and thus these two techniques are complementary to one another.

Exposure to harsh chemical cleaning regimes can cause membrane polymer chain scission and breaking reactions resulting in an ageing membrane that has lost its functional groups, thus making it more susceptible to failure.

11.4.1.4 Mechanical and thermomechanical characteristics

Mechanical properties of the membrane such as the ultimate tensile strength, breaking force, yield stress, and Young's modulus are measured to determine whether ageing has occurred. Physical ageing of the membrane would result in an increase in yield stress and Young's modulus and a decrease in tensile strength and breaking force, indicating that the membrane has become stiffer, more brittle, and mechanically weaker (Arkhangelsky et al., 2007; Rouaix et al., 2006). It should be noted that results from

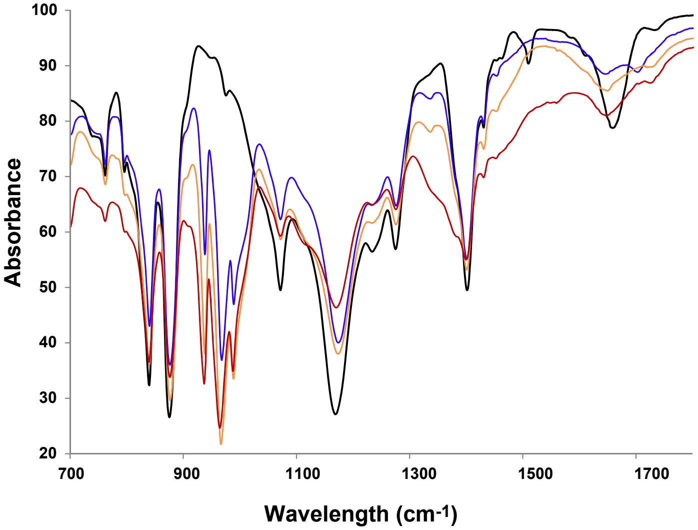


Figure 11.7 Typical Fourier transform infrared spectra for chemical functional group comparison.

each mechanical property have to be cross-referenced before a sound conclusion can be drawn with regard to the membrane's mechanical integrity.

Thermogravimetric analysis (TGA) is also used to detect loss of membrane material due to ageing (see Figure 11.8). TGA detects changes in the mass of the membrane sample as a function of both temperature and time. It is based on the principle that each polymeric material has a unique degradation temperature and disappearances of polymeric peaks at specific temperatures would indicate an alteration to the membrane's mechanical properties (Yadav, Morison, & Staiger, 2009).

11.4.1.5 Morphological characteristics

To have a better understanding of the membrane's surface morphology, microscopic visualisation techniques are used. Atomic force microscopy (AFM), scanning electron microscopy (SEM), and field emission scanning electron microscopy (FESEM) are visualisation techniques that can provide accurate, high-resolution images of various membrane characteristics.

AFM is widely used to determine surface morphology and roughness via a precision tip that is dragged along the membrane surface. The repulsive interaction between the surface and the tip is measured, and a micrograph based on the force is measured. The micrograph provides information on characteristics such as pore size distribution, surface roughness, and membrane surface charge interactions (Arkhangelsky et al., 2007; Hilal, Johnson, Bowen, & Williams, 2009). By comparing micrographs of the virgin and aged membrane samples, changes in the membrane's morphological characteristics can be detected and could help with assessing and predicting membrane ageing and failure.

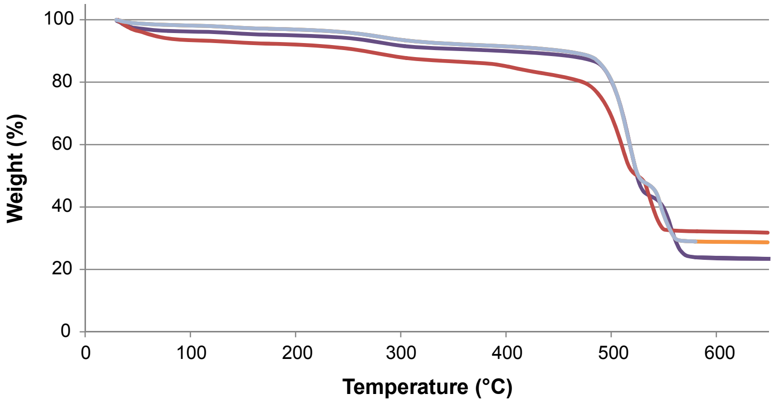


Figure 11.8 Typical thermogravimetric analysis thermogram profile of weight loss as a function of temperature.

SEM and FESEM are able to capture high-resolution images of the membrane surface and can provide detailed information that can aid in the understanding of degradation on the membrane surface. Through the captured high-resolution images, characterisation of the membrane's pore size, thickness, membrane symmetry, and physical damage that has occurred on the membrane surface can be performed. Changes in these parameters would indicate membrane ageing or failure. SEM is combined with energy dispersive X-ray spectroscopy (EDS) to characterise the chemical composition of the foulant on the membrane surface or the membrane itself (see Figure 11.9).

11.4.2 Membrane integrity tests

Membrane failure leads to the compromise of membrane integrity, resulting in pathogens being able to breach the membrane system and increase the microbial contamination risk of the treated water, and subsequently pose a serious threat to public health and safety (Phattaranawik, Fane, & Wong, 2008). Therefore, continuous

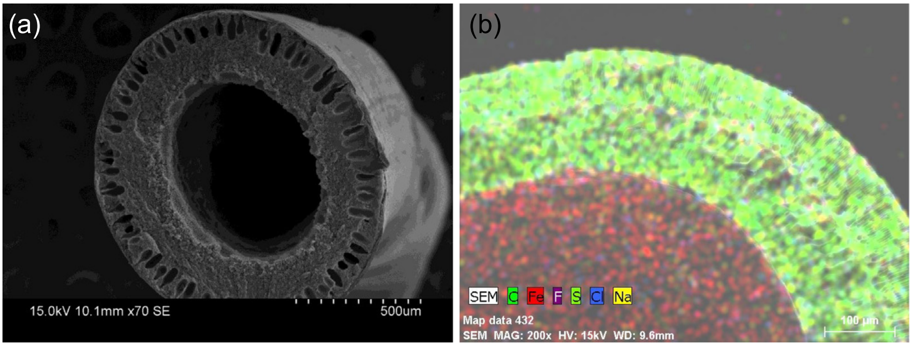


Figure 11.9 (a) Cross-sectional scanning electron microscopy image and (b) energy dispersive X-ray spectroscopy elemental map of a hollow-fibre membrane.

integrity monitoring and testing are required to ensure that pathogens are completely removed and the product water meets the regulatory guidelines. Membrane integrity testing can be divided into two groups, direct and indirect testing methods (Guo, Wyart, Perot, Nauleau, & Moulin, 2010).

11.4.2.1 Direct testing methods

Direct integrity testing methods refer to tests conducted on the membrane or membrane module directly and are the most obvious ways to determine membrane integrity. Table 11.3 below summarises the advantages and limitations of the conventional direct testing methods (Guo et al., 2010).

Pressure decay test

A PDT is a pressure-driven test that is widely used and accepted in the water industry as a way to evaluate the integrity of a membrane. During a PDT, one side of the

Table 11.3 Advantages and disadvantages of direct integrity tests

Direct integrity test	Advantages	Disadvantages
Pressure decay test (PDT)	• Independent of feed water quality • Ease of application • High sensitivity • High reliability • Low maintenance of test equipment • Well-established technique	• Performed offline • Limited by membrane's bubble point • Requires a large range of pressures • No information of filtrate quality
Diffusive air flow (DAF) test	• Independent of feed water quality • Higher sensitivity than PDT • Ease of application	• Performed offline • No information of filtrate quality
Vacuum decay test (VDT)	• Independent of feed water quality • Higher sensitivity than PDT	• Performed offline • No information of filtrate quality • Difficult for large-scale systems
Acoustic sound test (AST)	• High failure detection accuracy • Online operation • Simple and nondestructive	• No information of filtrate quality • Dependent on back-ground noise and interferences • Requires competent operator training

membrane is drained and pressurised up to the test pressure, which is set below the membrane's bubble point. The pressure is held for a specific duration, and the pressure decay is monitored. It is normal for minor pressure decay (0.5−1.5 kPa) due to air diffusion across the membrane; however, a faster decrease in pressure would indicate that the membrane's integrity has been compromised (ASTM, 2013).

PDT is a reliable membrane integrity monitoring technique, because it is sensitive to leak detection and integrity breaches, but can only be performed offline, resulting in membrane system downtime. Because the membrane is subjected to pressure during the PDT and with the effects of membrane ageing or the membrane being not wetted properly, membrane breakage can occur during PDTs, and thus may yield a false-positive result (USEPA, 2005).

Diffusive air flow test

The diffusive air flow (DAF) test is based on the same principle as the PDT. Instead of measuring the pressure decay rate in the PDT, DAF tests measure the rate of liquid displaced by the diffusive air flow. DAF is also limited by the same disadvantages as the PDT, but is more sensitive when detecting integrity changes at levels of greater than six LRV. Leaks in the additional pipework required for DAF tests could affect the sensitivity of the integrity tests and thus might not be feasible for routine use in large scale plants.

Vacuum decay test

The vacuum decay test (VDT) is very similar to the PDT, but instead of pressurising the drained side, a vacuum is applied, and the vacuum pressure decay is measured. This method is more sensitive than a PDT because it negates the effect of air diffusion through the membrane and can also detect points of leakage and is nondestructive. However, this method is rarely used in large-scale membrane systems (Guo et al., 2010).

Acoustic sound test

A more novel approach to direct integrity monitoring is the acoustic sound test (AST). This technique entails the use of an accelerometer to detect the vibrations generated by air leaks in the membrane module. This process is time-consuming and, in practice, is used in conjunction with a PDT. PDT is first used to detect any breaches in the module, and AST is then used to accurately pinpoint the location of the defect so the membrane can be isolated for replacement or repairs (Johnson, 1998). The advantage that AST has over other direct integrity tests is that it can be performed online while membrane operation is on, thus cutting down on the plant's downtime. However, AST's acoustic detection is hampered significantly by background noises and high-process flow rates; therefore, it has yet to be implemented in a large-scale system (Laîne, Glucina, Chamant, & Simonie, 1998).

11.4.2.2 Indirect testing methods

Indirect integrity testing methods often involve measuring a specific parameter of the product water and is used to represent the integrity of the membrane. The sensitivity of the chosen test should be relatively high so as to detect minor fluctuations in a measured parameter. This would ensure that the treated water achieves the targeted LRV and meets regulatory requirements. Table 11.4 summarises the pros and cons of indirect testing methods used by industry (Guo et al., 2010).

Particle counting and monitoring

Particle counting and monitoring is a laser-based light scattering technique used to count the number of particles of a specific size in the feed and filtrate. It is an

Table 11.4 **Advantages and disadvantages of indirect integrity tests**

Indirect integrity test	Advantages	Disadvantages
Particle counting	• Ease of application • Independent of membrane configurations • Online operation	• Low detection sensitivity • Dependent on feed water quality and operating conditions • Relatively high cost to install and maintain
Particle monitoring	• As per particle counters • Cheaper than particle counting • More sensitive than turbidity monitors	• As per particle counters • Not widely used in water industry
Turbidity monitoring	• As per particle monitoring • Well-established technique in water industry	• As per particle counters
Phage/Spore challenge testing	• Online operation • High sensitivity • High accuracy • Provides actual log removal value rates	• Long preparation time for microbial cultivation and analysis • Does not provide real-time integrity results
Powdered activated carbon (PAC) challenge testing	• Online operation • High sensitivity	• High PAC feed concentration required • Difficult to ensure uniform PAC particle size • May cause membrane fouling
Fluorescent/Magnetic particles challenge testing	• Independent of feed water quality • Online operation • High sensitivity • Can detect virus-sized breaches	• May cause membrane fouling • Not a well-established technique • Not tested on industrial scale

in situ monitoring technique and can be applied to membrane systems of varying configurations. The measurement sensitivity of the particle counter is directly related to the size or size distribution of the particles measured and increases as the particle measurement threshold is reduced (Guo et al., 2010). Therefore, the particle counter should have a low threshold that suits its application, because the more sensitive the counter is, the more expensive it becomes as well.

Particle counters do suffer from a number of distinct disadvantages. They can only measure particles of a specific size and thus have no selectivity in particle size measurements and would produce false readings when micro air bubbles are present in the permeate stream. In a full-scale plant study carried out by Landsness, in which fibres were progressively cut and the particle count measured, the particle count measurements were inconsistent, thus suggesting that particle counting might not be suitable for full-scale membrane plants (Landsness, 2001).

Particle monitoring uses the same principle as particle counters except that it provides a qualitative assessment of the particle size distribution of the feed or filtrate. It is therefore cheaper than particle counting, but is less sensitive (Banerjee, Lambertson, & Carlson, 1999).

Turbidity monitoring

Turbidity is described as the opaqueness of a fluid due to the presence of suspended solids and is measured in terms of nephelometric turbidity units (NTU). The turbidity of the feed and filtrate is monitored and a noncompromised membrane should be able to reduce the turbidity by at least 90%. This is cheaper than particle counting and monitoring; however, even treated water with a turbidity less than 0.1 NTU could still have bacterial contamination (Banerjee, Lambertson, Lozier, & Colvin, 2001). In the same study carried out by Landsness, an insignificant change in turbidity (0.024−0.037 NTU) was observed when 200 fibres were intentionally cut (Landsness, 2001). Consequently, turbidity monitoring has limited sensitivity for detection membrane breaches.

Phage and spore challenge testing

Phage and spore challenge tests are microbial integrity tests that are spiked into the feed water and subsequently measured in the permeate. Microbial tests are easy to implement, can be done online in situ with membrane system operation, and are nondestructive. Depending on the application and site-specific considerations, the correct surrogate should be chosen for the challenge tests.

Bacteriophages are virus-infected bacteria surrogates that are used in regulatory required challenge tests to determine membrane integrity and LRV of treatment plants. MS2 bacteriophage is the most common surrogate, given its similarly to enteric viruses (Antony et al., 2012). Despite the advantages of bacteriophage and spore challenge testing, there are also disadvantages. Microbial challenge testing requires the long lead time for preparation and cultivation of the surrogate phage. It also entails a lengthy analysis after sampling due to the complexity of plaque forming unit (PFU) counting; thus, bacteriophage challenge testing cannot provide real-time membrane integrity information (Gitis et al., 2006).

With microbial testing, it is difficult to distinguish whether microbial reduction was due to biological inactivation or retention on the membrane surface. Not only are these phages prone to contamination from other viruses, they can also accumulate in the permeate piping system and lead to false-positive membrane breach detection (Guo et al., 2010).

Powdered activated carbon challenge testing

An alternative that mitigates the disadvantages of microbial challenge testing is powdered activated carbon (PAC) challenge testing. It is based on the same principle as its microbial counterpart, with the only difference being small, controlled doses of PAC are spiked into the system instead of bacteriophage or spore surrogates. The PAC particle size has to be in the similar size range as *Giardia* and *Cryptosporidium* so as to mimic microbes (Van Hoof, Broens, Nahrstedt, Panglisch, & Gimbel, 2003). This method relies on particle counters and thus suffers from the drawbacks of particle counting. In addition, the sensitivity of the test is largely affected by the particle size distribution of PAC and could lead to membrane fouling if not monitored properly.

Fluorescent and magnetic particles challenge testing

Another novel surrogate challenge testing option is to either tag particles with fluorescent or magnetic materials. Fluorescent tagged particles can be easily detected by measuring the intensity of fluorescence. A high fluorescent intensity indicates a large amount of particles. It should be noted that the mass of the particle should be below 1 μg so as to maintain the linear relationship between mass and fluorescence. Likewise, particles tagged with magnetic materials such as iron can be easily detected and collected after the testing (Choi, Yang, Suh, & Cho, 2011). Notwithstanding these advantages, fluorescent and magnetic surrogates do experience similar disadvantages as the other challenge testing methods and thus are not widely used in the water industry.

11.5 Membrane ageing control methods

Membrane ageing and failure are the main challenges faced by water treatment plants that use membrane systems for water treatment and recycling. Membrane degradation and failure increases the rate at which the membranes would need to be replaced and thus makes membrane filtration more costly. Given that membrane ageing eventually leads to membrane failure, more emphasis should be placed on controlling membrane ageing so as to limit the occurrence of membrane failure.

11.5.1 Membrane train redundancies

The traditional “belt and braces” approach in engineering relies on implementation of multiple process redundancies. Redundancies can be either active or standby. In the water treatment industry, active redundant membrane systems reduce the load on one particular membrane train by sharing the overall processing load over multiple redundant trains when a surge in influent flow is detected. Standby trains, on the other hand, do not come into operation until a failure has occurred and the redundancy is called into service to maintain the water treatment system's functionality and treated water quality. Therefore, having standby redundancies would maintain the membrane filtration unit's efficiency and performance, but it will also lead to a higher capital and operational expenditure, thus highlighting the need for membrane process reliability modelling.

11.5.2 Membrane modification

Polymeric membranes are often used in various chemical-based environments and are highly susceptible to membrane degradation due to chemical exposure. Therefore, one effective way to mitigate this issue is to develop new polymeric membranes with surface modifications. The chemistry of the surface properties of microporous and semiporous membranes are changed via a surface coating. These coatings would render the membranes fouling resistant, antimicrobial, and chlorine resistant (Geise et al., 2010; Mansouri, Harrisson, & Chen, 2010).

From studies conducted, it has been proven that membranes become fouling resistant after different modifications. An increase in the membrane surface's hydrophilicity does decrease fouling, because this prevents hydrophobic organic foulants from being attracted onto the membrane surface. Changing the surface charge of the membrane can also aid the membrane in becoming more antifouling. Similar to increasing hydrophilicity, changing the surface charge would generate a repulsive force between the membrane surface and the charged ions of the foulant, thus preventing foulant deposition (Rana & Matsuura, 2010).

Formation of biofilms or membrane biofouling has adverse effects on both membrane filtration flux and the membrane's lifespan. Biofouling is unlike other forms of fouling that can be reduced by effective pretreatment of the feedwater due to the self-replicating nature of microbial organisms. Biofouling starts with the initial deposition of a film of organic molecules and is followed by bacterial colonisation. As the biofilm matures, a fouling layer builds up and thus leads to a decline in membrane flux. It has also been reported that biofouling in the feed channel can lead to a severe increase in internal pressure drop and, in some cases, result in deformation and damage to the membrane module (Mansouri et al., 2010).

To control biofouling, chlorine is often used as a disinfectant, but it suffers from the negative side effects of chlorine on membrane surfaces. Thus, chlorine resistance and surface modification are highly favoured modifications given the high cost involved in the dechlorination–rechlorination process and replacement of membranes in water treatment plants.

More recently, nanoclay nanocomposites have been added to flat sheet membranes to increase the membrane's abrasion resistance. The study concluded that the membrane with 1 wt% nanoclay showed superior abrasive resistance, with the membrane lasting two times longer than a normal membrane without the nanoclay addition. However, the nanoclay concentration would require further optimisation work because an increase in the concentration resulted in a decrease in the membrane's permeability and adverse changes in the membrane's essential mechanical properties (Lai, Groth, Gray, & Duke, 2014).

11.6 Conclusion

Currently, there are no standard protocols for assessing the membrane's mechanical integrity after prolonged membrane operation, and although there are multiple modes and mechanisms that can result in membrane failure, membrane ageing and degradation due to chemical attack via strong oxidants is the most common. With better characterisation of the effects and quantification of membrane ageing at different stages of a membrane's lifespan, membrane ageing can be mitigated, thus prolonging the lifespan of the membrane while still maintaining its resilience and reliability. With the ever-improving membrane modifications being developed, the effects of membrane ageing can be further controlled, thus making membranes more robust, cost-effective, and efficient for water treatment processes.

11.7 Future trends

The current state-of-the-art of membrane integrity monitoring tools is limited to detecting compromises via a variety of in situ and ex situ techniques and tools. Despite extensive research performed on membrane failure mechanisms and their resultant effects, these studies are often based on ex situ analytical techniques and can only provide information when a serious breach in membrane integrity is detected. Therefore, this highlights the need for the development of nondestructive, computer-aided modelling techniques to predict and quantify membrane ageing at various stages of membrane operation through to the end of the membrane's lifespan.

11.7.1 Membrane failure prediction

Apart from monitoring membrane ageing and detecting integrity breaches and failure, another method to limit and control membrane degradation is membrane failure prediction. Prediction of failure in membrane systems is achieved via a finite element method, known as finite element analysis (FEA). FEA is a computer-aided modelling technique that can perform mechanical analyses on structures to compute displacements from applied loads and is a tool that is widely used by structural and mechanical engineers (Nicholson, 2003). It has also been used by biomedical engineers to predict stress distribution within teeth for tooth fracture prediction (Xie, Swain, & Hoffman, 2009).

FEA can determine stress, strain, and displacements in complicated shapes by first dividing the complicated structure into smaller elements, and this process is known as discretisation. Simple equations are then used to solve each element. Once all the smaller elements are solved, the equation for the whole structure can then be solved, and thus generating the stresses, strains, and displacements on the entire structure. Through FEA, stresses at the locations where they are most likely to cause failure can be determined. Such analyses would aid in design of membrane modules and optimisation of operation protocols. FEA can also be diagnostic by providing supportive interpretations via simulation at similar operation conditions when performing autopsies on failed membranes and modules. FEA with ageing monitoring tools will yield a more comprehensive understanding of membrane aging and failure and their mechanisms, as well as allow for better process efficiency through improved module design.

11.7.2 Membrane reliability modelling

The evaluation of a membrane process unit's reliability should be an important part of its design and operation. However, this has traditionally been difficult to assess and quantify, and as a consequence, its management has largely been ignored. Reliability modelling can be used throughout the membrane module's life cycle to predict the failure and the subsequent process shortfalls. This would also yield significant savings on capital and operating costs via the implementation of better strategies derived from the simulation's results, while enabling utilities and plant designers to effectively manage and quantify the risk of noncompliance due to membrane failure. With the use of reliability modelling, membrane process performance is no longer just limited to membrane fouling, but can now encompass membrane ageing and failure.

List of acronyms

AST	Acoustic sound test
AFO	Amorphous ferric oxide
AFM	Atomic force microscopy
ATR−FTIR	Attenuated total reflectance−Fourier transform infrared
CIP	Cleaning in place
DAF	Diffusive air flow
EDS	Energy dispersive X-ray spectroscopy
FESEM	Field emission scanning electron microscopy
FEA	Finite element analysis
LRV	Log removal values
MF	Microfiltration
MLD	Megaliter per day
MTBF	Mean time between failure
MTTF	Mean time to failure
MTTR	Mean time to repair
MWCO	Molecular weight cut-off
NTU	Nephelometric turbidity units
PFU	Plaque forming unit
PAC	Powdered activated carbon

PDT	Pressure decay test
RCM	Reliability centred maintenance
RO	Reverse osmosis
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
TFC	Thin film composite
UF	Ultrafiltration
VDT	Vacuum decay test
XPS	X-ray photoelectron spectroscopy

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Mathematical modeling of membrane operations for water treatment

12

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12.1 Introduction

This chapter will review the mathematical modeling used in water treatment plants that incorporate membranes in the operation processes. Recently, more and more water treatment plants have chosen membranes as the alternative process in producing clean and potable water due to the process' advantages over conventional treatment processes. Hence, a short review about the different mathematical equations used in water treatment processes with different types of membranes should be carried out. The first section will briefly introduce the current development trend in the water treatment sector and the reasons behind the change. The second section will focus on the mathematical models used in membrane water treatment processes. It reveals the main mechanisms of transport in membranes, introduces the fundamentals of membrane fouling, elaborates the phenomenon of concentration polarization (CP), and the derivation of the equation. The design equation used in membranes processes, according to the type of membranes, will be briefly covered, too. The following sections will cover the design equations used in nanofiltration (NF) and reverse osmosis (RO) membranes and discuss the derivation and use of mathematical equations for microfiltration (MF)/ultrafiltration (UF) membranes under different conditions. The last part of this chapter provides information about the importance of mathematical modeling in membrane operations for water treatment plants and will look into the future trends and challenges.

12.1.1 Water treatment process and its trend

Water scarcity has becomes a worldwide problem that threatens our daily activities and sustainable developments. One of the main factors that contributed to this problem is the reduction in clean water resources due to pollution. Pollution, especially from industry and agriculture, has introduced toxins, pesticides, herbicides, heavy metals, and deleterious chemicals/residues into our watercourse. Conventional water treatment plants that use chemical and physical processes are not able to remove those contaminants and are unable to produce consumable water with required

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qualities (Gibs et al., 2007; Harisha, Hosamani, Keri, Nataraj, & Aminabhavi, 2010; Radjenović, Petrović, Ventura, & Barceló, 2008; Saitúa, Giannini, & Padilla, 2012; Sarkar, Venkateshwarlu, Rao, Bhattacharjee, & Kale, 2007).

Besides the limited clean water resources, several other challenges are also creating tension in potable water supply, such as high blooming population and rapid urbanization, stringent regulations for potable water, uncertainty in climate changes, overuse, and improper management of water resources. All these factors, coupled with the underperformance of conventional water treatment processes, have led to the search for new technologies for a better, safer, and stable potable water supply. One of the most popular alternatives is the membrane process in drinking water production plants. In recent years, membrane technology has emerged as one of the main processes to resolve the problem of water scarcity. The membrane process is very versatile, and it has been used for desalting, softening, and the removal of dissolved organics, color, particles, and microbes. Its performance has been proven to be better than conventional water treatment methods. Hence, the shortcomings of conventional water treatment processes and the strengths of membrane technology have been the reasons that contribute to the trend of membrane processes for water treatment.

Basically, four types of membranes, MF, UF, NF, and RO have been widely used in the drinking water industry. A number of water treatment plants have already implemented membrane-based processes, and the outcomes were encouraging, with the performances of membrane filtration better than those of conventional processes. Hence, the focus now is on the track to optimize the membrane filtration process and reduce the fouling problems that might affect a membrane's rejection capabilities.

12.2 Mathematical modeling

Modeling of membranes is very important because it will allow users to obtain useful information, especially on a membrane's ability in retaining certain solutes and allowing the permeation of particular substances. The mechanism of permeation and rejection of membrane is a complicated process. Thus, a good predictive model will enable the performance of the membrane to be predicted accurately without involving tedious and complicated procedures to obtain raw data for prediction and enhance the efficiency of the process by optimizing it. A reliable modeling will result in a smaller number of experiments and, consequently, a reduction in cost and time (Hilal, Al-Zoubi, Darwish, Mohammad, & Arabi, 2004). Normally, in the membrane process, two aspects of performance will be predicted by using modeling: flux prediction and rejection prediction (Van der Bruggen, Mänttäri, & Nyström, 2008). Several theories and models have been proposed for membrane transport mechanisms to derive an acceptable model. The models used for each membrane might be different due to the difference in membranes properties. Several types of fouling also affect the complication of the models. Further details will be elaborated in the following section.

12.2.1 Transport and fouling mechanisms for membranes

Transport mechanisms of solute/solvent molecules through membranes are shown in Figure 12.1. Generally, there are four types of transport mechanisms (Seader & Henley, 1998):

1. Bulk flow through pores
2. Diffusion through pores
3. Restricted diffusion through pores
4. Solution-diffusion through dense membranes

Different types of membranes will have different transport mechanisms applied on them. For example, an RO membrane is a dense membrane, so the transport of components through the membrane will be a solution-diffusion type, while for microporous membranes such as MF and UF, the transport mechanisms will involve the pore size of membranes. NF membranes show a behavior between dense and microporous membranes. In addition, size exclusion and electrostatic interaction are the two fundamental phenomena that govern the solute rejection by RO/NF. The transport mechanism will determine how the performance (flux and rejection) of membranes are being modeled in the water treatment process. Figure 12.2 shows a simple classification of transport models for the four membranes discussed in this chapter and the factors that affect the type of transfer models to be used in water treatment (Mulder, 1996; Shon, Vigneswaran, Kandasamy, & Shim, 2008; Wiesner & Buckley, 1996; Williams, 2003).

From Figure 12.2, it can be seen that the transport models used to predict and describe the water treatment process depend on the membranes used and the foulants in the raw water. Membrane class is further separated into porous and nonporous types, each one having its own suitable equations/theories for mathematical modeling. For foulants, its characteristic will determine which model is the most suitable and accurate in describing the retention mechanism. Indeed, transport mechanisms rely on a combination of several principles, including size exclusion and charge or dielectric exclusion (DE) (Yaroshchuk & Staude, 1992). For uncharged solutes, sieving effect or steric hindrance will be the main rejection mechanism. Solutes with larger molecular weight cutoff than the membrane will be retained. Besides that, the transport of uncharged solutes is also contributed by convection due to pressure difference and

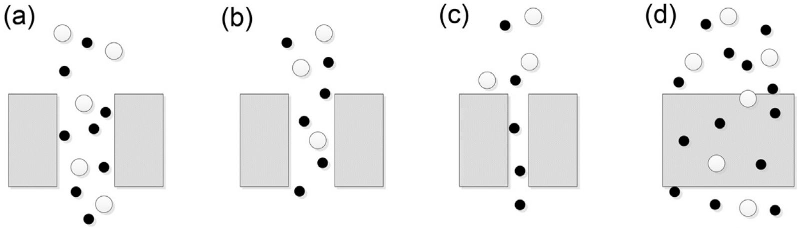

Figure 12.1 Transport mechanisms in membranes. (Flow is downward.) (a) Bulk flow through pores; (b) Diffusion through pores; (c) Restricted diffusion through pores; (d) Solution-diffusion through dense membranes.

Source: Adapted from Seader and Henley (1998).

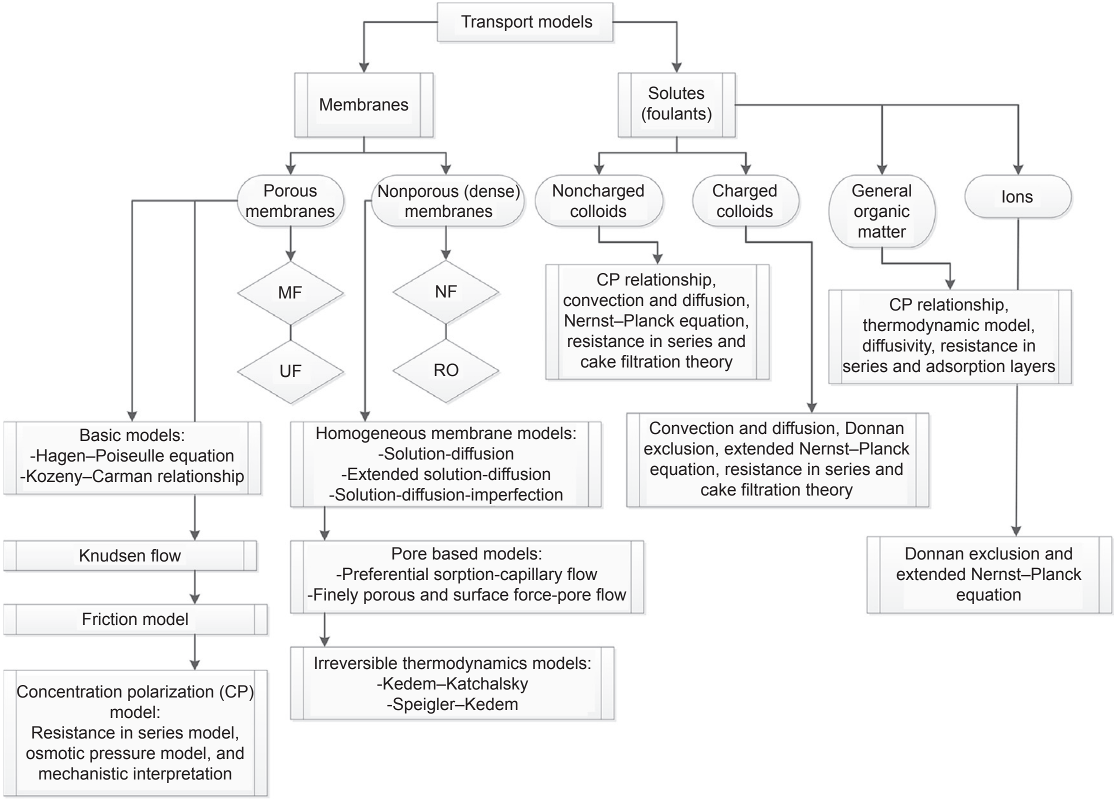

Figure 12.2 Classification of transport models according to the type of membranes and foulants.
Source: Adapted from Williams (2003), Mulder (1996), Shon et al. (2008) and Wiesner and Buckley (1996).

diffusion through a concentration gradient across the membrane. The main transport mechanism of charged solutes (ions) is charged exclusion or the Donnan effect, which involves the interaction between the rejection of co-ions and the fixed electric charges attached to the membrane matrix (Hassan, Ali, Abdull, & Ismail, 2007). Some of the commonly used transport models will be discussed in the following sections. It should be noted that so far, there is not any mathematical modeling that is valid for wide-range applications. Most of the established models are only applicable for certain and specific conditions.

Fouling is a major obstacle for membranes to be used widely. Fouling may exist in different forms (Field, 2010):

1. Adsorption—occurs when there are specific interactions between the membrane and foulant/solute in the solution,
2. Pore blockage—foulants/particles block and clog the pores of membrane,
3. Deposition—deposit of particles that grows layer by layer at the membrane surface (known as cake resistance fouling as well),
4. Gel formation—CP leads to the formation of a gel layer in the immediate vicinity of the membrane surface.

Fouling will affect membrane flux and rejection of unwanted components in water. Hence, modeling of membrane performance in water treatment should take into account membrane fouling, because fouling phenomena is unavoidable for current stage.

12.2.2 Concentration polarization

CP is a process of accumulation of retained solutes in the membrane boundary at the feed side. It is a natural consequence of membrane selectivity (Field, 2010). CP complicates the modeling of the membrane filtration unit, because the wall concentration of solute is not the same as the bulk feed concentration. It is difficult to determine the solute wall concentration. The boundary layer film model has been used to describe this phenomenon. Under steady-state conditions, the convective flow of solute to the membrane surface is equal to the solute that permeates through the membrane deduct, with diffusion of solute back to the bulk feed solution (as shown in Eqn (12.1)).

$$J \cdot C = J \cdot C_p - D_{ji} \frac{\mathrm{d}C}{\mathrm{d}z} \tag{12.1}$$

Integration of Eqn (12.1) with the following boundary conditions:

$$z = 0 \quad C = C_m$$

$$z = l_{bl} \quad C = C_b$$

will yield Eqn (12.2):

$$J = \left(\frac{D_{ij}}{l_{bl}}\right) \ln\left(\frac{C_m - C_p}{C_b - C_p}\right) \tag{12.2}$$

At the end, this equation derived from film theory model will be used to determine the solute concentration at the membrane surface. Rearranging Eqn (12.2) yields:

$$C_m = (C_b - C_p)\exp\left(\frac{J \cdot l_{bl}}{D_{ij}}\right) \tag{12.3}$$

Solute concentration at the membrane surface is very important because it will be used in many membrane transport models.

Usually, the term D_{ij}/l_b in Eqns (12.2) and (12.3) will be described as a mass transfer coefficient $k_{i,b}$, and it can be determined from conventional chemical engineering correlations, such as the Sherwood number (Sh), Reynolds number (Re), Schmidt number (Sc), and Peclet number (Pe) (Baker, 2000; Field, 2010). The bulk and permeate concentrations can be determined by using analytical instruments.

CP might have some negative effects on the performance of a membrane filtration unit. It will decrease the water flux and rejection of undesired solute, cause precipitation due to high surface concentration that exceeds the solubility limit, change the membrane separation properties, and enhance other fouling such as colloidal or particulate materials that will block the membrane surface. Hence, the design of the membrane module and operating conditions are important to prevent and reduce the impact of CP.

12.2.3 Mathematical modeling for RO membranes

RO is a process especially applied in desalination that uses membranes only permeable to water but impermeable to salt and other impurities. Many mathematical models have been proposed for the solute and solvent transport mechanism, and the most acceptable and widely applied is solution-diffusion transport mechanism. The water transport across the membrane can be expressed by Fick's law (Baker, 2000). With some assumptions and further derivation, the equation is reduced to a formula in which the water flux is linked to pressure and concentration gradients across the membrane. For solute flux, it depends on salt concentration at the feed side and permeate side.

Design equations for RO membranes will be based on the solution-diffusion transport mechanism. Water flux and solute flux are expressed as (Baker, 2000):

$$J_w = P_w(\Delta p - \Delta\pi) \tag{12.4}$$

$$J_s = P_s(C_1 - C_2) \tag{12.5}$$

One of the considerations when deciding on the operating pressure for RO is the osmotic pressure of the liquid feed. Osmotic pressure is being defined as the pressure required to be applied to a solution to prevent the inward flow of water across the membrane. For small to minimum concentration of solute, osmotic pressure, π, is directly proportional to the concentration of the solute and temperature, according to the experimental data done by other researchers (Senthilmurugan, Ahluwalia, & Gupta, 2005). Osmotic pressure can be calculated by using the formula proposed by Van't Hoff (Geankoplis, 2003) or using the Pitzer equation (Hu, Wu, & Gao, 1999). However, the calculation steps of the Pitzer equation are complicated, as shown in the reference cited. So here is the easier form of Van't Hoff equation:

$$\pi = \frac{n}{V_m} R_G T \tag{12.6}$$

However, this equation is suitable for dilute water solutions. For solutions with high concentration of solutes, modifications have to be made. For concentration of dissolved solids in the range of 20,000–50,000 ppm, the osmotic pressure can be calculated from the equation modified by (Kaghazchi, Mehri, Ravanchi, & Kargari, 2010):

$$\pi = 0.9524C^2 + 81633C - 236143 \tag{12.7}$$

Hence, the osmotic pressure gradient is:

$$\Delta\pi = \pi_m - \pi_p = 0.9524\left(C_m^2 - C_p^2\right) + 81633\left(C_m - C_p\right) - 23614 \tag{12.8}$$

in which the concentration of a solute at the membrane surface could be obtained from the CP correlation.

An industrial seawater RO desalination plant with a spiral-wound module was simulated using the solution-diffusion model, and the model was found to be able to predict the steady-state behavior of the plant with good accuracy. Tables 12.1 and 12.2 show the comparison between the actual results from the industrial unit and calculated data from the solution-diffusion model. It can be concluded that the mathematical model has a good accuracy of prediction for that particular seawater RO desalination plant (Kaghazchi et al., 2010).

Besides the well-known solution-diffusion model (under the category of nonporous or homogeneous membrane models as depicted in Figure 12.2), RO transport models can be derived from one of two main groups: irreversible thermodynamics models and porous models (Gambier, Krasnik, & Badreddin, 2007). Table 12.3 presents a summary of available transport models and basic equations for determining the solute and solvent fluxes for RO membranes (Malaeb & Ayoub, 2011). Details of derivation can be found in the reference cited.

Models based on irreversible thermodynamics treat the membrane as a black box. One of the irreversible thermodynamics models is the Spiegler–Kedem model. This black box approach allows the performance of the membranes to be characterized in terms of salt permeability, P_s, and the reflection coefficient, σ (Levenstein, Hasson, & Semiat, 1996; Schirg & Widmer, 1992; Xu & Spencer, 1997). No particular mechanism of solute transport and structure of membrane are required.

Table 12.1 **Simulation results of the first industrial unit**

Parameter	Industrial unit	Calculated	Error (%)
Permeate flow rate (m^3/s)	8.30×10^{-5}	7.53×10^{-5}	9.3
Permeate concentration (kg/m^3)	0.61	0.60	1.1
Concentrate flow rate (m^3/s)	2.25×10^{-3}	2.23×10^{-3}	0.9
Concentrate concentration (kg/m^3)	64.11	64.72	0.9

Source: Kaghazchi et al. (2010).

There are several assumptions being made for the classical hydrodynamic or pore model. It is assumed that (Nakao, 1994; Zhao, Zhou, & Yue, 2000):

1. The membrane is crossed by cylindrical pores with uniform radius and length,
2. Solute molecules are simulated as rigid spheres moving slowly inside the pores,
3. Poiseuille flow applies in the pores of the solvent,
4. Steady-state flow occurs, and
5. Solute concentration is so small that there is no interaction among solute molecules inside the pores.

Membrane is being considered as a charged porous layer by steric hindrance pore (SHP) model and Teorell—Meyer—Sievers (TMS) model. The partitioning effects are described by steric hindrance and electrostatics, and mass transfer through the membrane is based on the extended Nernst—Planck equation. Space charge models of Spiegler-Kedem provide a relatively stable numerical solution, but are computationally expensive (Malaeb & Ayoub, 2011).

Agriculture and industry, the two largest water consumption sectors, have produced and released a lot of new contaminants into our various drinking water sources. Pesticides, herbicides, insecticides, pharmaceutical products, and heavy metals are a few of the emerging trace contaminants that currently receive more attention in water treatment plants. With the health threats from the emerging and newly discovered trace

Table 12.2 **Performance comparison between actual and simulated first unit**

Parameter	Industrial unit	Calculated	Error (%)
Recovery	0.0259	0.0233	0.03
Rejection percent	0.9902	0.9905	0.03

Source: Kaghazchi et al. (2010).

Table 12.3 Available transport models for reverse osmosis membrane

Models	Model reference	Basic features/equations
Models based on irreversible thermodynamics	Kedem and Katchalsky (KK) model	• Describes the flow of solution and solute, in which performance is measured through the dissipation function and does not address the mechanism of rejection $J_v = L_p(\Delta P - \sigma\Delta\pi)$ $J_s = P_s(c_m - c_p) + (1 - \sigma)J_v$
	Kedem−Katchalsky−Zelman model	• Proposed for the multiple solute system in membrane filtration • Considers the differential equations for the transport of multiple solutes and involves the usage of finite-difference equations
	Spiegler−Kedem model	• Accounts for the variability of the concentration profile at large fluxes and high concentration gradients • Transport through membrane is characterized by solvent and solute permeability and reflection coefficient • Calculated based on the average concentration inside the membrane • Mostly used in single-solute systems $J_s = -P'\left(\frac{\mathrm{d}c}{\mathrm{d}x}\right) + (1 - \sigma)J_v$
	Extended Spiegler−Kedem model	• A one-dimensional model for multiple solutes, incorporating solute−solute interactions • Characterized by parameters estimated using the Levenberg−Marquardt method coupled with the Gauss−Newton algorithm and based on experimental data from the literature

Continued

Table 12.3 Continued

Models	Model reference	Basic features/equations
Stefan-Maxwell model	Peppas & Meadows (1983); Roberson & Zydney (1988)	• Have shown to be equivalent to models based on irreversible thermodynamics $J_s = -D_2 C x_s \frac{\mathrm{d}\ln(y_s x_s)}{\mathrm{d}z} + \frac{D_2}{D_1} J_v C x_s$ x_s is the solute mole fraction; y_s is the solute activity coefficient; C is the total molar concentration; and D_1 and D_2 are overall transfer coefficients given in terms of the binary Stefan-Maxwell diffusivities
	Teorell-Meyer-Sievers (TMS) model (Hassan et al., 2007)	• Describes the membrane electrical properties in terms of effective charge density and electrostatic effects • Assumes a uniform radial distribution of fixed charges and mobile species $\sigma_{\mathrm{salt}} = 1 - \frac{2}{(2\alpha - 1)\zeta + (\zeta^2 + 4)^{1/2}}$ $P_{\mathrm{salt}} = D_s(1 - \sigma_{\mathrm{salt}})\left(\frac{A_k}{\Delta x}\right)$
	Space charge model	• Suggests a radial distribution of the potential and concentration gradient across the pores • Ions are treated as point charges, so steric effects of the size of ions are neglected

		• The Nernst–Planck equation is used for ion transport, the nonlinear Poisson–Boltzmann equation for ion concentration and radial distribution of electric potential, and the Navier–Stokes equation for the force balance in narrow pores relative to pore length
Hydrodynamic or pore models	Pappenheimer (1953)	Solute flux due to diffusion only: $J_s^d = -D_o f(q) S_D A_k \mathrm{d}C/\mathrm{d}x - D_{\mathrm{eff}} A_k \mathrm{d}C/\mathrm{d}x$ S_D: steric factor restricting the entrance of the molecule into the pore $f(q)$: viscous drag at the wall once the molecule has entered the pore D_o and D_{eff}: diffusion coefficients in a free solution and in a pore, respectively A_k: corresponds to the membrane surface porosity $S_D = (1-q)^2 f(q) = 1/(1+2.4q)$
	Renkin (1954)	Solute flux is given in terms of both diffusion flow and convection flow: $J_s = D_o(q) S_D A_k (C_m - C_f) + f(q) S_c J_v C_m$ The restriction factor S_c for the convection flow is introduced: $S_c = 2(1-q)^2 - (1-q)^4$ $f(q) = 1 - 2.104q + 2.09q^3 - 0.95q^5$
	Verniory, DuBois, Decoodt, Gassee, & Lambert (1973)	• Modified the above classical pore models by adopting a wall correction factor and relating it to the treatment with thermodynamic and frictional forces: $J_s = D_o f(q) S_D A_k \Delta C_s / \Delta x + g(q) S_c J_v \overline{C_s}$ • Introduced the convective friction forces function, $g(q)$ in addition to $f(g)$: $f(q) = (1 - 2.105q^2 + 2.865q^3 - 1.7068q^5 + 0.72603)/(1 - 0.75857q^5)$ $g(q) = (1 - 2/3q^2 - 0.20217q^5)/(1 - 0.75857q^5)$

Continued

Table 12.3 Continued

Models	Model reference	Basic features/equations
	Steric hindrance pore (SHP) model	• Modified pore model by eliminating the wall correction factors used to predict pore radius and the ratio of membrane porosity to thickness • Particularly used for the permeation of a single neutral solute and not suitable for salt retention application $J_i = v_i k_i \left[H_{F,i} u_x c - H_{D,i} D_i \left(\frac{\mathrm{d}c}{\mathrm{d}x} + c\frac{z_i F \mathrm{d}\phi}{RT\mathrm{d}x}\right)\right]$ • The H_F and H_D parameters are for steric hindrance and frictional forces that impede convective and diffusive transport, respectively

Source: Malaeb and Ayoub (2011).

contaminants in natural water resources, membrane technology (RO/NF) has been suggested and accepted as the most appropriate method to remove them. Thus, mathematical modeling of the rejection of those trace contaminants is very useful in predicting the removal of deleterious substances in water.

The issue of boron in drinking water has received more attention judging from the increasing number of scientific investigations on the removal of boron by RO/NF membranes (Tu, Nghiem, & Chivas, 2010). Because boron exists in a solution in the form of boric acid and borate salts, the currently widely accepted solution-diffusion model can be used to explain the transport mechanism of boron through RO/NF membranes. Another model used to describe the transport of boron is the irreversible thermodynamics model developed by Kedem and Katchalsky (Kedem & Katchalsky, 1958). The transport equations of solution-diffusion and irreversible thermodynamics models have been presented above and in Table 12.3.

The detection of pesticides and endocrine compounds in natural water is of great concern to the public and especially potable water production plants (Cornelissen Verdouw, Gijsbertsen-Abrahamse, & Hofman, 2005). Pesticide removal by RO/NF is a complicated process. However, in general, there is ample evidence that the main mechanism that determines the retention of pesticides is size exclusion (sieving mechanism) (Plakas & Karabelas, 2012). For charged pesticides, both size exclusion and electrostatic interaction are the two mechanisms that are responsible in controlling the degree of separation. Few models have been applied to predict the trace organic rejection, and Table 12.4 shows the pros and cons of different models applied for modeling and predicting trace organic rejection by NF/RO membranes (Plakas & Karabelas, 2012).

In membrane water treatment processes, water temperature is an important factor that must be considered when operating the plants. Higher temperature will require lower operating pressure to produce the desired production capacity, and the reverse is true for low-temperature raw water. By assuming all the factors affecting performance of a membrane remain constant, the permeate flow at any temperature, relative to flow at 25 °C, can be estimated by (AWWA & ASCE, 2012):

$$Q_T = Q_{25^\circ\mathrm{C}} \times 1.03^{(T-25)} \tag{12.9}$$

This equation is applicable for both RO and NF membranes.

The selectivity of RO membranes normally will be measured as solute rejection coefficient as (AWWA & ASCE, 2012):

$$R = \frac{C_b - C_p}{C_b} \times 100\% = \left[1 - \frac{C_p}{C_b}\right] \times 100\% \tag{12.10}$$

Due to the high rejection of solute for RO membranes, the concentration of solute being retained at the membrane surface (feed side) will be very high. This leads to the problem of CP. The solute concentration at the membrane surface (feed side) will be different from bulk concentration. Hence, the film theory model is used to determine the solute wall concentration (as shown in the previous section). The solute wall concentration is required to obtain the real rejection percentage of the RO membrane.

Table 12.4 **Main advantages and disadvantages of the models applied for modeling and/or predicting trace organic rejection by nanofiltration/reverse osmosis membranes**

Models	Advantages	Disadvantages
Models based on irreversible thermodynamics (Spiegler—Kedem model, combined film theory-Spiegler—Kedem model, models with and without convection)	• No particular mechanism of solute transport and structure of membrane is specified (membrane treated as a "black box") • Suitable for predicting the performance of multiple solutes in nanofiltration/reverse osmosis systems	• Highly dependant on the driving forces (pressure and concentration gradients), which restricts their practical application • A number of assumptions made which in many cases are unrealistic • The system should not be too far from equilibrium in order for the model to be applicable • Valid for high rejection membranes
Mass transport models (solution-diffusion models, porous models, nonporous or homogeneous membrane models, etc.)	• Simple models providing estimates even for technically demanding separations • The linearization of these models facilitates rapid calculations	• Variation of the solute mass transfer coefficients with different water qualities and operating conditions; intrinsically membrane physicochemical properties constrains the model application from one system to another • Mainly applicable to single-solute systems • Solute mass transfer coefficients depend on the test unit scale (as different operating conditions may exist in these units), limiting the model accuracy in membrane scale-up
Artificial neural network models in conjunction (or not) with quantitative structure activity relationship models	• Easy to use • Do not apply any physical laws and transport phenomena, thus overcoming the problems of complexity • More accurate estimates than existing models • Valid models regardless of rejection performance of the membranes tested	• Specific; applicable in the range of experimental conditions employed for their development • Changes of membrane properties, as a result of fouling or swelling, influence the accuracy of models

Source: Plakas & Karabelas (2012).

The model equations for water and solute flux also will be changed after taking the CP effect into consideration. Concentration of solute at membrane surface could be obtained from the final derivation shown in previous subsection.

For rejection:

$$R_{\mathrm{CP}} = \frac{C_m - C_p}{C_m} \times 100\% = \left[1 - \frac{C_p}{C_m}\right] \times 100\% \tag{12.11}$$

The CP effect will be included in modeling for more precise prediction. An example is the incorporation of the CP ratio for tubular membranes in the turbulent region that has been derived out as shown below (Wiesner & Buckley, 1996):

$$\frac{C_m}{C_b} = \frac{1}{D_r} + \left[1 - \frac{1}{D_r}\right] \exp(k) \tag{12.12}$$

$$D_r = \frac{C_b}{C_p}$$

$$j_d = 0.023 Re^{-0.17}$$

By incorporating the CP ratio into the solution-diffusion transport equations for water and solute flux, the following equation could be obtained:

$$J_w = k_w\left(\Delta p - \Delta\pi\left(\frac{C_m}{C_b}\right) + \frac{\Delta\pi}{D_r}\right) \tag{12.13}$$

$$J_s = k_i C_b\left(\frac{C_m}{C_b} - \frac{1}{D_r}\right) \tag{12.14}$$

These equations allow the performance of RO membranes to be estimated and predict what the effect of CP would be on the given operating conditions.

12.2.4 Mathematical modeling for NF membranes

NF has been defined by many as a process between UF and RO. Indeed, NF is a very complex process. Generally, NF is a charged membrane, and the modeling must consider the interaction between the charged membrane and ionic solute. Many charged membrane transport theories have been proposed that account for electrostatic effects as well as diffusive and convective flow to describe the solute separation. Indeed, NF and RO membranes both share most of the same models, but under this subsection, a few models that are widely accepted for NF membrane will be discussed. One of them is the solution diffusion model, which has been depicted in the previous subsection. However, the most popular mathematical model for NF is the extended Nernst–Planck equation. It has been widely adopted for NF membrane modeling.

This equation consists of a few different terms that accounted for the different transport phenomena. Donnan effect and dieletric exclusion are included in this model.

The most commonly adopted form of the extended Nernst–Planck equation (Tsuru, Nakao, & Kimura, 1991) is:

$$J_i = K_{ic}c_iJ_v - D_{ip}\frac{\mathrm{d}c_i}{\mathrm{d}x} - \frac{z_ic_iD_{ip}}{R_GT}F\frac{\mathrm{d}\psi}{\mathrm{d}x} \tag{12.15}$$

The first term in Eqn (12.15) represents the solute flux contribution due to convection, the second term accounts for solute transport due to diffusion, and the last term describes the solute flux due to the Donnan potential (Williams, 2003). This extended Nernst–Planck equation will be the base model for other models. When a charged membrane is brought into contact with an electrolyte solution, the concentration partition of co-ions and counter-ions occurs at the membrane–solution interfaces on both the feed and permeate sides. The potential differences associated at these boundaries are called Donnan potentials, and Donnan potentials exist to maintain the electrochemical equilibrium (Nguyen, Bang, Cho, & Kim, 2009). The Donnan potential helps in repelling ions where co-ions are rejected because of the potential at the membrane-feed interface, whereas counter-ions are attracted (Greenlee, Lawler, Freeman, Marrot, & Moulin, 2009).

For uncharged solute transport through the membrane, the Donnan effect will not be considered, so the third term in Eqn (12.15) will be zero (Luo & Wan, 2011). The application of the modified extended Nernst–Planck equation for uncharged solutes can be obtained elsewhere (Bowen & Welfoot, 2005, 2002), and Figures 12.3 and 12.4 show the good agreement between the predicted and experimental data for organic solute (iminodiacetic acid, IDA, and glutamic acid, Glu) rejection by NF 270 membrane (Luo & Wan, 2011).

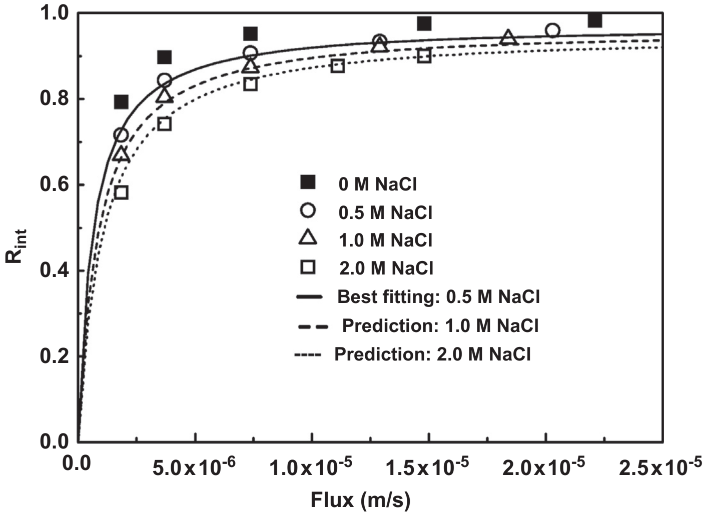

Figure 12.3 Measured and predicted iminodiacetic acid retentions for NF 270. Reprinted from Luo and Wan (2011), with permission from Elsevier.

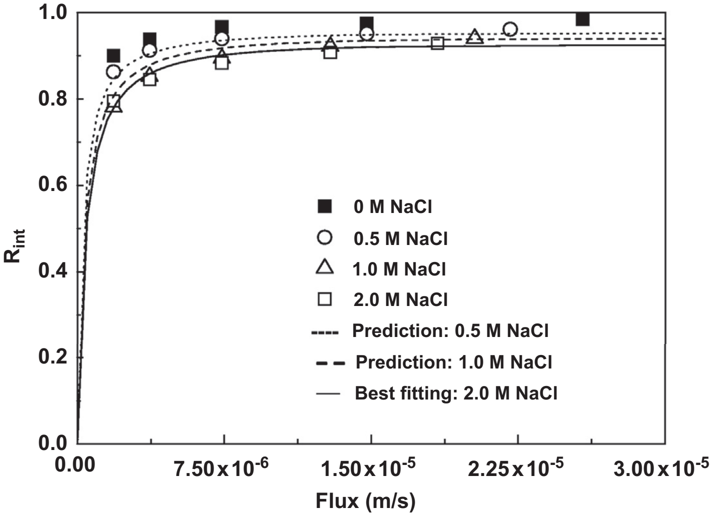

Figure 12.4 Measured and predicted glutamic acid retentions for NF 270.
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Various studies have used a model termed the Donnan-Steric-Pore model (DSPM) to predict the behavior of ionic rejections in NF membranes (Bowen & Mohammad, 1998; Bowen, Mohammad, & Hilal, 1997). DSPM is a model developed based on the extended Nernst—Planck equation in conjunction with the Donnan equilibrium. It has been widely accepted as one of the most effective models for NF membranes in predicting the rejection of ionic compounds (Mohammad, 2008). The potential gradient is:

$$\frac{\mathrm{d}\psi}{\mathrm{d}x} = \frac{\sum_{i=1}^{n} z_i \frac{J_v}{D_{ip}}\left[K_{ic}c_i - C_{ip}\right]}{(F/R_GT)\sum_{i=1}^{n} z_i^2 c_i} \tag{12.16}$$

With the inclusion of the steric effect (φ) and Donnan exclusion effect ($\Delta\psi$):

$$\frac{\gamma_i c_i}{\gamma_i^o C_i} = \varphi \exp\left(\frac{-z_i F}{R_G T}\Delta\psi_D\right) \tag{12.17}$$

The DSPM model has been further modified to include the DE effect for charged ions (Mohammad, Hilal, Al-Zoubib, Darwish, & Ali, 2007), and this model has been termed the DSPM-DE model. The DSPM-DE model differs from the DSPM model due to the inclusion of the DE effect in the partitioning coefficients of each ion as follows:

$$\frac{c_i}{C_i} = \varphi \exp\left(\frac{-z_i F}{R_G T}\Delta\psi_D\right)\exp\left(\frac{-\Delta W_i}{k_B T}\right) \tag{12.18}$$

The DE effect is represented by the Born solvation energy barrier. The electrostatic interactions between the ions of the solutions with the polarization charges induced by ions at the interfaces between the media of different dielectric constants (in this case, a membrane matrix and a solvent) will create DE (Bandini & Vezzani, 2003; Yaroshchuk, 2000). The derivations and the applications of the above equations are not within the scope of this chapter, and they could be obtained from the references cited.

12.2.5 Mathematical modeling for MF/UF membranes

Both MF and UF membranes are porous membranes, which indicate that the basic mechanism of rejection will be the sieving mechanism. Molecules with a greater size than the pores of membranes will be rejected. Hence, the pore flow model can be used to describe the flux through the membranes. According to Darcy's law, flux is proportional to applied pressure difference across the membrane, as shown in Eqn (12.19) (Baker, 2000):

$$J = P\cdot(p_f - p_p) = P\cdot\Delta p \tag{12.19}$$

This equation is the basic design equation used to model the performance of MF/UF (clean membranes) in water treatment processes. Unlike RO/NF membranes, the osmotic pressure of macromolecules (solutes being rejected from passing through MF/UF) is very low and can be neglected. So the osmotic pressure effect is not being considered for MF/UF (Geankoplis, 2003). The permeability constant, P, depends on the membrane structure (pore size distribution and porosity) and permeate quality (viscosity). There are two approaches normally used to define the permeability constant. The first approach is using the Hagen-Poiseuille law, in which the membrane structure can be assumed to be uniform capillaries (Seader & Henley, 1998):

$$v = \frac{D^2}{32\mu L}(p_f - p_p) \tag{12.20}$$

By combining the Hagen–Poiseuille equation, the porosity of membrane, ε, and the tortuosity of the pores, τ, the flux can be described by:

$$J = \frac{\varepsilon D^2}{32\mu\tau}\frac{\Delta p}{L} \tag{12.21}$$

In real porous membranes, the pores might not be cylindrical and straight, so another approach is assuming the membrane is an arrangement of near-spherical particles, in which Carman–Kozeny equation can be applied to obtain the flux as (Field, 2010):

$$J = \frac{\varepsilon^3}{K\mu S^2(1-\varepsilon)^2}\frac{\Delta p}{L} \tag{12.22}$$

However, both of the above two equations are idealized equations, because the real structure of the membrane deviates from the assumptions. Thus, usually a more commonly accepted equation will be used to describe the pure water flux of MF/UF, known as the osmotic pressure model (Ahmad, Chong, & Bhatia, 2006; Karode, 2001):

$$J = \frac{\Delta p - \Delta\pi}{\mu R_m} = \frac{\Delta p}{\mu R_m} \tag{12.23}$$

Because the osmotic effect for MF/UF membranes usually is very small, this term will be neglected. To have a better prediction on the membrane performance, the fouling effect has to be taken into consideration when treating the real water sample, which might contain foulants. Equation (12.23) will be modified to include the possible fouling resistance when the membranes are being used to treat nonpure water. This leads to the development of a widely used mathematical model known as the hydraulic model of filtration resistance (resistance in series model) (Konieczny, 2002; Rajca, Bodzek, & Konieczny, 2009; Shengji, Juanjuan, & Naiyun, 2008). This model is based on the equation that describes the correlation between permeate flux and pressure, taking into account the hydraulic resistance fluid meets flowing through a membrane. By looking at the equation below, it can be seen that the liquid flowing through the membrane will not only encounter the resistance from membrane itself, but also reversible and irreversible resistances ariseing due to fouling phenomena.

$$J = \frac{\Delta p}{\mu(R_m + R_\mathrm{t})} = \frac{\Delta p}{\mu(R_m + R_\mathrm{rev} + R_\mathrm{irr})} \tag{12.24}$$

Reversible fouling is a fouling process where the membrane capability can be recovered by either backwash or chemical cleaning methods, while irreversible fouling is the permanent loss of a membrane's productivity that could not be recovered by a cleaning method. The ways to obtain the values of resistance are shown elsewhere (Rajca et al., 2009). Figure 12.5 depicts the comparison between volume water flux obtained experimentally and calculated using Eqn (12.24) under different operating conditions. It was shown that this resistance model is capable of characterizing the water treatment process by UF membrane.

Another simple mathematical model that has been tried out to calculate the flux from the UF membrane water treatment process is the filtration model in a nonstationary process (relaxation model) (Konieczny, 2002). It uses the mass transport balance equation during membrane filtration in which the decrease in the permeate flux is proportional to its value:

$$\frac{\mathrm{d}}{\mathrm{d}t}(J - J_\infty) + \frac{1}{t_0}(J - J_\infty) = 0 \tag{12.25}$$

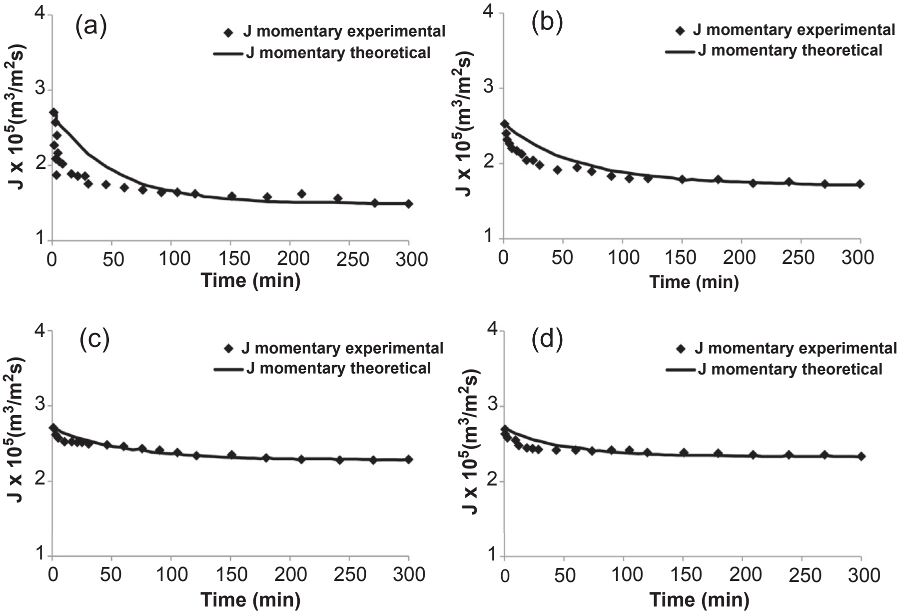

Figure 12.5 Comparison of experimental and theoretical volume flux for ceramic ultrafiltration (UF) membrane (a) Direct UF; (b) Coagulation $FeCl_3$-UF; (c) Coagulation $Al_2(SO_4)_3$-UF; (d) Coagulation PAX-25-UF.
Reprinted from Rajca et al. (2009), with permission from Elsevier.

$$\text{for } t = 0 \rightarrow J = J_0$$
$$\text{for } t = \infty \rightarrow J = J_\infty$$

After integration with the above boundary conditions:

$$J_t = (J_0 - J_\infty)e^{-\frac{t}{t_0}} + J_\infty \tag{12.26}$$

Figure 12.6 shows that the model curve (relaxation model) did not fit with the filtration results (feed water from raw water reservoir) initially, which might indicate that the system has not reached equilibrium yet. The model adequately fits into the membrane water treatment process.

In reality, natural water for the potable water treatment process might contain various contaminants/foulants. So to understand and describe the fouling mechanism (pore blocking) more precisely, a mathematical model that can give a clue on which pore blocking mechanisms should be developed and used. Such a model has been developed, and it is known as Hermia's model.

Most of the fouling mechanisms for porous membranes like MF and UF are related to their pores. As shown in Figure 12.7, porous membrane fouling mechanisms can be divided into four categories (Field, 2010).

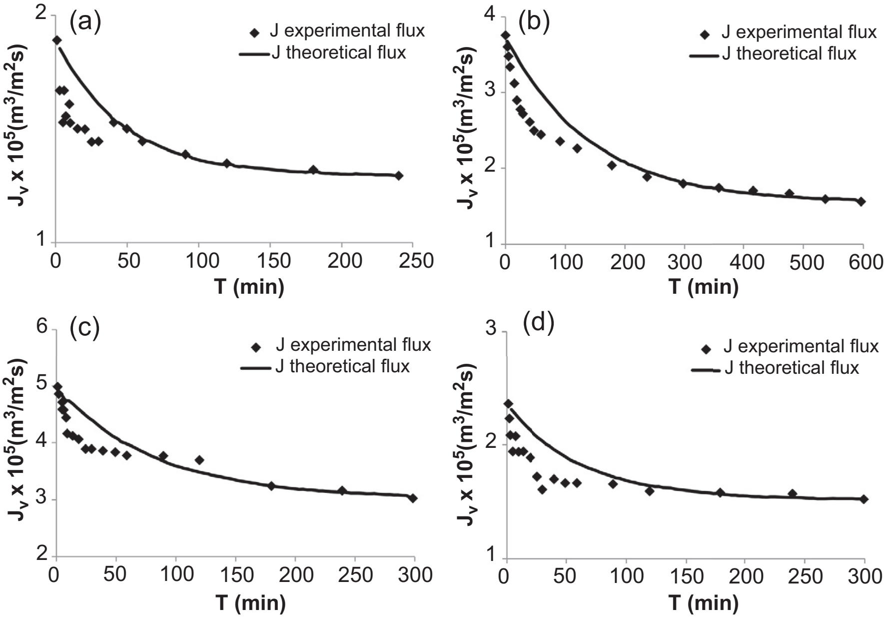

Figure 12.6 Comparison of experimental and theoretical volumetric flux (relaxation model) for MF membranes (a) Membrane 0.1 μm (0.1 MPa); (b) Membrane 0.2 μm (0.1 MPa); (c) Membrane 0.2 μm (0.2 MPa); (d) Membrane 0.45 μm (0.1 MPa).
Source: Reprinted from Konieczny (2002), with permission from Elsevier.

The transport equations for each case have been derived from Hermia's equation, and the results can be seen in Table 12.5 (Field, 2010; Field & Wu, 2011; Field, Wu, Howell, & Gupta, 1995). Those equations could be used to diagnose the type of fouling and predict the causes of it. Originally, these equations are

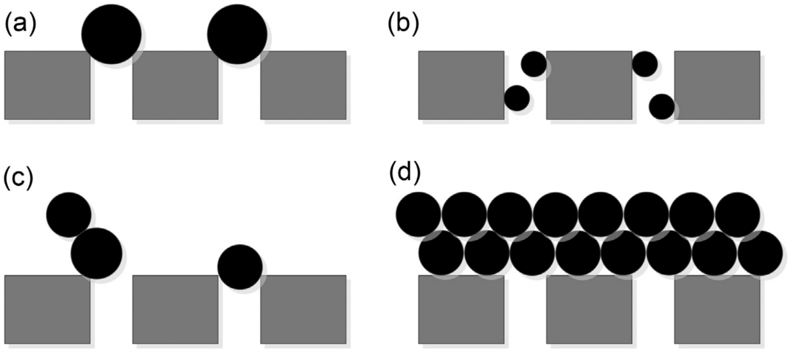

Figure 12.7 Fouling mechanisms of porous membranes (a) Complete pore blocking; (b) Internal pore blocking; (c) Partial pore blocking; (d) Cake filtration.
Source: Adapted from Field (2010) and Konieczny (2002).

Table 12.5 Fouling mechanisms, phenomenological background, and transport equations

Fouling mechanism	n	Phenomenological background	Flux equation for dead-end	Flux equation for crossflow
Complete pore blocking	2	Particles larger than the pore size completely block pores	$J = J_0 \exp(-K_b t)$	$J = (J_0 - J^*)\exp(-k_2 t) + J^*$
Internal pore blocking	1.5	Particles smaller than pore size enter the pores and get either adsorbed or deposited onto the pore walls; this restricts the flow of permeate	$J = J_0 \cdot \left(1 + \frac{1}{2} \cdot K_s \cdot (A \cdot J_0)^{0.5} \cdot t\right)^{-2}$	$J = J_0 \cdot \left(1 + \frac{1}{2} \cdot K_s \cdot (A \cdot J_0)^{0.5} \cdot t\right)^{-2}$
Particle pore blocking	1	Particles reaching surface may seal a pore or bridge a pore or partially block it or adhere on inactive regions	$J = J_0 \cdot (1 + K_i \cdot (A \cdot J_0) \cdot t)^{-1}$	$J = \frac{J^*}{\left[1 - \left(\frac{J_0 - J^*}{J_0}\right)\exp\left(-J^* k_1 t\right)\right]}$
Cake filtration	0	Formation of a cake on the membrane surface by particles that neither enter the pores nor seal the pores	$J = J_0 \cdot (1 + 2 \cdot K_c \cdot (A \cdot J_0)^2 \cdot t)^{-\frac{1}{2}}$	$k_0 t = \frac{1}{J^{*2}}\left[\ln\left(\frac{J}{J_0} \cdot \frac{(J_0 - J^*)}{(J - J^*)}\right) - J^*\left(\frac{1}{J} - \frac{1}{J_0}\right)\right]$

Note: J^* - critical flux, k_i - constant in a crossflow fouling equation ($i = 0,1,2$).
Source: Field and Wu (2011); Field (2010); Field et al. (1995).

applicable to dead-end filtration, but with some allowance for crossflow made, it can be applied to both modes of filtration.

Besides than the fouling effect, temperature will affect the flux performance of membranes as well. For MF and UF systems, the flow of permeate at any temperature, relative to the flow at 20 °C, can be estimated by using (AWWA & ASCE, 2012):

$$Q_T = \frac{Q_{20^\circ\mathrm{C}}}{e^{-0.0239(T-20)}} \tag{12.27}$$

This approximation is very useful and important because the effect from the fluctuation of raw water temperature can be minimized and the production of potable water can be controlled.

Another term used to define the performance of membranes is the removal percentage of unwanted solute (foulants) from the raw water. The solute rejection equation will be the same as the one being used in NF/RO membranes:

$$R = \frac{C_b - C_p}{C_b} \times 100\% = \left[1 - \frac{C_p}{C_f}\right] \times 100\% \tag{12.28}$$

If the CP effect is to be taken into consideration, then the concentration of solute at the membrane surface should be used instead of the concentration of solute in bulk solution.

12.3 Future work

Understanding the transport models and fouling mechanisms is very important and essential, especially for reliable plant performance. With better and accurate mathematical modeling, membrane water treatment plants can be controlled, monitored, and operated easily when the performance of the plants can be predicted precisely. This will be very beneficial to automated plants in which the systems are controlled by sophisticated automation systems. Without reliable mathematical modeling, the automated plants are vulnerable to membrane fouling because this problem could not be predicted properly in the initial stage, and it will be too late to prevent the fouling problem when it is discovered. Hence, study about mathematical modeling for the membrane water treatment process should be carried out more thoroughly. It is hoped that a predictive model that takes into account the effect of fouling and long-term process operation could be developed, because the main problem encountered by the membrane process is membrane fouling.

The challenge now is the ability to develop the mathematical models that can convey the fundamental understanding and simple quantification of the governing phenomena in a way that has the potential for industrial application. An accurate and precise mathematical modeling not only will ease the design stage of the membrane water treatment plant, but also will smooth the operation of the plant because the fouling propensity could be diagnosed earlier and preventive measures could be taken to curb it.

Thus, the models developed should be validated with real industrial data so that the applicability and validation of the models could be tested. With such a comparison, the weakness of the mathematical modeling can be identified and improved.

As shown in this chapter, currently more and more new substances that might prove to be detrimental to our health and environment have been discovered. Studies about the removal of pesticides have been carried out, and several models have been used to predict their retention by membranes. However, with the emerging deleterious components being discovered from time to time, it is unsure whether the currently available predictive models could be used for membrane rejection performance. Furthermore, it seems like the mathematical model used by the membrane water treatment plant does not only depend solely on the membrane used, but also the quality and foulant in the raw water will affect the suitability of the model used. Until now, there has not been any mathematical modeling that could be applied to all the membranes and source water. Hence, to have a better prediction on the membrane performance, several models might be required, and the computational steps might be tedious. Thus, works developing a simpler and compact model should be focused to benefit all membrane applications in the water treatment process.

12.4 Conclusion

Process modeling plays a very important role in membrane operations for water treatment applications. It allows users to obtain reliable prediction results that can be very helpful in membrane water treatment plants, from the design stage toward the commissioning, implementation, and maintenance phases. Mathematical modeling ensures that the fundamentals of the separation phenomena during the water treatment process of membranes can be understood. With that, specific preventative methods could be applied to avoid the fouling problems. In the earlier stage of designing, a good predictive model will result in a smaller number of experiments and subsequently save time and money. With the appropriate design equation for the membrane, the size of the water treatment system as well as the area of membrane required to meet certain production rate could be determined. Besides that, mathematical modeling can be incorporated into the control system to predict the fouling potential of the membrane system, and thus suitable measures can be taken to reduce and mitigate the problem of membrane fouling. Hence, it can be concluded that with a good predictive modeling for the membrane process, the problem of water scarcity could be mitigated with the wide acceptance of membranes in the water industry, because the water treatment plant can be controlled and operated stably.

Nomenclature

c_i	Concentration of ion i within pore (kg mol/m^3)
C	Solute concentration (kg/m^3, kg mol/m^3)
C_b	Feed solute concentration (kg/m^3, kg mol/m^3)
C_i	Ionic solute bulk solution concentration (kg mol/m^3)

C_{ip}	Ionic solute bulk permeate concentration (kg mol/m^3)
C_m	Membrane surface solute concentration (kg/m^3, kg mol/m^3)
C_p	Permeate solute concentration (kg/m^3, kg mol/m^3)
CP	Concentration polarization
D	Pore diameter (m)
D_{ij}	Diffusion coefficient of solute (m^2/s)
D_{ip}	Pore diffusion coefficient of ion i (m^2/s)
D_r	Desalination ratio (C_b/C_p)
DE	Dielectric exclusion
DSPM	Donnan-Steric-Pore-model
F	Faraday constant (96,487) (C/mol)
j_d	Chilton-Coburn factor
J	Volumetric flux (m^3/s m^2)
J_i	Molar flux of solute (kg mol/s m^2)
J_0	Initial flux (m^3/s m^2)
J_s	Solute flux (kg/s m^2)
J_t	Permeate flux at time t (m^3/s m^2)
J_v	Solvent velocity (m/s)
J_w	Pure water permeate flux (m^3/s m^2)
J_∞	Equilibrium flux (m^3/s m^2)
k	Mass transfer coefficient (m/s)
$k_{i,b}$	Mass transfer coefficient for concentration polarization (m/s)
k_B	Boltzmann constant ($1.38{,}066 \times 10^{-23}$) (J/K)
k_i	Membrane permeability coefficient for solute (m/s)
k_w	Mass transfer coefficient for water (m/s atm)
K	Constant for Carman−Kozeny equation
K_{ic}	Hindrance factor for convection of ion i
l_{bl}	Thickness of the mass transfer boundary layer
L	Length of pore (m)
MF	Microfiltration
n	Number of kg mol of solute
NF	Nanofiltration
p_f	Feed pressure (atm)
p_p	Permeate pressure (atm)
P	Permeability coefficient (m^3/s m^2 atm)
P_s	Solute permeability coefficient (m/s)
P_w	Water permeability coefficient (m^3/s m^2 atm)
$Q_{20\ ^\circ\mathrm{C}}$	Permeate flow at 20 °C (m^3/s)
$Q_{25\ ^\circ\mathrm{C}}$	Permeate flow at 25 °C (m^3/s)
Q_T	Permeate flow at temperature T (m^3/s)
R	Solute rejection
$R\mathrm{e}$	Reynolds number
R_{CP}	Solute rejection (after taking into CP effect)
R_G	Gas law constant (82.057×10^{-3}) (m^3 atm/kg mol K)
R_{irr}	Resistance due to irreversible fouling (1/m)
R_m	Membrane resistance (1/m)
R_{rev}	Resistance due to reversible fouling (1/m)
R_t	Resistance from foulants (total) (1/m)
RO	Reverse osmosis

$\boldsymbol{S}$	Specific area (m^2/m^3)
Sc	Schmidt number
SHP	Steric hindrance pore
$\boldsymbol{T}$	Temperature (K, °C)
TMS	Teorell−Meyer−Sievers
UF	Ultrafiltration
$\boldsymbol{v}$	Flow velocity (m/s)
$\boldsymbol{V_m}$	Volume of pure solvent water in m^3 associated with n kg mol of solute (m^3)
$\boldsymbol{x}$	Axial position within the pore (m)
$\boldsymbol{z}$	Thickness of boundary layer (m)
$\boldsymbol{z_i}$	Valence of ion *i*

Greek letters

$\boldsymbol{\tau}$	Tortuosity of membrane
$\boldsymbol{\varepsilon}$	Porosity of membrane
$\boldsymbol{\mu}$	Viscosity of liquid (kg/s m)
$\boldsymbol{\gamma_i}$	Activity coefficient of ion *i* within pore
$\boldsymbol{\gamma_i^o}$	Bulk activity coefficient of ion *i*
$\boldsymbol{\psi}$	Potential within the pore (V)
$\boldsymbol{\Delta\psi_D}$	Donnan potential (V)
$\boldsymbol{\Delta W_i}$	Born solvation energy barrier (J)
$\boldsymbol{\Delta p}$	Transmembrane pressure (atm)
$\boldsymbol{\Delta\pi}$	Transmembrane osmotic pressure (atm)
$\boldsymbol{\pi}$	Osmotic pressure (atm)
$\boldsymbol{\pi_m}$	Osmotic pressure at membrane surface (atm)
$\boldsymbol{\pi_p}$	Osmotic pressure at permeate side (atm)

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Part Three

Applications

Membrane technologies for seawater desalination and brackish water treatment

13

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13.1 Introduction

In past decades, the number of countries experiencing water scarcity has increased significantly owing to steady demographic expansion and the amplified demand for water in industrial activities, in agriculture, and for municipal (including domestic) purposes. In particular, agriculture accounts for about 70% of global freshwater withdrawal (FAO Water Report, 2012). Average consumption per capita of water per day spans from 150 L in Western countries to about 20 L on the African continent; the latter value dramatically approaches the lower limit fixed by the World Health Organization, which is sufficient to guarantee basic needs such as drinking, personal hygiene, and food preparation. The demand for water is expected to increase by 50% in the next 40 years, driving about 3.9 billion people under water stress (Mountford, 2011).

Paradoxically, water is one of the most abundant resources on earth (the estimated amount in the ocean is 1.4×10^9 km^3 (Bengtsson, 2010)). Seawater (SW) represents about 96.7% of total available water; the remaining part is underground and surface waters, mostly frozen in glaciers. Only 0.7% of the total amount (1.2×10^7 km^3) is available in lakes, rivers, and aquifers (Figure 13.1).

Water is classified primarily according to its salinity content: Freshwater has salinity up to 1500 ppm, brackish water (BW) has a saline content in the range of 1500−10,000 ppm, and SW salinity is between 10,000 and 45,000 ppm. For reference, the average salinity of SW is conventionally normalized at 35,000 ppm (‘standard SW’ is arbitrarily defined on the basis of certain samples taken from North Atlantic surface water, as first proposed by Martin Knudsen at the International Conference for the Exploration of the Sea, held in Stockholm in 1899 (Knudsen, 1903)). The main ionic constituents of SW are sodium (30%) and chloride (55%). Table 13.1 lists the composition of standard SW.

To date, SW and BW desalination represents the most reliable and economically sustainable way to produce drinking water for human consumption. The total global desalination capacity is currently around 66.4 million m^3/day and is expected to reach about 100 million m^3/day by 2015; the annual market growth is about 55%. SW represents the main source for the desalination industry (about 58.9%), whereas BW accounts for 21.2% (Global Water Intelligence).

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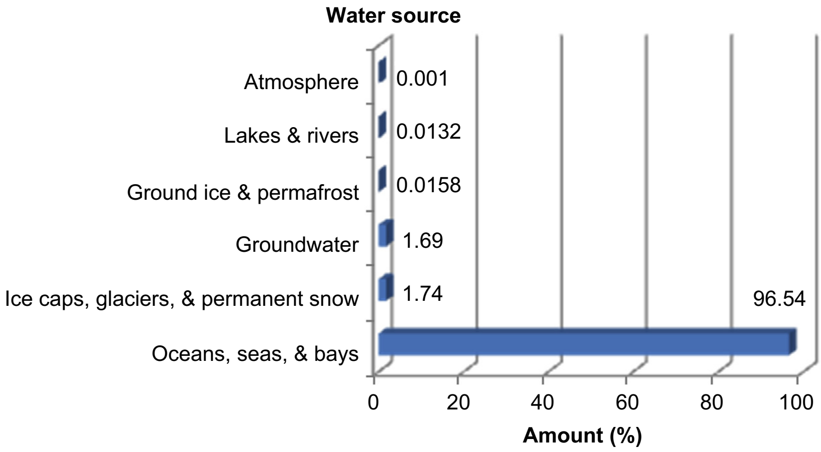

Figure 13.1 Rough estimate of global water distribution.
Data elaborated from Shiklomanov (1993).

Thermal desalination processes dominate in the Gulf region (more than 90% of total production), where water is generated together with electricity in large cogeneration plants. There, steam drives turbines and acts as a source for SW evaporation. Multistage flash (MSF) distillation is the prevalent desalination technology in the Middle East with more than 80% of installed capacity, followed by multiple effect distillation (MED) (IDA Media Analytics Ltd, 2007).

MSF consumes a larger amount of total energy than other desalination processes (around 17—18 kWh/m^3) with a gain output ratio (GOR) of 8—10 kg of distillate per kilogram of steam; however, its highly reliable performance (early plants began operation in 1978 with an expected life of over 30 years) makes MSF competitive in the Middle East—North Africa region. MSF plants are generally built to be large. The Jebel Ali MSF plant in Dubai, contracted by Fisia and officially opened in 2013, has a productivity of 6,26,400 m^3/day and 2060 MW/day of generated power (Borsani & Ghiazza, 2012).

MED plants are generally designed for operative temperature below 70 °C to limit scale formation on the outside surface of evaporator tubes; total energy consumption is 6—7 kWh/m^3 for a GOR of 8—16 kg of distillate per kilogram of steam. In recent years, the productivity of MED integrated with thermal vapour compression (TVC) units has increased exponentially. For example, the MED—TVC Marafiq Jubail (Saudi Arabia) desalination plant (27 units), completed in 2010 by Veolia's subsidiary, Sidem, produces a total of 8,00,000 m^3/day of desalted water with a GOR of 9.84 kg of distillate per kilogram of steam. Huge MED plants are in operation at Fujairah, United Arab Emirates (4,63,000 m^3/day), Ras Laffan, Qatar (2,86,000 m^3/day), and Al Hidd, Bahrain (2,72,000 m^3/day) (sidem-desalination.com, 2014).

Developed in the 1980s, mechanical vapour compression units have a small capacity with respect to MSF and MED (usually lower than 5000 m^3/day) and an average energy consumption of around 8 kWh/m^3 of electrical power (Lokiec & Ophir, 2007).

Desalination processes are classified according to the type of separation. Conventionally, two groups are identified: membrane systems and thermal technologies

Table 13.1 Standard seawater composition

Ion	Concentration (ppm)	Total salt content (%)
Chloride, Cl^-	19,345	55.03
Sodium, Na^+	10,752	30.59
Sulphate, SO_4^{2-}	2701	7.68
Magnesium, Mg^{2+}	1295	3.68
Calcium, Ca^{2+}	416	1.18
Potassium, K^+	390	1.11
Bicarbonate, HCO_3^-	145	0.41
Bromide, Br^-	66	0.19
Borate, BO_3^{3-}	27	0.08
Strontium, Sr^{2+}	13	0.04
Fluoride, F^-	1	0.003

Source: Millero, Feistel, Wright, and McDougall (2008).

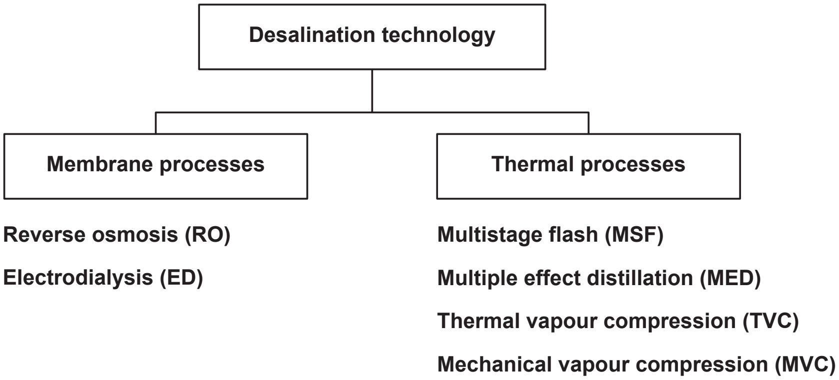

Figure 13.2 Classification of major technologies currently in use for seawater and brackish water desalination.

(Figure 13.2). The first group includes reverse osmosis (RO), which currently dominates desalination technology; the second is electrodialysis. Both membrane operations require electrical energy.

Currently, the largest SWRO plant, with a productivity of 6,24,000 m^3/day is installed in Sorek, Israel, and is operated by IDE Technologies. The SWRO plant in Ashkelon, Israel, operated by Veolia Water since 2005, reaches a daily productivity of 3,20,000 m^3/day. Feed water passes through 32 modules that decrease salt concentration down to 30 mg/L with a cost of 0.50 Euro/m^3. The SWRO plant installed in Perth, Australia, designed and built in only 18 months by Multiplex Degrémont Joint Venture in 2006, produces 1,44,000 m^3/day of desalinated water (Clemente & Mercer, 2011).

Electrodialysis and electrodialysis reversal (EDR) are electrochemical separation processes in which ions are transferred through ion exchange membranes under direct current; both are typically operated for BW desalination purposes. One of the major facilities installed in Europe is the 57,000-m^3/day EDR plant operated in Sant Boi de Llobregat, Spain (Segarra, Iglesias, Pérez, & Salas, 2009).

13.2 Principle of RO

RO allows dissolved ions to be separated from feed water using semipermeable membranes operated under the driving force of a difference in chemical potential (function of pressure, concentration, and temperature). From a phenomenological point of view, RO separation is based on countering the natural osmotic process by applying hydrostatic pressure to the side contacted by SW, thus driving the solvent flux in the opposite direction with respect to that established by natural osmosis.

The value of osmotic pressure Π (defined as the equilibrium pressure at which the net flux of solvent stops) depends on the salt concentration, c_i, according to the following equation (Fell, 1995):

$$\Pi = RT\sum_i \nu_i c_i \tag{13.1}$$

The osmotic pressure of SW is typically around 2.3 MPa. As long as the applied hydrostatic pressure, ΔP, is higher than the osmotic pressure difference $\Delta \Pi$ between the feed and permeate solutions, the solvent (water) will flow from the more concentrated solution (feed) to the dilute solution (permeate), and the trans-membrane flux will reverse from the direction of natural osmosis, as illustrated in Figure 13.3.

The solution-diffusion model is frequently adopted with the aim of describing the transport phenomenon in RO (Merten, 1966). It is assumed that the volumetric flux of water (J_v) and the flux of solutes (J_s), both of which occur by diffusing through the membrane, are related to their mobility, driving force (effective pressure difference of $\Delta P - \Delta \Pi$), and salt concentration gradient:

$$J_v = -\frac{k_w D_w \overline{V}_w}{RT}\left(\frac{\Delta P - \Delta \Pi}{\delta}\right) \tag{13.2}$$

$$J_s = k_s \frac{D_s}{\delta}\left(c_s^f - c_s^p\right) \tag{13.3}$$

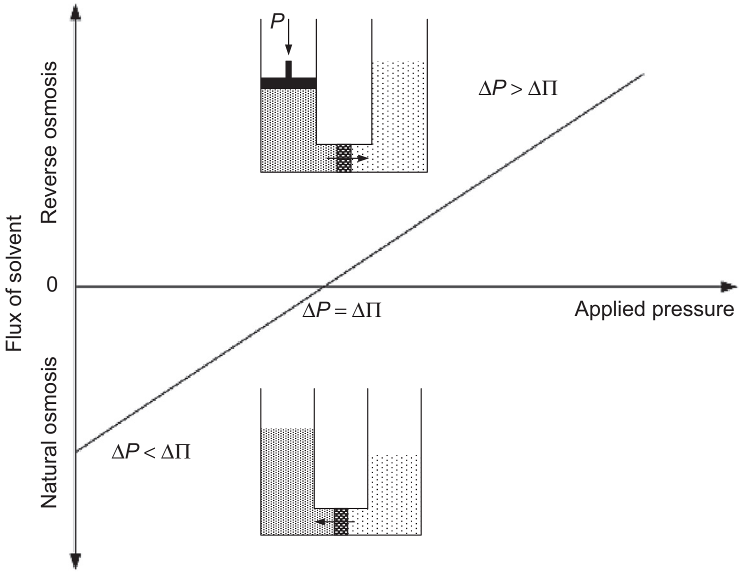

Figure 13.3 Trans-membrane flux of solvent through an ideally semipermeable membrane as a function of applied hydrostatic pressure.

13.3 RO membranes and modules

The RO membrane market is essentially based on thin-film composite (TFC) polyamide membranes, generally consisting of a polyester web used as a support (120—150 μm thick), a microporous interlayer usually made of polysulphonic polymer (40—50 μm), and a top ultrathin barrier layer with selectivity properties and low resistance to mass transfer of permeate (~0.2 μm). The selective layer, which is generally able to provide salt rejection higher than 99.5% to NaCl, is commonly made of 1,3-phenylenediamine (also known as 1,3-benzenediamine) and tri-acid chloride of benzene (Figure 13.4) (Lee, Arnot, & Mattia, 2011). Historically, RO technology started with cellulose acetate (CA) membranes. Although they are characterized by higher resistance to chlorine (extensively used as a disinfectant to prevent bacterial growth on membranes), asymmetric CA or triacetate hollow-fibre modules are much less frequently installed in RO plants because of their lower rejection ability. Among the unresolved challenges, the boron rejection of any commercially available membrane is still insufficient (~93%) to meet WHO water drinking standards by one-pass RO process (Kumano & Fujiwara, 2008).

With few exceptions, RO membranes are prepared in the flat-sheet form and are assembled in spiral-wound module (SWM) configuration with a high specific membrane surface area (the packing density is about 500—800 m^2/m^3) and low replacement cost (Pearce, 2007). In SWM, two rectangular flat-sheet membranes are placed back to back and sealed on three sides to form an envelope. One or multiple envelopes are wound around a collector tube connected to the fourth side, which remains open.

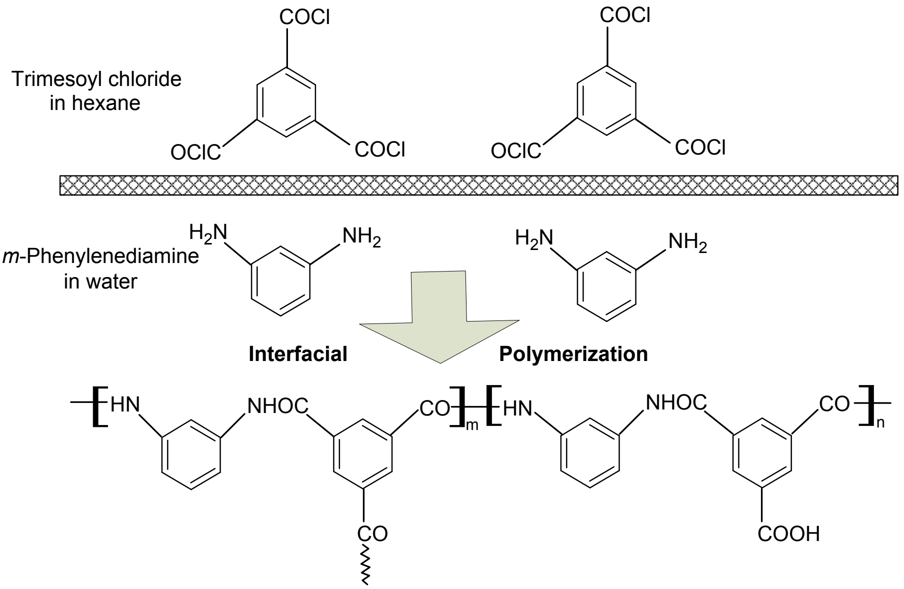

Figure 13.4 Sample scheme of interfacial polymerization for the preparation of the top layer of a thin-film composite, fully aromatic polyamide membrane.

Feed water enters tangentially in the module and the permeate goes through the membrane and flows perpendicularly in the collector tube, while the retentate leaves the module at the opposite end.

Advances in membrane desalination (innovation in membrane materials, optimization of module fluid dynamics, and improvement in process design, pretreatment, and energy recovery systems) resulted in progressive enhancement of membrane rejection and a decrease in overall energy consumption, as illustrated in Figure 13.5.

Currently, some major suppliers of RO membrane modules are Dow (Filmtech), Toray, Hydranautics (Nitto Group), and Koch Membrane Systems. Standard modules for current SWRO desalination plants are 8 inches in diameter. However, recent developments in module design and hydrodynamics optimization are moving towards larger modules (Yun, Gabelich, Cox, Mofidi, & Lesan, 2006). Tables 13.2 and 13.3 summarize the main characteristics of eight modules commercialized by these companies.

SWMs are contained in pressure vessels consisting of a cylindrical housing, each hosting typically six to eight modules. From a technical point of view, each group of parallel connected vessels forms a ‘stage’. Connection in parallel leads to an increase in productivity. A configuration ratio of 2:1, representing the ratio between the number of pressure vessels from one stage to the next, is generally adopted in RO plants. SWRO plants are typically composed of two stages to increase the total water recovery factor to 50—60% at an operating pressure of 50—70 bar. The number of ‘passes’ identifies the number of times that permeate is treated in the system. Additional passes are necessary whenever high permeate quality is requested. A single-pass RO plant typically guarantees a total dissolved solids (TDS) content around

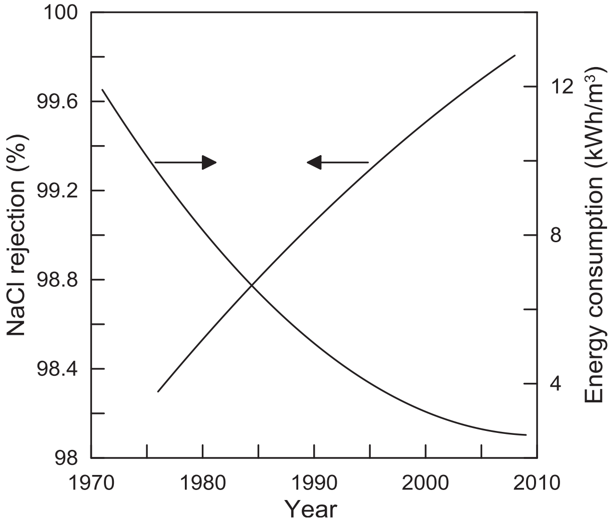

Figure 13.5 Improvement in salt rejection (%) and energy consumption (kWh/m^3) of SWRO technology.
Data from Lee, Arnot, and Mattia (2011).

500 mg/L, whereas a two-pass configuration decreases TDS below 300 mg/L. Stages interconnected in series form a 'train'; SWRO plants are generally composed of several trains. Typical examples of RO flow sheets are given in Figure 13.6(a) and (b).

13.4 Fouling and pretreatment strategies

Composition and characteristics of BW and SW used as a feed in desalination plants directly affect the efficiency of membrane processes (El-Manharawy & Hafez, 2001). The presence of sparingly soluble salts, colloids and suspended matters, organic compounds, or microorganisms, if not appropriately controlled, might result in a severe impact of fouling phenomena on the performance of RO plants, leading to irreversible damage to membranes and a significant decrease in their lifetime (see Figure 13.7 for an overview).

Membrane damage primarily results from oxidation and hydrolysis of the polymeric material. In general, membranes cannot tolerate residual chlorine concentrations, which are used extensively in desalination processes to prevent biological growth. Adjustment of the pH to recommended operational values is therefore required to fit optimal operation protocols and mitigate scaling (acidification is usually made by adding sulphuric acid). Moreover, oxidizing agents and dissolved oxygen must be removed by adding appropriate reducing compounds such as sodium thiosulphate or sodium bisulphite. More details on pretreatment procedures are provided in paragraph 15.4.1.

Scaling refers to the precipitation of sparingly soluble salts onto the membrane surface, often exacerbated by concentration polarization. In fact, owing to the progressive

Table 13.2 Product specifications of selected brackish water desalination modules

Element model	**Dow™ Filmtec™ BW30-365**[a]	**Toray Standard BWRO TM720-370**[b]	**Nitto/Hydranautics ESPA1**[c]	**Koch Membrane Systems/Fluid Systems® TFC®-FR 400-34**[d]
Active area (m^2)	34	34	37.1	37.2
Permeate flow rate (m^3/day)	36	36	45.4	41.6
Stabilized salt rejection (%)	99.5	99.7	99.3	99.55
Diameter (inch)	8	8	8	8
Membrane type	Polyamide thin-film composite	Cross-linked, fully aromatic polyamide composite	Composite polyamide	TFC polyamide

Note:

[a] Test conditions: 2000 ppm NaCl, 15.3 bar, 25 °C, 15% recovery, pH 8.

[b] Test conditions: 2000 ppm NaCl, 1.55 MPa, 25 °C, 15% recovery, pH 7.

[c] Test conditions: 1500 ppm NaCl, 1.05 MPa, 25 °C, 15% recovery, pH 6.5–7.

[d] Test conditions: 2000 ppm NaCl, 1.55 MPa, 25 °C, 15% recovery, pH 7.5.

Table 13.3 **Product specifications of selected seawater desalination modules**

Element model	**Filmtec™ SW30HR-380**[a]	**Toray Standard SWRO TM820C-400**[b]	**Nitto/Hydranautics SWC4-LD**[c]	**Koch Membrane Systems/Fluid Systems® TFC®-SW 400-34**[d]
Active area (m^2)	35	37	37.1	37.2
Permeate flow rate (m^3/day)	23	24.6	24.6	27.2
Stabilized salt rejection (%)	99.7	99.75	99.8	99.75
Diameter (inch)	8	8	8	8
Applied pressure (bar)	55	55	55	55
Membrane type	Polyamide thin-film composite	Cross-linked, fully aromatic polyamide composite	Composite polyamide	TFC polyamide

Note:
[a] Test conditions: 32,000 ppm NaCl, 55 bar, 25 °C, 8% recovery, pH 8.
[b] Test conditions: 32,000 ppm NaCl, 5.52 MPa, 25 °C, 15% recovery, pH 7.
[c] Test conditions: 32,000 ppm NaCl, 5.5 MPa, 25 °C, 10% recovery, pH 6.5—7.
[d] Test conditions: 32,800 ppm NaCl, 5.52 MPa, 25 °C, 7% recovery, pH 7.5.

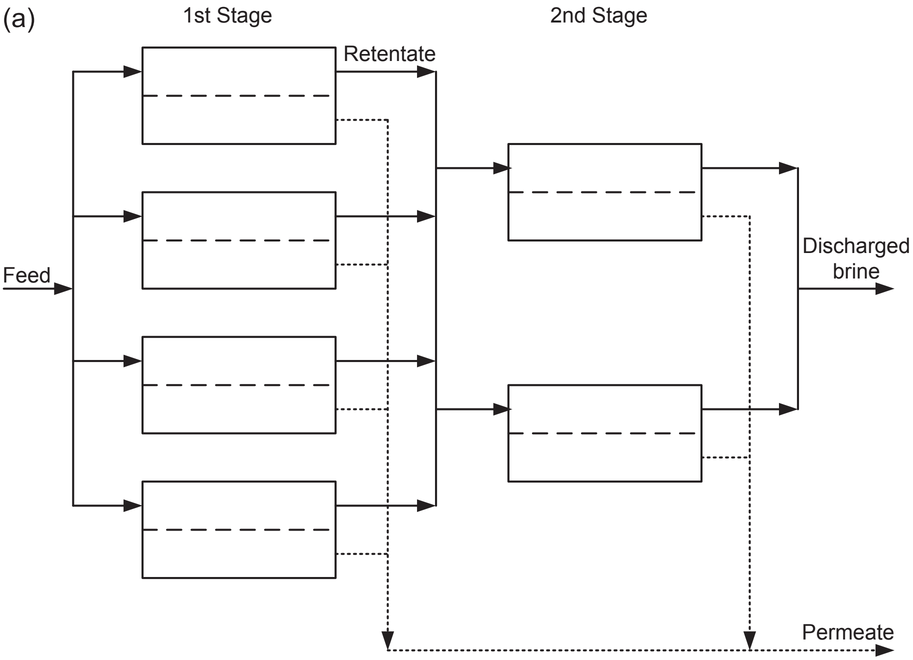

Figure 13.6 Reverse osmosis train configuration: (a) single-pass/two stages. Example: Tampa Bay SWRO plant, United States; (b) two-pass/two stages per pass. Example: Point Lisas SWRO plant, Trinidad.

removal of solvent through the membrane, the solubility limit of some components dissolved in the feed (typically calcium carbonate, magnesium carbonate, calcium sulphate, silica, barium sulphate, strontium sulphate, and calcium fluoride) may be exceeded (van de Lisdonk, Rietman, Heijman, Sterk, & Schippers, 2001).

The scaling propensity of a given feed water is usually evaluated by the Langelier saturation index for BW (Pátzay, Stáhl, Kármán, & Kálmán, 1998), and by the Stiff and Davis stability index for SW (Al-Shammiri & Al-Dawas, 1997). Scaling does not occur for negative values of these indexes.

Typical countermeasures to limit scaling problems are to:

- reduce the water recovery factor to operate below solubility limits
- decrease pH by adding acids to regulate the calcium carbonate speciation (moving solubility equilibrium towards the formation of carbonates and bicarbonates into carbon dioxide)
- add inhibitors or antiscalants that delay the induction time of precipitation
- eliminate calcium and magnesium to limit the risk of calcium/magnesium carbonate precipitation (softening)
- use ion exchange resins to eliminate undesirable ions.

Particulate fouling is caused by particles and suspended colloidal matter present in solution. Clogging can be mitigated by limiting the amount of particles by conventional coagulation—flocculation (a critical issue is the appropriate dosage of

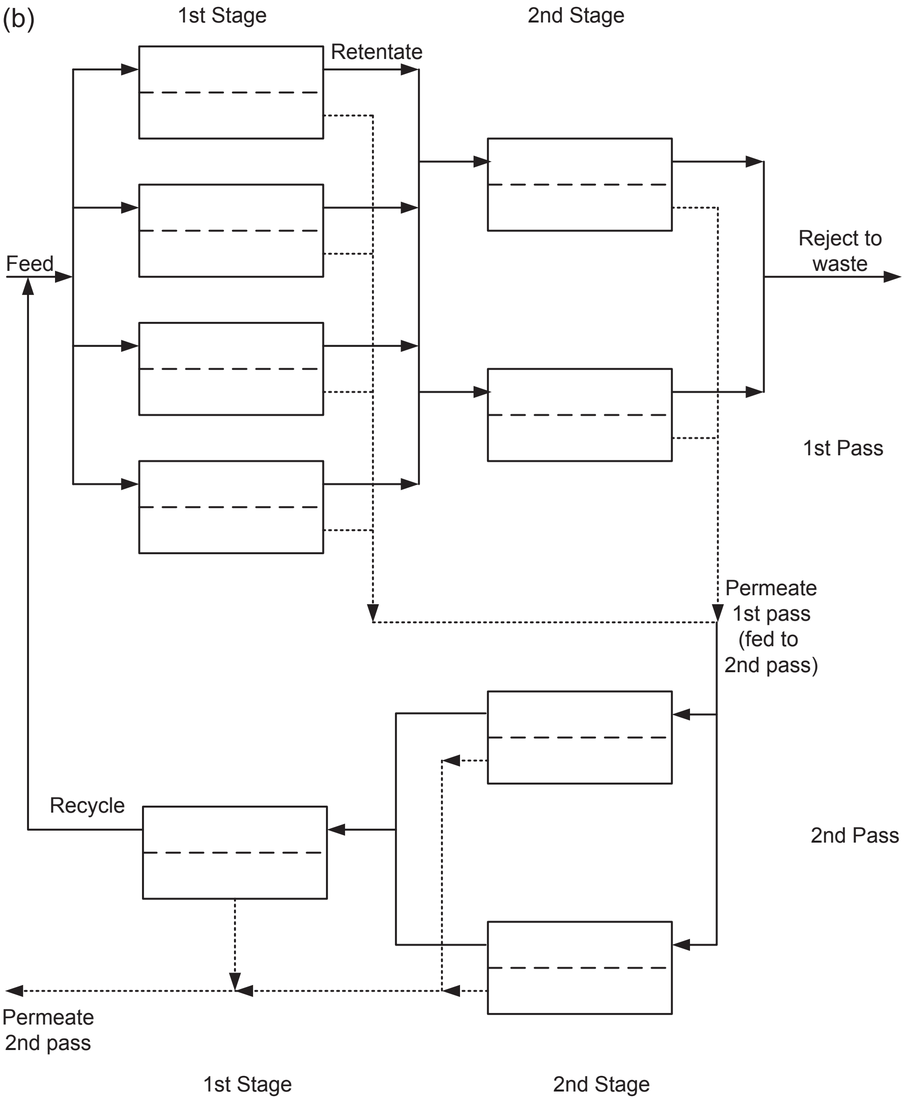

Figure 13.6 Continued.

coagulant–flocculants that might damage membranes) or by pressure-driven membrane operations (microfiltration (MF) or ultrafiltration (UF)) (Ning & Troyer, 2007). To quantify the potential of particulate fouling, a gravimetric procedure is normally used to express the concentration of particles in terms of total suspended solids. In addition, turbidity measurements, expressed in nephelometric turbidity units (NTU), provide quick and easy measurements for low solid concentrations.

Colloidal fouling is caused by the accumulation of colloids on the membrane surface, leading to the formation of a cake layer. As a result, the permeate flux decreases

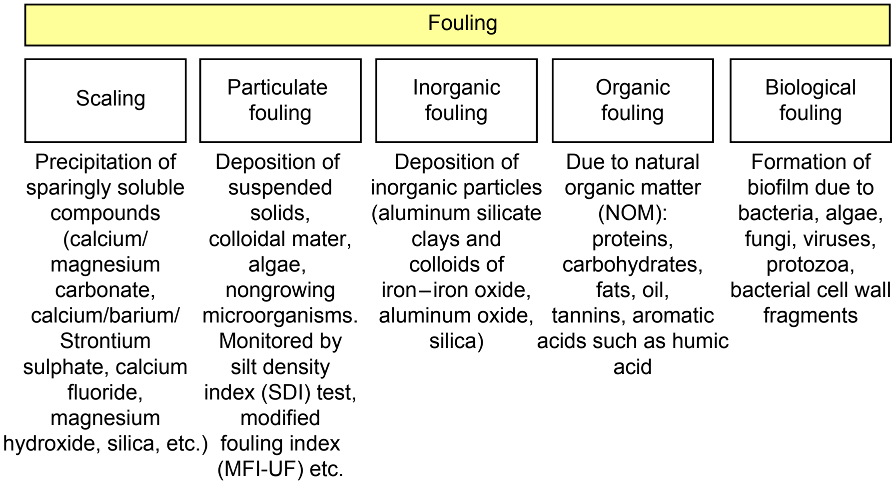

Figure 13.7 Qualitative classification of fouling phenomena.

because of the additional cake layer resistance; moreover, the hindered back-diffusion of salt ions within the deposit layer increases the ion concentration at the membrane surface, thus enhancing the osmotic pressure and decreasing the net driving force.

Biological fouling originates from the growth of colonies of bacteria or algae on the surface of the membrane (Nguyen, Roddick, & Fan, 2012). Washing with biocides may be necessary to prevent the development of biomass; for membranes resistant to chlorine, shock chlorination is the preferred option.

Natural organic matter (NOM) is considered a major foulant among all species present in natural water (Pressman et al., 2012). NOM is a complex mixture of both inorganic and organic components, characterized by a wide range of molecular weight and functional groups (phenolic, hydroxyl, carbonyl groups, and carboxylic acid), originated by allochthonous (terrestrial and vegetative debris) and autochthonous input (algae). Particularly aggressive fouling is caused by dissolved organic matter composed of humic substances, polysaccharides, amino acids, proteins, fatty acids, phenols, carboxylic acids, quinines, lignins, carbohydrates, alcohols, etc. (Zularisam, Ismail, & Salim, 2006). Fouling mechanisms of NOM typically include preliminary adsorption on the surface, followed by the formation of a continuous gel. The structure of the gel layer depends on both chemical conditions (pH, ionic strength, and the presence of multivalent cations) and physical conditions (permeate flux and cross-flow velocity). The presence of inorganic ions in solution exacerbates the fouling problem (for example, through NOM–calcium complexation), resulting in the formation of a dense and highly resistant fouling layer (Lee, Cho, & Elimelech, 2005).

Cleaning procedures partially restore the efficiency of a membrane process. As a rule, membrane elements should be cleaned whenever a critical performance parameter (usually permeate flux, salt rejection, or trans-membrane pressure) changes by at least 10–15%. Cleaning methods are usually classified into four groups: mechanical, hydrodynamic, air–water cleaning, and chemical.

Mechanical cleaning is accomplished by promoting high shear forces at the membrane surface by mechanical action (for example, using sponge balls for cleaning tubular membranes or using ultrasound waves causing the cavitation of fluids and the consequent increase in turbulence and promotion of shear forces at the membrane surface); mechanical cleaning is not frequently applied on an industrial scale (Al-Amoudi & Lovitt, 2007).

Hydrodynamic cleaning methods consist in a temporary increase of cross-flow velocity, in a pulsed feed flow, or in a temporary reversal of the flow through the membrane elements. In particular, periodic back-washing of membranes is an effective and commonly used method to remove accumulated cake, although it is energetically expensive (Sagiv & Semiat, 2010). Air bubbling (periodic injection of compressed air) also increases turbulence and results in high shear forces at the membrane surface (Cornelissen et al., 2007).

Chemical cleaning methods aim to dissolve, complexate, oxidize, inactivate, solubilize, hydrolyze, and denature membrane fouling (Madaenl, Mohamamdi, & Moghadam, 2001; Zondervan & Roffel, 2007). Common cleaning agents are:

1. acid cleaning agents used to dissolve inorganic precipitates caused by scaling ($CaCO_3$, $FeSO_4$, FeO, FeOH, $Al_2(SO_4)_3$, $BaSO_4$, $SrSO_4$, $CaSO_4$, etc.) or the inorganic matrix in a biofilm. Most frequently used chemicals are citric acid, sulphuric acid, and phosphoric acid
2. alkaline cleaning agents used to dissolve organic deposits. Typically used chemicals are NaOH and/or Na_2CO_3
3. complexing or anti-precipitating agents used to remove metals (mostly bivalent ions) and other precipitating ions from the solution. For example, ethylenediaminetetraacetic acid removes Ca^{2+} and Mg^{2+} ions
4. biocides used to inactivate microorganisms (for example, chlorine, chloramines, organic peroxides, glutaraldehyde, sodium bisulphite)
5. detergents or surfactants that reduce the surface tension of the water, resulting in better hydration and solubility of the fouling layer
6. enzymatic cleaning agents, aiming at hydrolyzing the extra polymeric substances formed by microorganisms
7. chaotrophic cleaning agents that induce denaturation of proteins, resulting in the better solvability of organic compounds

13.4.1 Conventional pretreatment

Conventional pretreatment operations for an SWRO plant usually include: (1) screens for preliminary coarse prefiltration; (2) chlorination and acidification steps; (3) addition of flocculation agents and coagulation/flocculation units; (4) single or double media filtration; (5) dechlorination and addition of antiscalants; and (6) cartridge filtration before RO trains. Main disadvantages of conventional pretreatment systems include high sensitivity to fluctuations of feed characteristics; difficulties in supplying feed a constant silt density index (SDI) less than 3.0; and large footprint owing to slow filtration velocities. A schematic representation of a conventional pretreatment system is illustrated in Figure 13.8.

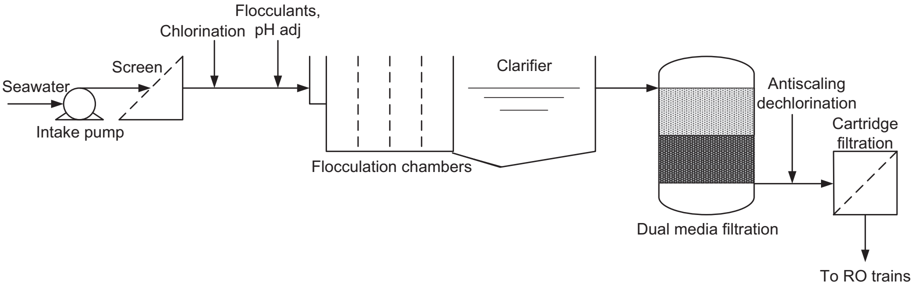

Figure 13.8 Typical conventional SWRO pretreatment system.

Screens are used to protect water pumps from particle clogging and remove coarse floating solids from the feed (used for both BW and SW). To limit the environmental impact, screens are designed to reduce the risk of impingement on marine organisms. Traditional travelling water screens are equipped with revolving wire mesh panels with 6- to 9.5-mm openings.

Chlorination is a standard disinfection method aiming at destroying or inactivating pathogenic microorganisms (bacteria, amoebic cysts, algae, spores, and viruses). In general, sodium hypochlorite is dispersed in SW, where the following reaction occurs:

$$NaOCl + H_2O \rightarrow HOCl + NaOH$$

In principle, chlorine gas can be injected directly into the feed stream: it readily dissolves in water to a maximum concentration of 3500 mg/L and reacts as:

$$Cl_2 + H_2O \rightarrow HOCl + HCl$$

However, direct injection is not a common practice in large desalination plants. In solution, hypochlorous acid dissociates to hydrogen and hypochlorite ions. The sum of Cl_2, NaOCl, HOCl, and OCl^- is indicated as free residual chlorine; this value should be maintained within 0.5−1.0 mg/L along the pretreatment line to prevent biofouling. Contact or detention times of 10−120 min may be required, which depend on the level of residual chlorine (Shams El Din, Arain, & Hammoud, 2000).

Coagulation/flocculation is applied to remove fine suspended solids (size range of 1 nm to 1.0 μm), soluble organic and toxic substances, and trace metals. Coagulants such as aluminum sulphate (or alum), ferric sulphate or ferric chloride, quicklime, and synthetic cationic/anionic/nonionic polymers are efficiently dispersed in flocculation chambers by diffuser grids, chemical jets, or in-line blender systems. Flocculation is achieved through slow mixing using paddles or propellers. Usually, several flocculation chambers are built in series with successively decreasing mixing velocities. Alum is the most commonly used primary coagulant; theoretically, 1 mg/L of alum will consume approximately 0.50 mg/L of alkalinity (as $CaCO_3$) and produce

0.44 mg/L of carbon dioxide. If the natural alkalinity of the water is not sufficient to react with the alum and buffer the pH, alkalinity is increased by adding lime or soda ash (coagulant aids).

After the coagulation/flocculation stage, simple and inexpensive slow sand filtration (SSF) can be successfully applied to treat feed with a turbidity of less than 50 NTU. SSF consists of the filtration of BW or SW through a bed of fine sand at low velocity, which causes the retention of organic and inorganic suspended matter in the upper 0.5−2 cm of the filter bed. Slow sand filters are also appropriate for removing pathogenic organisms that are eventually present in surface waters. Scraping off the top layer cleans the filter and restores its original efficiency. Although sludge handling is negligible and close control by an operator is not strictly necessary, slow sand filters require a large footprint, huge quantities of filter medium, and extensive labour for manual cleaning.

Dual media filtration (DMF) more efficiently removes suspended solids and pathogens and reduces the turbidity of the RO feed water to about 0.4 NTU with an SDI typically around 2.5 or slightly less. DMF consists of coarse anthracite coal over a bed of fine sand (Zouboulis, Traskas, & Samaras, 2007). Cleaning is usually required when water head loss through the filter exceeds 1.5−2.5 m.

Before entering the cartridge filters, the pH value of feed water has to be reduced at moderate values to prevent calcium carbonate scaling and damage to RO membranes. Sulphuric acid is typically injected to adjust the pH to around 7.5. The addition of antiscaling agents is also requested for SWRO systems operated with a recovery greater than 35% (Hasson, Drak, & Semiat, 2003). In past decades, sodium hexametaphosphate (SHMP) was extensively used as an antiscalant; today, it has been replaced by polymeric compounds such as polyphosphates and polyacrylates, because of the eutrophicating properties of SHMP and associated disposal problems. Dechlorination has to be performed before the RO stage to avoid oxidation damage by residual chlorine in the feed water (Saeed, 2002). Commonly, sodium metabisulphite (SMBS) is used for dechlorination owing to its high cost effectiveness: 3.0 mg of SMBS is used to remove 1.0 mg of free chlorine.

Cartridge filters with a pore size of 5−10 μm represent the last pretreatment stage before RO trains; they are used to capture contaminants and particles throughout the whole thickness of the filtering medium.

13.4.2 Membrane pretreatment

Interest in pretreatment operations based on membrane technology has recently increased. MF is a low energy-consuming membrane unit commonly used to remove suspended solids, reduce the chemical oxygen demand below 25 mg/L, and achieve an SDI less than 5. UF is a versatile separation process able to retain suspended solids, bacteria, macromolecules, and colloids; turbidity is also significantly decreased (less than 0.4 NTU) and SDI is below 2 in the permeate stream. The main benefits of integrated MF/UF pretreatment technologies are (Buscha, Chub, Kolbe, Meng, & Li, 2009; Vial & Doussau, 2002): (1) the potential for higher RO flux and water recovery factor; (2) a low footprint with respect to the conventional coagulation/flocculation/

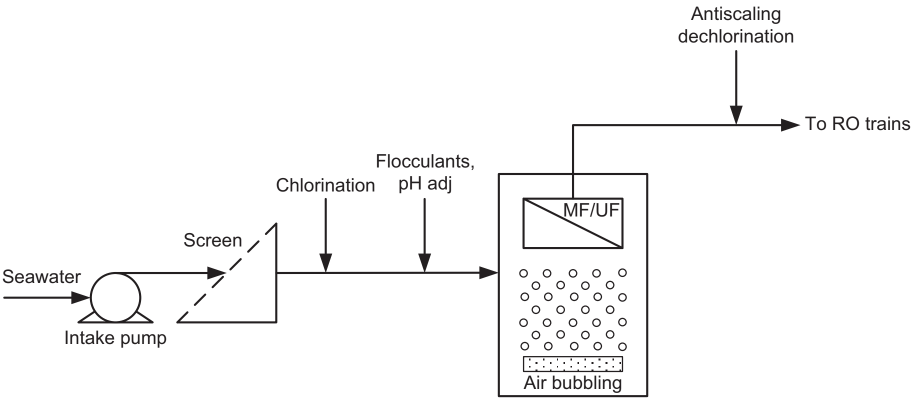

Figure 13.9 Seawater pretreatment based on submerged MF/UF unit (Di Profio, Ji, Curcio, & Drioli, 2011). Integration of standard MF/UF modules is also frequently applied.

DMF method; (3) improved membrane lifetime; and (4) a significant reduction in chemical dosing.

Although the capital cost of membrane pretreatment still exceeds that of conventional processes by about 10% (for instance, membranes are about twice as expensive as dual media filters), this is compensated for by the reduction of operation and maintenance (O&M) costs in subsequent RO trains. Whereas a typical annual replacement rate for RO membranes operated with a conventional pretreatment system is 15–20%, it is reduced to 10–15% when MF/UF pretreatment technology is used. The frequency of RO cleaning is also shortened. As the desalination industry gains long-term experience with membrane pretreatment systems, MF and UF are expected to become the standard for the next generation of BWRO and SWRO plants (operational scheme in Figure 13.9) (Voutchkov, 2010).

13.5 Energy requirements for RO plant

The energy consumption of modern large SWRO desalination plants is currently around 4 kWh/m^3, which makes membrane desalination the most energy-efficient technology for drinking water production (Darwish, Hassabou, & Shomar, 2013). Because of the lower salinity of the treated feed, BWRO requires less energy input (0.15–0.8 kWh/m^3) than a corresponding SWRO plant. About 80% of the total energy input is absorbed by high-pressure pumps that pressurize the feed entering RO trains; therefore, increasing of energy efficiency of both BWRO and SWRO trains is a critical issue. According to this perspective, various energy recovery devices (ERDs), such as the Francis turbine and Pelton wheel, and the turbochargers, DWEER and Pressure Exchanger, have been used over the past 15 years.

The goal of Pelton wheels and Francis turbines is to recover the energy of RO retentate (pressurized at 60–70 MPa) in the form of mechanical energy (Figure 13.10).

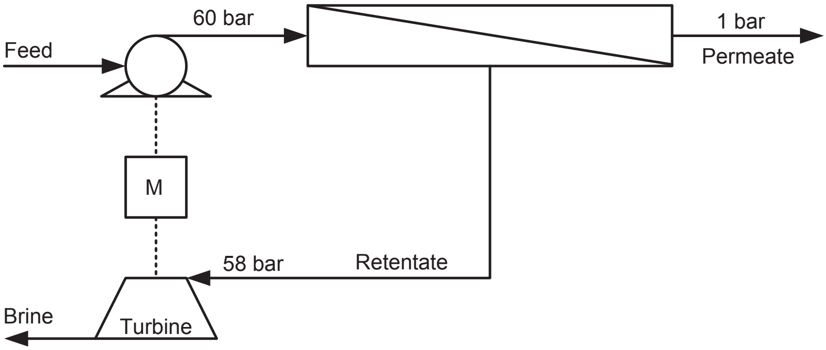

Figure 13.10 Scheme of an SWRO desalination unit with a Pelton wheel energy recovery device (ERD).

Pelton wheels and Francis turbines (usually denoted as Class III ERD) convert the hydraulic energy of the reject stream into rotational energy, which is delivered in the form of mechanical shaft power. Although these systems can reach 80—88% efficiency in converting hydraulic energy into rotational mechanical power, a second conversion is needed to obtain useful hydraulic energy. Overall, the real net transfer efficiencies fall to 63—76% (MacHarg, 2001).

Hydraulically driven pumps, such as hydraulic turbochargers, Pelton-drive pumps, and hydraulic pressure boosters, are centrifugal in nature and belong to the second class of ERDs; their hydraulic energy transfer efficiency is less than Class III devices.

Class I energy recovery technologies use the principle of positive displacement: Energy is transferred directly from the reject stream to an incoming SW stream that combines with the total feed stream to the RO membranes (operational principles of Desalco's Work Exchanger Energy Recovery (DWEER) system and Energy Recovery Inc.'s Pressure Exchanger (PX) are illustrated in Figure 13.11(a) and (b)). Positive displacement devices achieve net energy transfer efficiencies between 91% and 96% (Clemente & Mercer, 2011). Theoretically, Class I devices are able to decrease the energy consumption of SWRO plants to about 2 kWh/m^3 (MacHarg, 2001).

13.6 Energy from SW

The sea is more than just a potentially unlimited source of drinking water. Thermodynamic considerations based on evaluation of the energy of mixing suggest that a huge amount of energy can be potentially generated when waters of different salinities are mixed together (salinity gradient power generation). Vermaas et al. (2013) showed that the theoretical obtainable Gibbs free energy of mixing typical SW (30 g/L NaCl) and river water (1 g/L NaCl), both at a flow rate of 1 m^3/s, is 1.39 MW (Vermaas et al., 2013).

The global potential for salinity gradient power is reported to be 1650 TWh/year. In the United States, with a total flow of rivers into the ocean of about 1700 km^3/year, this

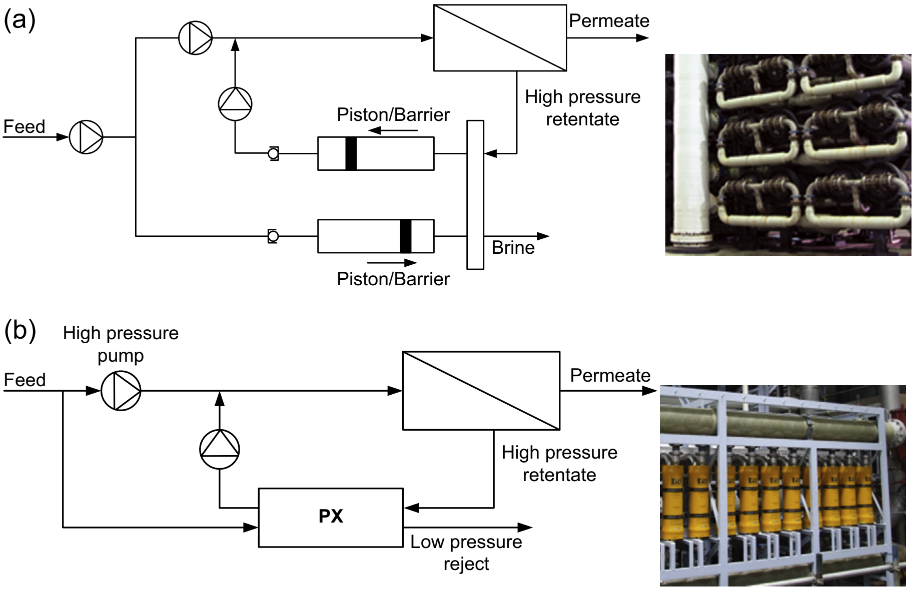

Figure 13.11 Operational schemes of: (a) DWEER system (Ashkelon SWRO plant, Israel); and (b) PXs (Qingdao SWRO plant, China).

technology could generate about 55 GW assuming an energy conversion efficiency of 40% (Thorsen & Holt, 2009).

Theoretical calculations using the van't Hoff equation (Eqn (13.1)) show that the maximum extractable energy from mixing freshwater with SW is 0.75 kWh/m^3 (assuming 0.55 M NaCl concentration); this value increases to 1.5 kWh/m^3 when considering SWRO brine from a desalination plant operating at a 50% recovery factor (Helfer, Lemckert, & Anissimov, 2014).

To date, pressure retarded osmosis (PRO) and reverse electrodialysis (RE) are the most investigated technologies to recover energy from saline gradients.

In PRO, a semipermeable membrane separates a low-concentration and a high-concentrated salt solution (also called a draw solution). Under the difference of osmotic pressure, water flows from the low-concentration compartment to the opposite side, thus increasing the volume of the concentrate flow. A turbine is coupled to the pipe containing the increased pressure flow to generate power. In the scheme of Figure 13.12, PRO is used to recover the osmotic energy of SWRO brine by operating with SW.

The performance of PRO strictly depends on the properties of the membrane. So far, membranes specifically developed for forward osmosis and PRO are almost exclusively commercialized by Hydration Technology Innovations (HTI), although the market is now accelerating driven by renewed interest in osmotic processes. PRO laboratory tests using commercial flat-sheet cellulose triacetate forward osmosis (FO) membranes from HTI resulted in the generation of a power density of 2.2 and 2.7 W/m^2 membrane area when operating with SW/BW and SW/pure water,

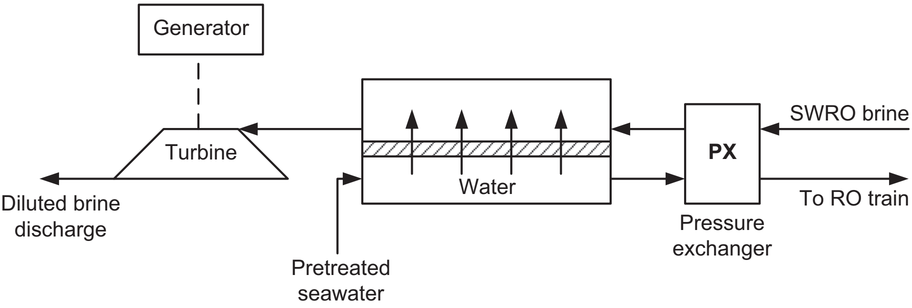

Figure 13.12 A possible scheme of pressure retarded osmosis (PRO) system to recover osmotic power from SWRO brine.

respectively (Achilli, Cath, & Childress, 2009). When using SWRO brine (6% NaCl), lab-made TFC hollow fibres specifically developed for PRO resulted in a power density higher than 10 W/m^2 (Wang, Tang, & Fane, 2012).

The first osmotic power plant prototype, with a designed capacity to generate 10 kW of electricity, was constructed by the Norwegian state-owned power company Statkraft in 2009. It is currently operated by Sintef Energy Research, a research division of the Sintef Group (Melanson, 2014).

RE is an emerging technology with the potential to generate energy from salinity gradients power (SGP). In a typical SGP-RE module, cation exchange membranes and anion exchange membranes are stacked alternately in a module (Figure 13.13).

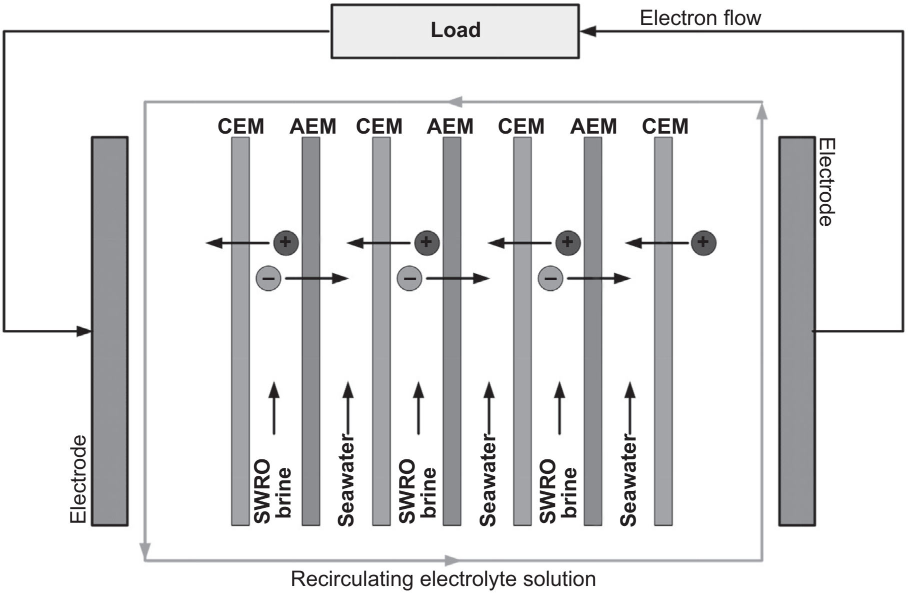

Figure 13.13 Scheme of an reverse electrodialysis (RE) unit operated with SWRO brine and seawater.

Driven by a concentration gradient, the diffusive flux of ions generates an electrochemical membrane potential recorded as a voltage across electrodes (Tedesco, Cipollina, Tamburini, van Baak, & Micale, 2012).

RE-SGP investigations carried out with aqueous NaCl solutions mimicking SW and river water salinity reached a power density of about 2 W/m^2 (Dlugolecki, Gambier, Nijmeijer, & Wessling, 2009; Post et al., 2010; Vermaas, Saakes, & Nijmeijer, 2011) and energy efficiency around 50%. Daniilidis, Vermaas, Herber, and Nijmeijer (2014) achieved a power density of 6.7 W/m^2 of total membrane area using 0.01 M NaCl solution against 5 M at 60 °C; in general, the power density increased monotonically for high-concentrated feed solutions (Daniilidis et al., 2014).

Theoretical predictions on a 12-cell stack equipped with Fujifilm ion exchange membranes and operated with 0.5 M/5.4 M NaCl dilute/concentrate solutions resulted in a maximum gross power density of 2.4 W/m^2 (Veerman, Saakes, Metz, & Harmsen, 2009).

13.6.1 Environmental impact of membrane desalination plants

Coastal and near-shore constructions (including intake and outfall structures), use of large quantity of SW causing impingement and entrainment of marine organisms, and disposal of large amount of brines and chemicals severely impact the environment.

Open intakes (the most common option in large desalination plants) and single open outfall or diffuser systems, when placed above the seafloor, may cause wave refractions and a change in current patterns, thus interfering with marine sediment. The local increase of turbidity results in an increased level of pollutants or a reduced level of dissolved oxygen, burying benthic flora and fauna. Moreover, structures above the seafloor might provide a substrate to which algae, anemones, or mussels might attach; these species attract echinoderms and crustaceans and ultimately result in a significant alteration in the marine community (Latterman & Hopner, 2008). Intake screens represent a high-mortality source for larger marine organisms and fish owing to impingement (causing suffocation, starvation, or exhaustion); for these reasons, the intake velocity of SW should be reduced as much as possible.

However, the highest impact on the marine environment is caused by the rejected SWRO concentrate stream. A typical plant operating at 50% recovery factor produces a brine with a salinity of about 70 that has a density of 1.053 kg/L (higher than the SW density of 1.025 kg/L) at room temperature. The brine spread through multi-port diffuser systems over the seafloor affects benthic communities. Studies on *Posidonia oceanica* showed that salinity around 45 causes about 50% mortality in 15 days (Latorre, 2005).

13.6.2 Membrane distillation

Membrane distillation (MD) is a membrane contactor technology with the potential to significantly reduce the amount of RO concentrate to be discharged. In MD, a microporous hydrophobic membrane contacts a heated solution on one side (‘feed’ or ‘retentate’). The hydro-repellent nature of the membrane avoids the permeation of any liquid

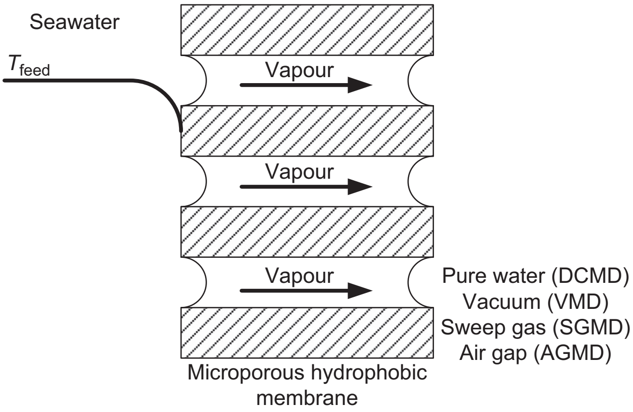

Figure 13.14 Principle of membrane distillation.

while sustaining a vapour—liquid interface at the entrance of each pore. There, water evaporates (whereas nonvolatile solutes are retained), diffuses across the membrane, and condenses on the opposite side ('distillate') of the module (Figure 13.14).

The specific method used to activate the vapour pressure gradient across the membrane (driving force) has four major MD configurations. In the most common and simplest arrangement, direct contact MD, the permeate side of the membrane consists of condensing pure water. Alternatively, the water vapour can be extracted by vacuum, recovered on a condensing metallic surface separated from the membrane by an air gap (AGMD), or removed by a sweep gas.

Ideally, MD guarantees the complete rejection of nonvolatile solutes such as macromolecules, colloidal species, and ions. Low-temperature gradients are generally sufficient to establish an acceptable trans-membrane flux (1—20 kg/m^{2}h); typical feed temperatures vary in the range of 50—80 °C, permitting the efficient recycle of low-grade or waste heat streams as well as the use of alternative energy sources (solar, wind, or geothermal). An interesting advantage with respect to RO is that MD does not have the limitations of concentration polarization; therefore, it can be applied to RO brines to increase the water recovery factor and decrease the amount of disposed brine.

Currently, no MD systems have reached a large industrial scale or are available on the market; most installations are at the pilot stage. The Swedish company Scarab Development provides flat-plate MD modules. Production rates of 10—20 kg/h are reported for high-temperature gradients across the membrane. These modules were also tested within European Union (EU)-funded project MEDESOL (SW desalination by innovative solar-powered MD system) (psa, 2014).

The Memstill® process was developed by TNO (The Netherlands) for SW desalination using air gap MD carried out in a countercurrent flow configuration. Cold SW flows through a condenser with nonpermeable walls, through a heat exchanger, and from there into the membrane evaporator. The wall of the evaporator is a microporous hydrophobic membrane through which water vapour diffuses and liquid salted water is retained (Hanemaaijer et al., 2006).

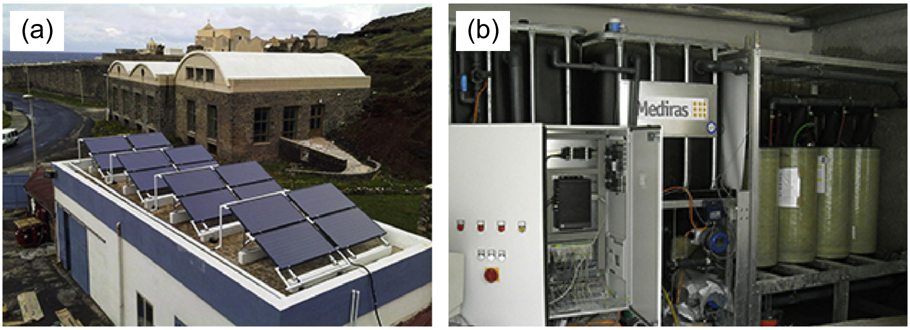

Figure 13.15 MEDIRAS project: Membrane Distillation (MD) pilot plant installed in Pantelleria, Italy. (a) Solar thermal collectors; (b) multi-module MD system.
From MEDIRAS Project website (2014) with kind permission.

Within the EU-funded project MEDIRAS (Membrane Distillation in Remote Areas), a two-loop MD system with a nominal production of 5 m^3/day was installed in an 8-MW diesel power plant on Pantelleria island, Italy. The system, which uses thermal energy (20%) from 40 m^2 of solar collectors and waste heat (80%) at 90 °C from the refrigeration of engines, is an example of a prototypal solar MD unit (Figure 13.15).

Air gap MD modules integrated with an appropriate heat recovery system were developed by SolarSpring GmbH, a Fraunhofer spin-off company. The module setup consists of three channels: condenser, evaporator, and distillate (Figure 13.16). Condenser and distillate channels are separated by a metallic foil, whereas a microporous hydrophobic membrane is interposed between the evaporator and the distillate channels. The hot SW (typically at 80 °C) is directed in the evaporator channel; there, water vapour diffuses across the membrane and condenses at the metallic foil surface where the heat of evaporation is partially recovered. Cold feed water (around 20 °C) enters in the distillate channel (in countercurrent with respect to the flow direction of the evaporator stream) to increase the temperature when in contact with the condensate foil (Koschikowski, Wieghaus, & Rommel, 2009).

The concept of integrated membrane desalination systems with MD operated on the RO retentate to increase the water recovery factor and reduce the volume of discharged

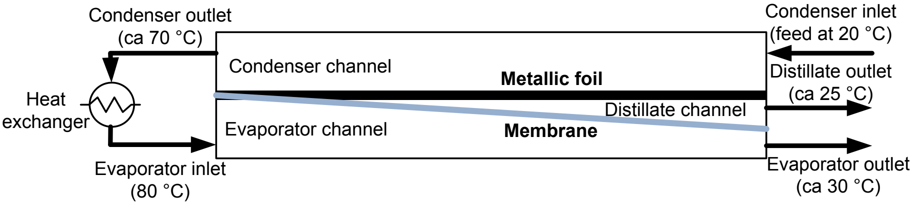

Figure 13.16 Principle of AGMD module with integrated heat recovery developed by SolarSpring GmbH.

brine (thus approaching the concept of zero liquid discharge) was developed within the EU-funded project MEDINA (membrane-based desalination, an integrated approach) (Al Obaidani et al., 2008; Macedonio, Curcio, & Drioli, 2007). The possibility of driving MD towards concentrations overcoming the saturation levels of salts dissolved in solution (MD—crystallization) led to the recovery of pure crystallized salts (sodium chloride, epsomite, etc.) from SW brine (Drioli, Criscuoli, & Curcio, 2005; Ji et al., 2010).

13.7 Economics of membrane desalination

Over the past 3 decades, the unit cost of water produced by SWRO desalination processes has progressively decreased (Figure 13.17). In particular, the economics of membrane desalination was found to be sensitive to the plant capacity. Despite a higher initial capital investment, plants with large capacities reduce the unit cost of water to 0.5—0.7 \$/m^3. Table 13.4 reports the estimated unit water cost produced in some large industrial SWRO desalination plants. On the other hand, the cost of desalinated water unit produced from BW by RO plants with a capacity less in 1000 m^3/day might range between 0.6 and 1 \$/m^3 (Karagiannis & Soldatos, 2008).

The unit cost of water (\$/m^3) is obtained by dividing the total annual cost (\$/year) and the annual yield (m^3/year).

The annual yield is determined by multiplying the maximum daily water production (m^3/day) and the annual plant utility (number of days on-line per year × percentage of daily plant capacity).

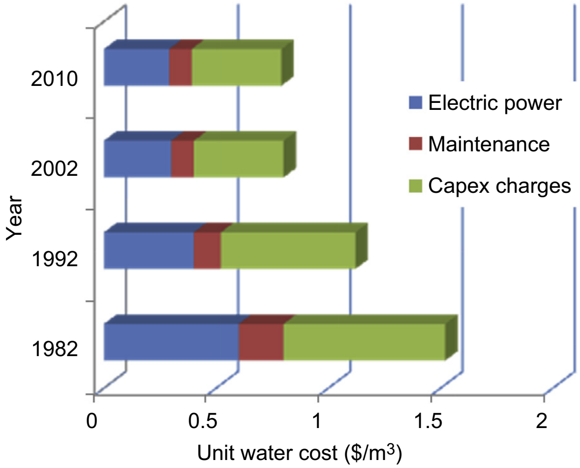

Figure 13.17 Historical trend of unit cost of drinking water produced by SWRO desalination. Data from Water Reuse Association (2012).

Table 13.4 **Unit water cost of some large SWRO plants**

SWRO plant	Start-up	Productivity (m^3/day)	Unit water cost (\$/m^3)
Ashkelon (Israel)	2001	3,20,000	0.52
Palmachim (Israel)	2005	83,000	0.78
Perth (Australia)	2006	1,44,000	0.75
Carlsbad (California)	2006	1,89,000	0.76
Skikda (Algeria)	2008	1,00,000	0.73
Hamma (Algeria)	2008	2,00,000	0.82
Hadera (Israel)	2010	3,48,000	0.63

Source: Ghaffour, Missimer, and Amy (2013); Pankratz (2009).

The total annual cost is determined by: (1) the annual cost of debt service on capital items ($/year), and (2) the annual operating and maintenance cost ($/year).

The annual cost of debt service on capital items ($/year) is composed of: (1.1) the annual debt service on water conveyance ($/year), and (1.2) the annual debt service of water production ($/year). (1.1) is calculated by multiplying the total capital cost of conveyance ($) by the capital recovery factor (CRF); (1.2) is calculated by multiplying the total capital cost of concerns and treatment ($) by the CRF.

The total capital cost of conveyance refers to the cost of constructing pipelines and any accessories and turnout on the pipeline route, including water storage tanks. The total capital cost of concerns and treatment includes both the cost of the contract associated with the delivery of the desalination plant and the cost of the engineering, legal, and administrative tasks associated with developing the contract documentation and executing the contract.

The CRF is calculated on the basis of a net present value of the asset, defined for a given discount rate (usually 6%) and a series of future payments over a defined period of time (usually serviced over 25 years).

The annual O&M costs, which emerge after plant commissioning and during plant operation include: (2.1) the cost of energy (in RO plants primarily electrical power, typically in the range of 3.5−5 KWh/m^3); (2.2) chemical costs (typically chlorine for disinfection, acid against calcium carbonate precipitation, antiscaling agents, coagulants and flocculants, caustic soda, etc.); (2.3) membranes and filtration media replacement; (2.4) maintenance costs covering all activities and consumables associated with scheduled and emergency servicing of mechanical equipment, calibrating and servicing instrumentation, data acquisition and electrical systems, and monitoring (collecting, analysing, and reporting on water quality data); and (2.5) labor costs.

A rough breakdown of total capital costs and O&M costs is provided in Figure 13.18(a) and (b).

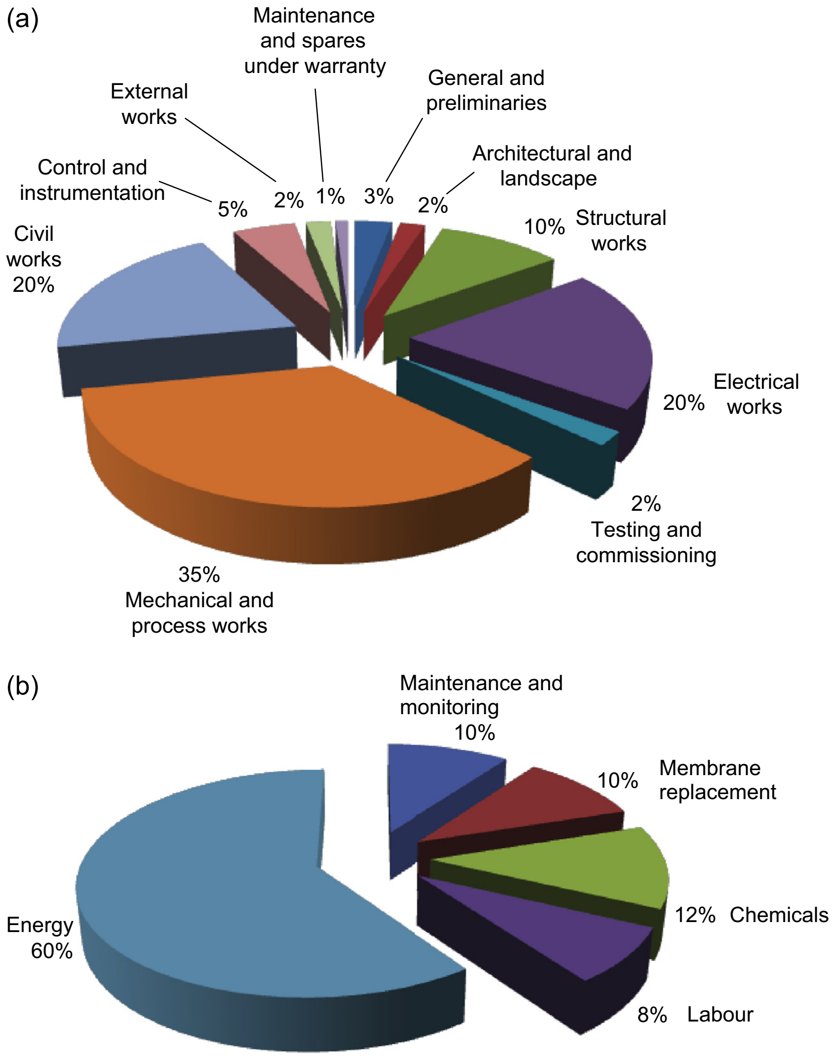

Figure 13.18 Percent breakdown of: (a) capital costs elements and (b) O&M cost elements. After UNESCO Centre for Membrane Science and Technology (2008).

13.8 Conclusions

Driven by RO, membrane science has exponentially grown over the past 40 years to become the leader in technology for BW and SW desalination. Despite this enormous success, many technological challenges still need to be addressed.

The recent development of ERDs has resulted in a drastic improvement in the energetic efficiency of desalination plants; however, the large energetic potential of concentrated streams remains unexploited. In this regard, emerging technologies such as PRO and RE promise a considerable reduction in the energy input and ultimately the unit water costs.

Further advances are expected to come from new RO membrane materials and module designs, and in particular from larger-diameter SWMs and high-flux membranes with enhanced selectivity.

Driven by rapid technological development, MF/UF operations are expected to increase in acceptance as standard pretreatment methods in the near future, with major benefits in terms of improved water quality and a lower RO membrane replacement rate.

Today, extensive expansion in the number and capacity of coastal desalination plants exacerbates the negative impact of rejected concentrate on the fauna and flora of the surrounding seas. Although far from being fully implemented on an industrial scale, MD and related operations (such as membrane crystallization) have emerged as an interesting answer to the brine disposal problem in the logic of zero liquid discharge.

In general, considering the strategic relevance of the desalination industry for many countries, continuous multidisciplinary research efforts are mandatory to make BWRO and SWRO affordable worldwide.

List of symbols

Italic font

c	Molar concentration
D	Diffusion coefficient
J_s	Solute molar flux
J_v	Volumetric flux
k	Partition coefficient
R	Ideal gas constant
T	Absolute temperature
$\overline{V}$	Partial molar volume

Greek font

δ	Membrane thickness
ν	Van't Hoff coefficient
Π	Osmotic pressure

Superscripts

f	Feed
p	Permeate

Subscripts

i	ith ion
s	Solute
w	Water

List of acronyms

AEM	Anion exchange membrane
AGMD	Air gap membrane distillation
BW	Brackish water
CA	Cellulose acetate
CEM	Cation exchange membrane
COD	Chemical oxygen demand
CRF	Capital recovery factor
DCMD	Direct contact membrane distillation
DMF	Dual media filtration
DOM	Dissolved organic matter
ED	Electrodialysis
EDR	Electrodialysis reversal
EDTA	Ethylenediaminetetraacetic acid
ERD	Energy recovery devices
GOR	Gain output ratio
LSI	Langelier saturation index
MD	Membrane distillation
MED	Multiple effect distillation
MENA	Middle East and North Africa
MF	Microfiltration
MSF	Multistage flash
MVC	Mechanical vapour compression
NOM	Natural organic matter
NTU	Nephelometric turbidity units
O&M	Operating and maintenance (costs)
PRO	Pressure retarded osmosis
PX	Pressure exchanger
RE	Reverse electrodialysis
RO	Reverse osmosis
SDI	Silt density index
S&DSI	Stiff and Davis stability index
SHMP	Sodium hexametaphosphate
SMBS	Sodium metabisulphite
SGMD	Sweep gas membrane distillation
SGP	Salinity gradient power
SSF	Slow sand filtration
SW	Seawater
SWM	Spiral-wound module
TCA	Cellulose triacetate
TDS	Total dissolved solids
TFC	Thin-film composite
TSS	Total suspended solids
TVC	Thermal vapour compression
UF	Ultrafiltration
VMD	Vacuum membrane distillation
WHO	World Health Organization

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Membrane technologies for municipal wastewater treatment

14

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14.1 Introduction

14.1.1 Membrane technologies for advanced wastewater treatment

Membrane technology is increasingly becoming popular for the advanced treatment of municipal wastewater. This is mainly because of growing concerns about water quality and pollution trends in relation to more complex global challenges such as rapid urbanisation, and increasing water demands in the domestic and industrial sectors. In the past few decades, wastewater treatment and reuse has gained interest, and so has advanced wastewater treatment technologies. Among these new technologies, membrane-assisted ones offer consistently high-quality treatment of effluent. Membrane technologies have also been shown to be promising in the removal of emerging compounds such as endocrine disturbing compounds (EDCs) and pharmaceutically active compounds (PhACs). It is projected that membrane-assisted technologies will be among the most reliable systems for water reclamation in coming decades (Shannon et al., 2008). Membrane technologies encompass a wide range of membrane processes depending on the desired quality of the effluent. For instance, by itself, microfiltration (MF) can remove particulate and colloidal forms of contaminants, whereas as a part of a membrane bioreactor (MBR), MF forms an integral part of a biological treatment system. Various membrane-assisted configurations for wastewater treatment exist, all of which have their own advantages and disadvantages depending on various factors such as effluent quality, energy consumption, and system complexity. Often, membrane technologies are employed in a combination of physical, chemical, and biological processes, resulting in an efficient process configuration for a particular scenario of wastewater treatment. For example, MBR technology combines activated sludge processes (ASPs) or an anaerobic biodegradation process with MF or ultrafiltration (UF); and MF or UF is also integrated as a posttreatment for tertiary treatment of municipal wastewater to achieve high effluent quality.

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14.1.2 Drivers and barriers to membrane technologies for municipal wastewater treatment

14.1.2.1 Advantages

Membrane technologies for municipal wastewater treatment, particularly MBRs, have been considered a reliable option for applications requiring a smaller footprint and/or higher effluent quality. In most cases of domestic wastewater treatment in developed urban areas, carbon (usually indicated by biochemical oxygen demand [BOD]) and nitrogen (NH_4-N and total nitrogen (TN)) removal are achieved using biological aerobic (BOD oxidation and nitrification) and anoxic treatment (denitrification) as part of the ASP. The conventional activated sludge process (CASP) is normally designed and operated at a mixed liquor suspended solids (MLSS) concentration of less than 4 g/L and a lower range of solids retention times (SRTs) to maintain the MLSS. In MBRs, however, the typical MLSS range between 8 and 15 g/L allows the intensification of microbial suspended growth and raises the possibility of reusing existing units to increase the plant's capacity with little or no increase in the footprint (Kraemer et al., 2012). In general, an advantage of membrane technology is the capital costs of construction/installation, which are similar to or lower than those of conventional technologies; although membrane cost can have an important role depending on the market trend in coming years. Current membrane technologies generally demand a high level of automation because of their need for continuous management of fouling. Consequently, membrane-assisted technologies can be controlled by computerised monitoring and control systems. This means that they can also be widely applied in decentralised and household systems in the coming decade.

14.1.2.2 Disadvantages

Clear disadvantages of MBRs can be seen in regions where conventional secondary wastewater treatment plants have already established. In this regard, although it would be possible to use existing bioreactors or clarifiers for the membrane basins, major retrofit modifications and reconstruction are required to meet the requirements of process geometry, the number of basins, and provisions for high mixed liquor recycle flow rates. Regarding retrofitting, it might be possible to use the clarifiers for other purposes: e.g. sludge storage. In the case of posttreatment membrane technologies (MF or UF units), the cost of membrane modules and operation are compared against the resulting high effluent quality after tertiary treatment.

In addition, there are limitations to the widespread application of membrane technologies in municipal wastewater treatment: e.g. energy consumption, membrane cost, and process complexity. Moreover, the scarcity of operational and equipment standards is evident. Although standardisation was contemplated in the European region through the European Commission's Amadeus project (de Wilde, Richard, Lesjean, & Tazi-Pain, 2007), this has not been widely considered successful so far. Membrane manufacturers have their own membrane module configurations and features and they also differ in recommended process unit geometry and sizes (Kraemer et al., 2012). Other operational disadvantages have been observed: e.g., the limited peak flow capacity and performance abilities compared with conventional clarifier-based systems. As a result of high energy consumption and, in some cases, chemical consumption, the operational costs of membrane technologies are still higher than those of conventional technologies, although the trend of energy consumption has recently decreased based on some new process modifications and the use of new materials.

14.2 Process fundamentals and indicators

14.2.1 Membrane-assisted processes and technologies

A membrane can be defined as a barrier that allows some components, either physical or chemical, to pass more freely through it than others. As normally applied to water and wastewater treatment, membranes are perm-selective. Main components in the process of membrane filtration are:

1. The permeate that passes through the membrane
2. The retentate that is rejected by the membrane

Membranes can be classified depending on their pore size, applied pressure, molecular weight cutoff, and permeability. Commonly accepted classifications in the field of water and wastewater treatment include MF, UF, nanofiltration (NF), and reverse osmosis (RO). Coarser membranes are associated with MF and the most selective membranes are associated with RO processes. As shown in Figure 14.1, the first two membranes operated at low pressures (0.1—5 bar) are normally used in MBR systems. They are capable of retaining bacteria, pathogens, and large fraction of viruses; the NF and RO membranes operated at higher pressures (3—100 bars) are able to reject soluble

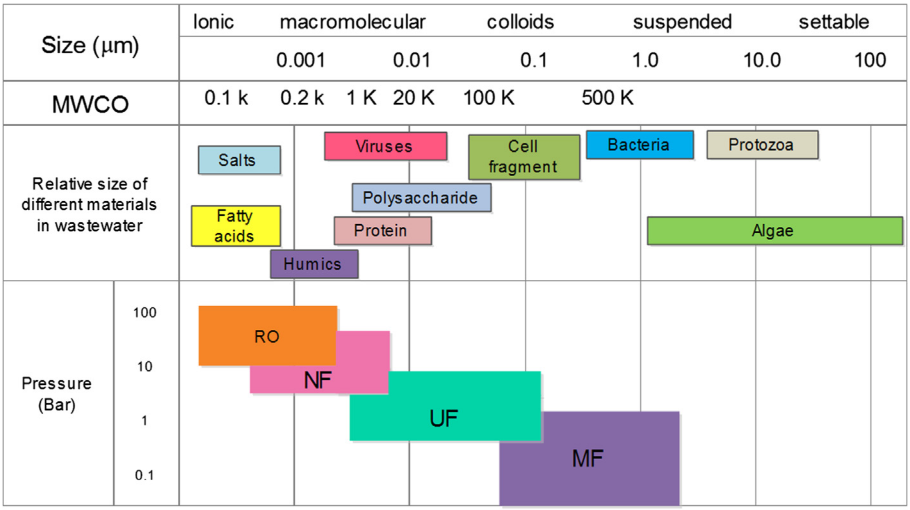

Figure 14.1 Various pressure-driven membrane processes.

organic compounds, EDCs, and PhACs. Reverse osmosis can also remove monovalent ions, e.g. sodium (Na^+). These well-established capabilities of various types of membrane processes are used in the design and operation of wastewater treatment systems.

There are several commonly observed operational issues with membrane processes in wastewater treatment. The rejected constituents in the retentate tend to accumulate at the membrane surface. This leads to various phenomena and a reduction in the water flow rate at a given transmembrane pressure (TMP), or conversely an increase in the TMP for a given flux (Judd, 2011). These phenomena are collectively referred to as fouling. A number of physicochemical and biological mechanisms are related to an increased deposition of fouling materials onto the membrane structure. Important factors in the type and the extent of fouling are the membrane material, feed water composition, and flux through the membrane.

14.2.2 Membrane-assisted systems in wastewater treatment

Because water quality in wastewater treatment and reuse applications is crucial, advanced treatment technologies are used to achieve the desired level of effluent quality. Principal unit operations and processes as well as constituent classes are listed in Figure 14.1. As suggested by Asano, Burton, Leverenz, Tsuchihashi, and Tchobanoglous (2007), an almost endless number of treatment processes can be applied in water reuse applications to improve the quality of treatment effluent for various purposes, such as different water reuse scenarios. Table 14.1 shows different processes and their capability of removing various classes of contaminants. Most established wastewater treatment processes employ biological treatment to remove BOD, total suspended solids (TSS), and even for total nitrogen and phosphorus. In membrane-assisted processes, membranes have an important role in removing residual suspended solids and improving the effectiveness of disinfection.

14.2.2.1 Conventional treatments versus MBRs

The main aerobic biological processes of municipal wastewater treatment applications can be categorised into three groups:

- Suspended growth biological treatment processes: In these processes, microorganisms are maintained in liquid suspension by mixing and aerating. The ASP is one of the most successfully applied processes for biological wastewater treatment. Various reactor types are used in the design of suspended growth processes for municipal wastewater treatment, such as completely mixed reactor and sequencing batch reactor.
- Attached growth processes: A medium, e.g. a rotating disc or fixed packing, is used to which microorganisms attach and form a biofilm. Then the biofilm microorganisms come in contact with wastewater and oxidise the organic matters.
- Hybrid processes: These use a combination of attached growth and suspended growth reactors to meet different conditions. An example of such processes is moving biofilm bioreactor technology.

These processes form the fundamental components of widely applicable biological wastewater treatment. In conventional treatment systems, these processes are applied

Table 14.1 Unit operation and processes used to remove various constituents in wastewater

Unit process	Suspended solids	Colloidal solids	Particulate organic matter	Dissolved organic matter	Nitrogen	Phosp-horous	Trace constituents	Total dissolved solids	Bacteria	Protozoan cysts and oocysts	Viruses
Secondary treatment	*			*							
Secondary + nutrient removal				*	*	*					
Depth filtration	*								*	*	
Surface filtration	*		*						*	*	
Micro-filtration	*	*	*						*	*	
Ultrafiltration	*	*	*						*	*	*
Dissolved air flotation	*	*	*							*	*
Nanofiltration			*	*			*	*	*	*	*
Reverse osmosis				*	*	*	*	*	*	*	*
Electro-dialysis		*						*			
Carbon adsorption				*			*				
Ion exchange					*		*	*			
Advanced oxidation			*	*			*		*	*	*
Disinfection				*					*	*	*

Source: Asano et al. (2007).

combined with well-established solid–liquid separation unit operations such as sedimentation tanks or clarifiers. The major advantage of applying these conventional treatment processes is that they are well understood; therefore, coping with the operation and maintenance is relatively simple. The other benefit is that automation of these processes is possible to a certain extent. However, conventional systems may not be most suitable, especially in an area with a lack of sufficient land. The effluent quality is also relatively lower than that of advanced membrane technologies. Table 14.2 compares conventional processes and MBRs.

Combined with conventional biological treatment processes, membrane processes can form robust membrane technologies, offering a higher level of treatment. For example, MBR technology, which combines membrane technology and the high-rate biological process, forms a unique technology for municipal wastewater treatment (Stephenson, Judd, Jeferson, & Brindle, 2000). Membrane bioreactors use two main configurations for solid–liquid separation:

- Side-stream MBR (sMBR): In this configuration, the membrane module is separated from the main reactor (Figure 14.2(a)). The mixed liquor in the bioreactor is pumped into a membrane module and a concentrated stream is retained by the membrane and returned to the bioreactor. Two major developments have been made in this configuration: A suction pump was added on the permeate side to increase flexibility and simultaneously decrease the cross-flow rate and energy consumption.
- Submerged or immersed MBR (iMBR): This configuration was introduced by Yamamoto, Hissa, Mahmood, and Matsuo (1989) with the aim of reducing energy consumption associated with the recirculation pump in the side-stream configuration. In this configuration, a membrane is directly immersed in the reactor (Figure 14.2(b)). As a result, only a suction pump is applied on the permeate side to create the TMP. Table 14.3 compares sMBR and iMBR.

Membrane bioreactors produce high effluent quality with a greater reuse potential. Table 14.4 compares the effluent quality of conventional treatments with a typical MBR system. In addition, the footprint of an MBR is much smaller than a conventional treatment process, mainly because of the higher SRT and higher MLSS in the bioreactor, and the small footprint of the membrane separation units. The Nordkanal plant in Germany, e.g., has five main parts: the sludge mechanical dewatering process, lidded sludge, the sludge liquor holding tanks, a grit chamber, the fine screen, the coarse screen, the MBR with nitrification and denitrification tanks, and process control. The plant has consistently achieved acceptable purification results: e.g. the chemical oxygen demand (COD) removal is about 97%. The biochemical oxygen demand (BOD) detected in effluent is below 3 mg/L when the average BOD in raw water is 300 mg/L. The elimination rate of TSS is 100%. In addition to this plant and other commissioned plants, various pilot studies have shown that MBR technologies are reliable for water reuse and/or can be applied to decentralised and household-scale wastewater treatment systems. It is evident that wastewater treatment plants that employ MBRs can produce effluent (Table 14.4) that can meet various requirements for reuse standards: e.g. landscape and agricultural irrigation and surface water discharge. For example, the Urban Wastewater Treatment Directive in Europe provides mandatory minimum design rules for sewerage systems as well as treatment plants (minimum

Table 14.2 Advantages and disadvantages of conventional treatment processes versus MBRs

Advantages	Disadvantages
Conventional wastewater treatment processes	
Technologies are well understood	Greater sludge production
Process potentials are universally accepted	More bio-solids handling and costs required
Different configurations allow the process to be designed to maximise contact time between macromolecules and microorganisms	Clarifier performance is reduced owing to development of filamentous organisms or poor settling sludge in aeration process
Energy requirement is less	Limited suspended solid removal that requires a high level of disinfection
Slow rate of kinetic reaction	Large footprint
Skilled operation and maintenance personnel are available	Subsequent filtration is needed for effective disinfection
MBRs	
Very high and stable effluent quality	High capital and operation costs
High potential for water reuse scenarios	More energy consumption
Smaller footprint and compact design	More extensive pretreatment required
Low sludge production	More chemical cleaning
Possibility of growth of specific microorganisms	Inevitable membrane fouling formation
Low suspended solid concentration and removal of large particles leads to more effective disinfection	Fouling mechanism and control still under investigation
	Lower effluent production capacity
Possible to add nutrient removal processes	Low oxygen transfer efficiency
Effluent quality independence from influent quality based on buffering effect of high MLSS values	Pilot scale often needed for full-scale design
	Membrane replacement is relatively expensive
Adaptable to decentralised and satellite technologies	Complicated control systems
Automation is fairly achievable	No standard configuration is available
High rate of nitrification owing to longer retention of nitrifying bacteria	

Source: Adapted from Asano et al. (2007).

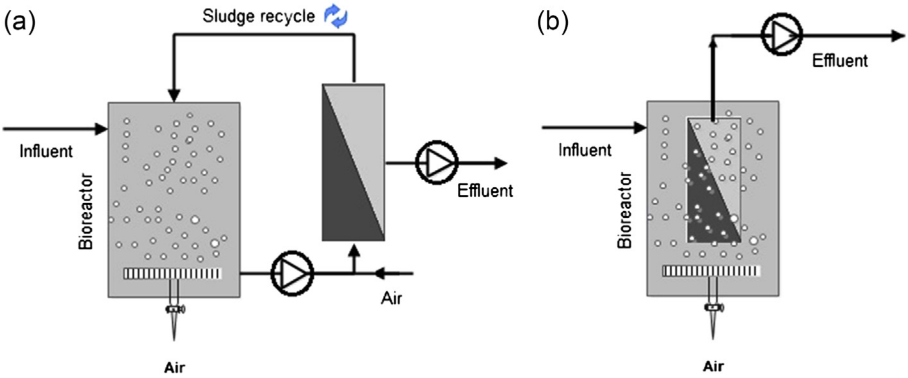

Figure 14.2 Configurations of (a) side-stream and (b) submerged MBRs.

Table 14.3 **Comparison of sMBRs and iMBRs**

	Side-stream MBR	Immersed MBR
Complexity	High	Fair
Flexibility	High	Low
Robustness	High	Fair
Flux	High (40–100 L/m^2·h)	Low (10–30 L/m^2·h)
Fouling	Cross-flow	Air bubble agitation
	Air lift	Back-washing (not always possible, e.g. flat-sheet [FS] membranes)
	Chemical cleaning	Chemical cleaning
Membrane packing density	Low	High
Energy consumption	High (2–10 kWh/m^3)	Low (0.2–0.4 kWh/m^3)

design requirement is the highest maximum weekly average load throughout the year). European regulations state that regardless of water reuse/wastewater treatment purposes, effluent from wastewater treatment plants in Europe must not exceed 25 mg/L BOD and 125 mg/L COD (Bloch, 2005).

14.2.2.2 Emerging membrane-assisted technologies: application of NF/RO after biological treatment

After the conventional secondary or MBR-based treatment, the level of treatment can be further improved by using membranes with tighter pore sizes. When an advanced level of removal of dissolved organics and inorganics is desired, membrane technologies such as NF and RO can be applied. The process of removing dissolved constituents can be accomplished by a pressure-driven separation process. Nanofiltration and RO require hydrostatic pressure to overcome the osmotic pressure of the feed stream, whereas MF and UF separations are based on the pore size and porosity of the membranes and the size of the contaminant constituents. Osmotic pressure can be seen where two solutions with different solute concentrations are separated by a thin, semi-permeable tissue, e.g. a membrane. If a difference in chemical potential exists across the membrane, water will diffuse through the membrane from the lower concentrated side (higher chemical potential) to the higher concentrated side (lower chemical potential) until a potential equilibrium occurs (the concentrations on both sides are similar).

Nanofiltration and RO are very similar in terms of rejection mechanisms and operation. However, some fundamental differences make these two technologies distinguishable from each other for wastewater treatment applications. Nanofiltration and RO remove particles with a molecular weight (MW) of 300−1000 g/mol and lower than 300 g/mol, respectively. Reverse osmosis is capable of removing monovalent ions, e.g. sodium and chloride, from 98% to 100%, whereas NF can reject these ions in the 50−90% range. They are also different in terms of water reuse application: NF is usually used for water softening and reducing the concentration of TDS in reclaimed water, whereas RO is used to desalinate seawater and brackish water. The characteristics and main applications of each technology are presented in Table 14.5.

14.2.3 Membrane modules

All commercial membrane modules have a particular membrane geometry and orientation in relation to the water flow. All membrane designs permit modularisation and provide limited economy scale with respect to membrane costs; these are directly proportional to the membrane area that correlates directly with the flow (Judd, 2011). The other factor is promoting turbulence, which results in a significant increase in energy costs and is adversely affected by high packing densities. A lower packing density would be preferred for promoting turbulence and hence reducing fouling. On the other hand, low packing densities can lead to high membrane unit costs. For an efficient module, narrowing the retentate flow channels is preferred to produce a high membrane packing density. Six types of membrane modules are commonly applied on an industrial scale:

- Flat sheet (FS)
- Hollow fibre (HF)
- Multi-tubular (MT)
- Capillary tube (CT)
- Pleated filter cartridge (FC)
- Spiral wound (SW).

Flat sheet, HF, and MT are suitable for MBR technologies owing to the reasons mentioned above, as well as for effective cleaning. Modules SW and HF are normally used in NF and RO technologies, mainly because of their high packing densities and small pores.

Table 14.4 Typical range of influent and effluent quality after CASPs and MBRs

Constituent	Unit	Untreated water	Conventional activated sludge	Activated sludge with biological nutrient removal (BNR)	MBR
TSS	mg/L	120–400	5.0–25.0	5.0–20.0	£1.0
BOD	mg/L	110–350	5.0–25.0	5.0–15.0	<1.0–5.0
COD	mg/L	250–800	40–80	20.0–40.0	<10.0–30.0
Total organic carbon	mg/L	80–260	10.0–40.0	8.0–20.0	0.5–5.0
Ammonia nitrogen	mg N/L	12–45	1.0–10.0	1.0–3.0	<1.0–5.0
Nitrate nitrogen	mg N/L	0 to trace	10.0–30.0	2.0–8.0	<10.0[a]
Nitrite nitrogen	mg N/L	0 to trace	0 to trace	0 to trace	0 to trace
Total nitrogen	mg N/L	20–70	15.0–35.0	3.0–8.0	<10.0[a]
Total phosphorous	mg P/L	4–12	4.0–10.0	1.0–2.0	0.5–2.0[a]
Turbidity	NTU	<15	2.0–15.0	2.0–8.0	£1.0
Volatile organic compounds	mg/L	100–400	10.0–40.0	10.0–20.0	10.0–20.0
Metals	mg/L	1.5–2.5	1.0–1.5	1.0–1.5	Trace
Surfactants	mg/L	4.0–10.0	0.5–2.0	0.1–1.0	0.1–0.5
TDS	mg/L	270–860	500–700	500–700	500–700
Trace constituents	mg/L	10.0–50.0	5.0–40.0	5.0–30.0	0.5–20.0
Total coliforms	No./100 mL	10^6–10^9	10^4–10^5	10^4–10^5	<100
Protozoan cysts and oocysts	No./100 mL	10^1–10^4	10^1–10^2	0.0–10.0	0.0–1.0
Viruses	Plaque–forming units/100 mL	10^1–10^4	10^1–10^3	10^1–10^3	10^0 to $<10^3$

Note:

[a] With BNR process.

Source: Adapted from Asano et al. (2007).

Table 14.5 Characteristics of NF and RO applications

Factor	Nanofiltration	Reverse osmosis
Membrane driving force	Hydrostatic pressure difference	Hydrostatic pressure difference
Separation mechanisms	Sieve, electrostatic repulsion, solution/diffusion, exclusion	Electrostatic repulsion, solution/diffusion, exclusion
Pore size (nm)	Microspores (<2.0)	Dense (<2.0)
Operating range (mm)	0.001–0.01	0.0001–0.001
Molecular weight cutoff (Da)	300–1000	<300
Typical removed constituents	Small molecules, colour, hardness, bacteria, viruses, proteins, multivalent ions	Very small molecules, colour, hardness, bacteria, viruses, proteins, nitrate, sodium, multivalent and monovalent ions
Operating pressure (bar)[a]	3.5–5.5	12.0–18.0
Energy consumption (kWh/m^3)[a]	0.6–1.2	1.5–2.5
Membrane configuration	Spiral wound (SW), hollow fibre (HF)	SW, HF
Typical application	Water softening (to reduce the concentration of multivalent ions leading to water hardness) and water reuse (used for both non-potable and potable water reuse applications)	Desalination (removing dissolved organics and inorganics for both seawater and brackish water), water reuse (used for both nonpotable and potable water reuse applications)

Note:
[a] Based on treating reused water with a TDS concentration in the range of 1000–2500 mg/L. It is widely believed that higher operating pressures are needed for seawater.
Source: Adapted from Asano et al. (2007).

14.2.4 Operational factors of membrane technologies in wastewater treatment

As one of the most important operational factors, flux (J), or permeate, is the quantity of fluid passing through a unit area of membrane per unit area ($m^3/m^2 \cdot s$ or $L/m^2 \cdot h$). The regular flux unit used in wastewater applications is metres per day (m/d) or litres per metre square per hour ($L/m^2 \cdot h$ or LMH). Membrane bioreactors are normally operated at 0.025–0.400 m/d of permeate. Transmembrane pressure is another important operational parameter; it defines the driving force for solid—liquid separation in MBRs or MF/UF applications as posttreatment.

Other parameters are used to describe the operational characteristics of membrane processes in municipal wastewater treatment. For example, resistance (R) is the ratio of the pressure difference (ΔP) to the flux and viscosity (η). It is inversely correlated to the permeability (K). The units normally used for resistance and permeability are m^{-1} and LMH/bar, respectively. The resistance in membrane processes for municipal wastewater treatment consists of different components:

1. Membrane resistance: This component mainly depends on membrane characteristics such as material, pore size, and surface porosity.
2. Resistance of the fouling layer: This is normally correlated with filtration mechanisms depending on feed constituents and/or microbial products.
3. Solution interfacial region: This component is associated with concentration polarisation (CP).

14.3 Membrane fouling in wastewater treatment

Membrane fouling refers to the adsorption and deposition of constituents on a membrane surface or in the membrane pores. Consequently, fouling leads to a reduction in membrane permeability. Fouling in general is divided into two subgroups:

- Reversible fouling, usually formed on the membrane surface. It can be removed by physical cleaning.
- Irreversible fouling, which designates internal fouling in the membrane pores and can be removed only by chemical cleaning.

14.3.1 Characteristics of membrane fouling

Common compounds and materials (foulants) causing membrane fouling can be categorised into four groups (Table 14.6):

- Particulate components: Small particles can accumulate on the membrane surface, consequently forming a filter cake. This type of fouling is common in MBRs using MF and UF.
- Organic compounds: Adsorption of dissolved organics on membrane surface results in membrane fouling. Natural organic matters (NOMs), e.g. humic substances, in drinking water filtration processes have a significant role. In membrane processes for wastewater treatment, organics remaining after biodegradation also can contribute to fouling.
- Biofouling: This refers to the adhesion and growth of microorganisms on the membrane surface. It results in a loss of membrane performance. Membrane processes other than MF and UF commonly used in MBRs and posttreatment after conventional ASP, NF, and RO may have more biofouling (Jiang, 2007).
- Scaling: This occurs when dissolved salts exceed their solubility product. This phenomenon is of main concern in the operation of NF and RO with regard to the deposition of salts such as $CaCO_4$, $CaSO_4$, $BaSO_4$, $SrSO_4$, $MgCO_3$, and SiO_2 (Baker, 2012).

The interaction between foulants and membrane mainly concerns the phenomenon involving colloidal and macromolecular organic matter rather than the particulates. A number of factors can affect this complex interaction (Table 14.6).

14.3.1.1 Electrostatic repulsion

If a colloid or microorganism contains a similar charge to a membrane surface, it will be repelled by the membrane surface as a result of electrostatic forces. As a consequence, the adsorption will be much less. Therefore, manufacturers develop membrane modules with appropriate membrane surface properties.

14.3.1.2 pH

Various organics compounds present in a wastewater matrix will be more negatively charged at higher pH conditions because of the proton deficiency. This increases the dissociation of protons into the solution. In other words, pH is likely to influence electrostatic repulsion.

14.3.1.3 Hydrophobicity

Opposite hydrophobicity in the microorganisms and the membrane surface also leads to hydrophobic repulsion; this also causes adsorption. Many membranes are made of hydrophilic materials (or coated), which is advantageous in terms of high permeability and low affinity with various NOMs.

14.3.1.4 Ionic strength

Adsorption of microorganisms and colloids to the membrane is reduced by the low ionic strength of the feed water. For example, in the filtration of proteins and NOMs, screening of the charges is decreased at a low ionic strength. As a result, these molecules repel each other at the membrane surface.

14.3.2 Concentration polarisation

Concentration polarisation relates to the continuous transport of polluted influent to the membrane surface and the selective retention of some constituents that leads to the accumulation of some solutes on or near the membrane surface. Over the operation time, their concentration increases; consequently, a boundary layer of higher concentration is created. This layer contains near-stagnant fluid and the velocity at the membrane surface is zero. It means that the only transport mode within this layer is diffusion. The concentration build-up causes a particle back-transport flux into the bulk. Cross-flow filtration can improve particle back-transport and reduce fouling, because higher flux leads to higher diffusion.

14.3.3 Fouling mechanisms in MBRs

Fouling mechanisms observed in MBRs can be divided into four different groups.

14.3.3.1 Complete blocking

Complete blocking refers to the situation in which each particle, upon arriving at the membrane surface, participates in blocking some pore with no superposition of particles. These particles have sizes comparable to the membrane pore sizes.

Table 14.6 Characteristics of different types of foulants

	Particulate fouling	Organic fouling	Biofouling	Scaling
Foulants	Colloid suspended solids	Organic matters	Microorganisms	Salts, metal cations
Major factors affecting fouling	Concentration particle size distribution compressibility of particles	Concentration, charge, hydrophobicity, pH, ionic strength, calcium	Temperature, nutrients	Temperature, concentration, pH
Fouling prediction indicator	Silt density index, Modified fouling index, specific resistance to fouling	Dissolved organic carbon (DOC), ultraviolet$_{254}$ (UV$_{254}$), specific ultraviolet adsorption (SUVA)	Assimilable organic carbon, biofilm formation rate	Solubility
Feed water pretreatment	Coagulation, MF, and UF	Adjustment of pH, coagulation	Sand filtration, biofilter, coagulation, flocculation, MF, UF	Acid, antiscalant

Source: Jiang (2007).

14.3.3.2 Standard blocking

This mechanism refers to conditions under which particles are deposited onto the internal pore walls. This leads to a decrease in pore volume.

14.3.3.3 Cake filtration

Cake filtration is defined as a phenomenon in which each particle locates on the other deposited particles. It implies that there is no room for particles to directly obstruct the membrane area.

14.3.3.4 Intermediate blocking

Intermediate blocking is pronounced when each particle can either settle on other particles that have already arrived or directly block some membrane area. It may be considered an intermediate step between complete blocking and cake filtration (Bowen, Calvo, & Hernández, 1995).

14.3.4 Fouling control: chemical and physical cleaning

Membrane cleaning is achieved by physical and chemical cleaning. Physical cleaning is usually accomplished by backwashing and relaxation in wastewater treatment by membrane-assisted technologies. Backwashing is simply referred to reversing the flow toward membranes, whereas relaxation is defined as ceasing permeation to scour the membrane with aeration (air bubbles). On the other hands, chemical cleaning is achieved with some mineral and organic acids, caustic soda, and sodium hypochlorite. Sometimes the cleaning process can be carried out with backwashing with the addition of a lower concentration of a chemical agent (chemically enhanced backwash). Table 14.7 compares various cleaning methods.

In most membrane-assisted technologies, fouling control is determined by considering the balance between flux, physical and chemical cleaning, and CP control. Controlling and reducing CP-related fouling can be divided into two methods (Judd, 2011):

- Promoting turbulence: This reduces the thickness of the boundary layer. Promoting turbulence in iMBRs and sMBRs can be achieved by increasing membrane aeration and increasing cross-flow velocity, respectively.
- Reducing flux: This decreases fouling formation on the membrane surface.

A successful MBR project, the cleaning method at the Nordkanal wastewater treatment plant in Germany, is summarised (Blastakova, Engelheardt, Drensla, & Bondik, 2009):

- Physical cleaning: by employing air scouring, backwashing, and relaxation of filters during the time of low inflow when the installed capacity is reduced by 12.5%.
- Chemical cleaning: by using backwashing with chemical cleaning agents for maintenance cleaning in place in biomass and/or on air, and occasional intensive cleaning out of place.
- Additional mechanical cleaning to remove debris from the membrane modules after COP when necessary.

Table 14.7 Comparison between physical and chemical cleaning

	Physical cleaning	Chemical cleaning
Methods	Backwashing without air	Base (e.g. caustic soda, citric, oxalic)
	Backwashing with air	Acid (e.g. hydrochloric/sulphuric, citric/oxalic)
	Relaxation	Oxidant (e.g. hydrogen peroxide, hypochlorite)
Advantages	Simpler and less complex	Much higher cleaning efficiencies (generally)
	No chemical needed; consequently, no chemical waste	Capable of returning flux to original or better conditions
	No membrane degradation Capable of removing gross solids	Capable of removing tenacious materials from membrane surface

14.4 Design, operation, and control of membrane processes in municipal wastewater treatment

Various process components of the entire technology need to be considered when designing membrane-assisted technology. Wastewater characteristics and the purpose of wastewater treatment are important factors in the design of membrane technologies.

The required membrane surface area is a function of the membrane flux and hydraulic load. The net flux is an important parameter that characterises the average flow rate including the relaxation and backwash phases (Li, Fane, Ho, & Matsuura, 2008). With the help of net flux, the treatment capacity of the whole plant is estimated. The normal range for the maximum fluxes of iMBRs in municipal wastewater treatment is 25–30 L/($m^2 \cdot h$), with a net flux about 20% lower. In terms of the optimal operation of a pilot-scale plant, it is usually recommended to record the initial flux and test different cleaning strategies to reconcile fouling control measures, cleaning procedures, and required flux. Estimation of recycle ratio and an appropriate flow regime and filtration tank are important steps in the design and operation of membrane technologies. Some important parameters and their value ranges for NF and RO are summarised in Table 14.5. Regarding operational issues, the membrane lifetime is important. It is directly correlated to operation and maintenance costs, e.g. repair, replacement, and operation efficiencies. Operating efficiencies can be considered a consequence of the membrane lifetime and performance stability (Asano et al., 2007). The following factors have a high impact on the operational efficiency of all membrane technologies in municipal wastewater treatment (Celenza, 2000):

- Consistent membrane fouling involving frequent and long regeneration times
- Membrane failure and then replacement
- Failure of high-pressure pumps
- Failure of membranes and pumps as a result of abrasive waste materials and components.

14.5 Optimisation of membrane processes in municipal wastewater treatment

14.5.1 Cost assessment

Cost assessment in most membrane technology projects is divided into capital costs (CAPEX) and operation and maintenance (OPEX) costs. Generally, it is challenging to obtain an appropriate cost assessment. It is evident that membrane prices have gradually decreased and are still slowly dropping. Judd (2011) reported that the prices of MBRs in the United Kingdom decreased from 320 to 80 €/m^2 membrane surface area from 1992 to 2000. However, the other parts of these systems (e.g. aeration devices, control systems, cleaning devices, and pipes) are almost at the same prices. Moreover, it is reported that at different wastewater treatment plants with MBRs, e.g. the plant at Nordkanal, Germany, the space requirement could be significantly reduced compared with conventional design capacity planning (Blastakova et al. 2009; Henze, van Loosdrecht, Ekama, & Brdjanovic, 2008). Consequently, capital costs would be substantially decreased. Investment costs for the Nordkanal MBR wastewater treatment plant amounted to €21.5 million (including VAT). In addition, approx. €3.2 million was spent for engineering, special consults, acquisition of land, and charges for environmental compensation (Blastakova et al., 2009). Life cycle cost analysis, which can be defined as a sensitivity analysis on uncontrollable expenditures, shows that although the capital cost often needs enormous investment, a more capital intensive technology might be selected when the O&M costs are more reasonable and controllable (Li et al., 2008).

14.5.2 Energy efficiencies and operational costs

There are a number of equations and evaluation methods for energy efficiency in water reuse technologies, but according to Li et al. (2008), most of these formulas, which were developed a few decades ago, have not been updated and reconsidered properly. Therefore, it is necessary to revisit these evaluation methods, especially because of the development of new technologies with different materials and methods of construction. Various factors are associated with energy consumption and operational costs. Hydraulic factors have an important role in improving energy efficiency. Aging infrastructures and redundant equipment should also be taken into consideration. Other important factors for this evaluation are the appropriate adaptation and replacement of membranes and other parts of membrane-assisted technologies to ensure acceptable energy efficiency.

The aeration process may be considered a major part of total energy demand and operational costs. The energy consumption of aeration in MBRs in a normal wastewater treatment plant is about 0.4 kWh/m^3 effluent whereas in CASPs it is in the range of 0.25−0.40 kWh/m^3 (Krause, 2005). Fouling control is another main part of energy consumption. The cost of chemical cleaning, regardless of the energy demand, is about 0.2−1.0 €/m^2 membrane surface area per year (Li et al., 2008). Based on a biological activated sludge model study of the Schilde MBR, the energy consumption of the entire MBR is 0.63 kWh/m^3 with a yearly average permeate production of 220 m^3/h. Therefore, the energy cost can be determined as 220 m^3/h × 24 h/d × 365 d/yr × 0.63 kWh/m^3 × 0.08 €/kW = 97,130 €/yr. In this evaluation, the energy consumption for coarse bubble aeration, compressors, warming of the permeate for cleaning, mixing energy, and pretreatment are 35.2%, 3.1%, 6.6%, 7.0%, and 2.6%, respectively, for a total of 54.0% of the total energy when the system is operated at 220 m^3/h (Greenlee, Lawler, Freeman, Marrot, & Moulin, 2009). Blastakova et al. (2009) reported that with the Nordkanal wastewater treatment plant at full capacity, specific energy consumption ranges between 0.4 and 0.8 kWh/m^3 wastewater. On average, the energy demands of membrane air scouring, process aeration, bioreactor mixing, permeate suction, and biomass circulation are 49%, 12.1%, 11.5%, 2.7%, and 1.3%, respectively. The remaining 23.2% is consumed by pumping stations, pretreatment, dewatering units, and miscellaneous process units (Blastakova et al., 2009; Judd, 2011).

Membrane lifetime is also an important factor in cost assessment. Studies have shown that membrane lifetime relates to the composition and pretreatment of the wastewater, membrane material, module construction, and cleaning strategies (Li et al., 2008). Moreover, toward the end of an effective membrane lifetime, energy consumption can increase to 170% owing to the reduced flow rate (Fenu et al., 2012).

14.6 Future trends and conclusion

Emerging global issues such as rapid urbanisation, increasing water pollution, and climate change have resulted in water scarcity in many regions of the world. As a result, improvement in water quality treatment technologies and a move toward water reuse are increasingly being adapted to satisfy growing water demand. From a sustainability point of view, wastewater treatment and reuse will be essential, placing resultant responsibility on wastewater treatment companies to provide clean water to suite end users. Membrane-assisted technologies are an undisputed part of high-quality wastewater treatment and reuse systems. However, there are still various challenges and issues, e.g. high CAPEX and OPEX costs, low flow rate, and operational complexities. In looking to develop new approaches, it is important to be able to meet both existing and new water reuse regulations and guidelines consistently. Regarding future regulations and guidelines, the additional issue is to consider removing micropollutants and emerging contaminants such as PhACs, endocrine-disruptive compounds, and personal care products; legislation should clearly require their removal.

Furthermore, development of new membrane technologies is needed that can be less expensive in terms of investment and OPEX and/or more effective in terms of water quality. New membranes have been successfully developed using different materials but they still need improvement. For example, according to Howell (2004) it is possible to make HF membranes with different materials; the membranes can be concentric, leaving an annular gap that can be filled by microorganisms so as to create an MBR in which feed streams and product streams can be totally separated or where different nutrients can be supplied from two different streams. Various ongoing developments may lead to the emergence of cost-effective and energy-efficient membrane technologies that can transform municipal wastewater treatment practices for high effluent-quality production with a high potential of water reuse.

List of acronyms and abbreviations

AnMBR	Anaerobic biodegradation process
ASM	Activated sludge model
ASP	Activated sludge process
BOD	Biochemical oxygen demand
CAPEX	Capital costs
CASP	Conventional activated sludge process
CIP	Cleaning in place
COD	Chemical oxygen demand
COP	Cleaning out of place
CP	Concentration polarisation
CT	Capillary tube
DOC	Dissolved organic carbon
EDCs	Endocrine disturbing compounds
FC	Pleated filter cartridge
FS	Flat sheet
HF	Hollow fibre
iMBR	Immersed membrane bioreactor
K	Permeability
MBBR	Moving biofilm bioreactor
MBR	Membrane bioreactor
MF	Microfiltration
MLSS	Mixed liquor suspended solids
MT	Multi-tubular
MW	Molecular weight
MWCO	Molecular weight cutoff
NF	Nanofiltration
NOMs	Natural organic matters
OPEX	Operation and maintenance costs
PCPs	Personal care products
PhACs	Pharmaceutically active compounds

R	Resistance
RO	Reverse osmosis
RSS	Residual suspended solids
sMBR	Side-stream MBR
SOCs	Soluble organic compounds
SRT	Solids retention time
SUVA	Specific ultraviolet adsorption
SW	Spiral wound
TMP	Transmembrane pressure
TN	Total Nitrogen
TSS	Total suspended solids
UF	Ultrafiltration
UV_{254}	Ultraviolet_{254}
η	Viscosity
ΔP	Pressure difference

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Membrane technologies for the removal of micropollutants in water treatment

15

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15.1 Introduction

In the treatment of natural water for drinking and household needs and industrial wastewaters, pressure-driven membrane techniques are principally applied. Other processes are taken into consideration as well, such as electrodialysis (ED) and electrodeionization (EDI), Donnan dialysis (DD) and diffusion dialysis, membrane contactors, and bioreactors. The choice of an appropriate membrane process depends on the scope of removed effluents and admixtures present in water. They can be used to remove effluents as independent processes or be combined with unit complementary processes, forming a treatment process line. Potential membrane techniques in the treatment of natural waters and wastewaters are:

- Reverse osmosis (RO), which retains monovalent ions and most low-molecular organic compounds - principally desalination of waters and removal of inorganic and organic micropollutants
- Nanofiltration (NF), which retains colloids, low-molecular organic compounds, and bivalent ions - softening and removal of micropollutants from water
- Ultrafiltration (UF) and microfiltration (MF), clarification methods for the removal of turbidity, retention of suspended substances and microorganisms, and disinfection
- Hybrid processes covering membrane techniques, especially UF and MF, with coagulation, adsorption onto activated carbon and in bioreactors, and treatment of drinking water and wastewaters
- Processes with ion-exchange membranes (ED and EDI, and DD and diffusion dialysis) to remove inorganic pollutants
- Membrane bioreactors (MBRs) for the removal of organics and to some extent inorganics.

Increasingly numerous micropollutants occur in the degenerated water environment, mainly in surface waters, but also in underground waters. Micropollutants in surface waters come from rainfall, sewage, industrial wastewaters, and landfill leachate as well as earth flow from the drainage area. The concentration of micropollutants in surface waters depends on their source and the pollution grade of the drainage area and sewage. Pollutants and organic additives present in natural waters are mainly dispersed substances and microorganisms, organic compounds, including natural organic matter

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(NOM), endocrine active compounds (EAC), and pharmaceutical residues and personal care products, as well as inorganic substances such as heavy metals and toxic anions.

15.2 Inorganic micropollutant removal

A number of inorganic compounds including anions (nitrate (V); chlorate (VII), (V), and (III); bromate (V); arsenate (III) and (V); borate and fluoride) and heavy metals have been found at potentially harmful concentrations in natural water sources and wastewaters (Bodzek & Konieczny, 2011a, 2011b; Bodzek, Konieczny, & Kwiecinska, 2011; Crespo, Velizarov, & Reis, 2004; Velizarov, Crespo, & Reis, 2004; Velizarov et al., 2008). Some of these compounds are highly soluble in water and dissociate completely, resulting in the formation of ions that are chemically stable at normal water conditions. The maximum permissible levels of these compounds in drinking water and wastewaters discharged to environment, set by the World Health Organization (WHO) and a number of countries, are very low (in the range of micrograms per liter to a few milligrams per liter). Thus, most of them can be referred to as charged micropollutants.

Pollution of the aquatic environment with metals and anions may be of either natural or anthropogenic origin. Several common treatment technologies, including coagulation—sedimentation—filtration, chemical precipitation, adsorption, ion-exchange, classical solvent extraction, evaporation, and biological methods, which are currently used to remove inorganic contaminants from natural waters or wastewaters, represent serious exploitation problems (Bodzek & Konieczny, 2011a, 2011b; Crespo et al., 2004; Velizarov et al., 2004, 2008). Increasingly, membrane processes are applied to remove inorganic micropollutants from the aquatic environment. Primarily RO, NF, UF, and MF in hybrid systems, DD, and ED, as well as these combined with extraction (liquid membranes) and bioreactors, are used (Bodzek & Konieczny, 2011a, 2011b; Bodzek et al., 2011; Crespo et al., 2004; Velizarov et al., 2004, 2008).

15.2.1 Anion removal

15.2.1.1 Pressure-driven membrane processes

The RO process is highly efficient in directly removing inorganic anions during drinking water production. In addition, it guarantees safe detoxification. However, complete desalination is undesirable because of possible corrosion problems and remineralization requirements (Kołtuniewicz & Drioli, 2008). Water with a hardness below 50 mg/L is corrosive to copper, iron, zinc, and other metals (Bodzek & Konieczny, 2011a, 2011b; Bodzek et al., 2011). As a result, other processes suitable for selective removal of toxic anions and moderate desalination are desired. Nanofiltration fulfills such requirements because it enables selective desalination, i.e., the separation of polyvalent ions from monovalent ions with the higher capacity obtained for lower transmembrane pressures compared with RO process. Asymmetric membranes used in

NF have a negative electrical charge in neutral and alkaline solutions. Thus, the separation of anions consists of the difference in the rate of transport through a membrane, but also the electrostatic repulsion between anions and the membrane surface charge, which is greater for polyvalent ions than for monovalent anions (Velizarov et al., 2004). Charge of the surface of NF membranes results in the presence of functional groups possessing an electrical charge, but also in the adsorption of anions from water. Hence, the charge of a membrane surface depends on the concentration of anions in the solution (Velizarov et al., 2004) and varies from negative values to zero in the isoelectric point of a membrane, up to positive values in an acidic environment (usually $pH < 4$) when the adsorption of cations takes place. The NF process is much more sensitive to the ionic strength and pH of raw water than RO; hence, the selection of proper process conditions is crucial to its application. Many studies considering the removal of toxic anions from natural waters and purified wastewaters by means of RO and NF have been performed. Promising results were obtained in a significant part of them (Bodzek & Konieczny, 2011a, 2011b; Velizarov et al., 2004).

The pollution of natural waters with nitrates (V) is a result of the application of nitrogen fertilizers and the disposal of municipal and industrial solid and liquid wastes into the environment (Bodzek & Konieczny, 2011a, 2011b). Ion exchange, RO, ED, and biological denitrification are the methods most often used to remove excessive amounts of nitrates (Bodzek & Konieczny, 2011a, 2011b; Kołtuniewicz & Drioli, 2008). Nitrates can have several adverse effects on human health; the most notable are methemoglobinemia, gastric cancer, and non-Hodgkin's lymphoma (Raczuk, 2010). The RO process allows the amount of NO_3^- in drinking water to be decreased to the level established in regulations (10 mg N/L). Reverse osmosis membranes are characterized by high values for the retention coefficient of inorganic salts. Thus, the required decrease in NO_3^- concentrations in drinking water can be achieved by mixing permeate and raw water (Bodzek & Konieczny, 2011a; Kołtuniewicz & Drioli, 2008). Nitrates as monovalent ions are not totally retained by NF; for example, the retention coefficient of NO_3^- for an NF-70 membrane (Dow/FilmTec) is equal to 76%, which is lower than for an RO membrane (Van der Bruggen & Vandecasteele, 2003). Nanofiltration can be also used as a first step in the NO_3^- removal process in combination with RO or ion exchange (Bodzek & Konieczny, 2011a; Kołtuniewicz & Drioli, 2008). However, the presence of sulfates decreases the retention coefficient of NO_3^- ions during NF. Under such conditions, NF membranes practically do not eliminate NO_3^-, nevertheless, they retain multivalent ions (Ca and Mg), which has a positive effect on RO and ion-exchange performance. Relative purification costs of both processes are comparable with the costs of ion exchange and ED, including the costs of disposing the concentrate.

Reverse osmosis and NF membranes used to remove nitrates from water are twice as expensive as membranes applied in low-pressure membrane processes. Moreover, their application is much more energy-consuming because they require a much higher pressure. Hence, alternative methods consisting of UF membranes and surfactants or polymers complexing nitrate ions are applied (Kołtuniewicz & Drioli, 2008). Complexes or micelles containing nitrate ions can be retained by UF membranes. For the application of UF membranes at a surfactant concentration below the critical concentration of micelle formation, the rate of removal of nitrate ions exceeds 79% depending on the type and dose of surfactant used (Kołtuniewicz & Drioli, 2008).

Contamination of drinking water with bromates (V) (BrO_3^-) is usually associated with the formation of disinfection by-products (DBP) during ozonation of waters containing bromides (Br^-). The concentration of BrO_3^- in natural waters varies between 15 and 200 μg/L, whereas the larger content appears in the groundwater. Removal of BrO_3^- in the NF process reaches up to 75–100% with an initial content of 285 μg/L, whereas for the RO process an average retention coefficient of 97% is obtained (Butler, Godley, Lytton, & Cartmell, 2005). Prados-Ramirez, Ciba, and Bourbigot (1995) observed 77% removal of BrO_3^- and 63% of Br^- using NF membranes to treat river water at the initial concentration of BrO_3^- amounting to 300 μg/L. They found that the NF was more economical in terms of cost, mainly as a result of the lower pressure applied. Disadvantages of these techniques include the deep deionization of permeate, which requires remineralization and the formation of a waste stream, i.e., retentate (concentrate), which needs to be treated before discharge into the environment.

Because of widespread use, high mobility in natural waters, and a low tendency to degrade, chlorates (VII) constitute a serious environmental problem mainly because of their toxicity and negative impact on the development and function of the human organism. Studies have shown that RO and NF can be applied to remove ClO_4^- from aqueous solutions (Bodzek & Konieczny, 2011b; Lee et al., 2008). For NF, ClO_4^- retention amounts are up to 75–90%, whereas for RO it is 96% at an initial concentration of 100 mg ClO_4/L (Bodzek & Konieczny, 2011a, 2011b). High-pressure RO membranes allow even 99.9% of ClO_4^- ions to be removed; for low-pressure RO membranes, the retention coefficient of ClO_4^- is lower (95%) (Anonymous, 2008). Hence, in some cases additional treatment of permeate before its introduction into the water network may be required, e.g., by means of ion exchange, or adsorption on activated carbon or in bioreactors (Anonymous, 2008). In principle RO can be used as a standalone technology to remove chlorates (VII) during the production of drinking water only at low ClO_4^- concentrations. Because RO and NF are not destructive processes, retentate contains chlorate (VII) and other pollutants that must be removed before discharge into the environment. In general, biological treatment and evaporation are taken into consideration (Anonymous, 2008).

The appearance of fluorides (F^-) in natural waters is a result of their presence in the lithosphere and anthropogenic industrial activity. According to the WHO, the maximum fluoride concentration in drinking water is established at 1.5 mg/L (Kołtuniewicz & Drioli, 2008; Velizarov et al., 2004). Adsorption, coagulation with sedimentation, ion exchange, and membrane processes, i.e., RO, NF, and ED, are the main methods proposed to remove fluorides from water (Bodzek & Konieczny, 2011a, 2011b). The application of RO to fluoride removal is connected with the partial demineralization of water, which is the main disadvantage of the process (Kołtuniewicz & Drioli, 2008). Reverse osmosis membranes for water desalination allow the removal of 98–99% of salts, which results in the almost total retention of fluorides, e.g., below 0.03 mg/L compared with the initial content range of 1.3–1.8 mg/L (Sehn, 2008). During the treatment of water characterized by a high fluoride content, the application of NF is beneficial because the remineralization of permeate is not always required. The final concentration of F^- ions in permeate obtained for commercially available NF membranes, i.e., NF-90 and NF-270 (FilmTec) and TR-60 (Toray) was in the range of 0.05—4.0 mg/L, depending on the initial concentration and membrane type (Tahaikt et al., 2008). Results obtained during similar studies confirmed the possibility of producing drinking water from brackish water with a high fluorides content using other commercial NF membranes, i.e., NTR-7250, NTR-7450, F-70 (FilmTec), Desal-5-DL and Desal 51-HL (Osmonics), MT-08 (PCI), and SR-1 (Koch) (Hu & Dickson, 2006). Analysis of the retention of monovalent ions for NF membranes indicates that smaller ions (fluorides) are retained more efficiently than other halogen ions (e.g., chlorides). The difference in selectivity results from differences in the hydration energy of particular ions because higher energy causes better retention (a hydration energy of F^- equals 515 kJ/mol whereas for Cl^- it is 381 kJ/mol) (Hu & Dickson, 2006). This explains the possibility of selective desalination of brackish water containing F^- using NF and allows drinking water to be produced less expensively than when RO is applied.

Besides RO and NF, a membrane coagulation reactor (MCR), i.e., a combination of coagulation and MF, can be used to remove fluorides during drinking water production (Zhang, Gao, Zhang, & Gu, 2005). In the MCR, aluminum salt is used as the coagulant and its hydroxide is the adsorbent. Sodium hydroxide can be added to provide hydroxide ions and adjust the pH during coagulation and adsorption. Hydrolysis (Eqn (15.1)), coprecipitation (Eqn (15.2)), and adsorption (Eqn (15.3)) may occur when $A1_2(SO_4)_3$ and NaOH are simultaneously added into raw water. The primary fluoride removal mechanism results in the low solubility constant of $Al(OH)_3$ (solubility product -1.9×10^{-33}) and hard dissolution of the aluminum—fluoride complex. Thus, they are precipitated out of the solution or can be separated by the MF membrane.

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3\downarrow \tag{15.1}$$

$$Al^{3+} + (3 - x)OH^- + xF^- \rightarrow Al(OH)_{3-x}F_x\downarrow \tag{15.2}$$

$$Al(OH)_3 + xF^- \rightarrow Al(OH)_{3-x}F_x\downarrow + xOH^- \tag{15.3}$$

Boron appears in the environment mainly in the form of boric acid (H_3BO_3) and its salts (Bick & Oron, 2005; Kołtuniewicz & Drioli, 2008). At a lower pH the hydration of boric acid does not occur, which causes its low retention during membrane separation. The dissociated form of the contaminant is totally hydrated and is characterized by a greater diameter and negative ion charge, resulting in higher retention (Bick & Oron, 2005). In the European Union, the permissible concentration of boron in drinking water is 1.0 mg/L, whereas for industrial wastewater disposed to sewage it is 10 mg/L (Bick & Oron, 2005). Boron is removed from the environment mainly by means of coagulation and electrocoagulation, adsorption, and ion exchange, as well as membrane processes, i.e., RO, NF, ED, and polymer-enhanced UF (PEUF) (Bick & Oron, 2005; Bodzek & Konieczny, 2011a, 2011b; Bodzek et al., 2011). However, only two of those methods are used in the industry: i.e., RO at high pH conditions and ion exchange (Bick & Oron, 2005).

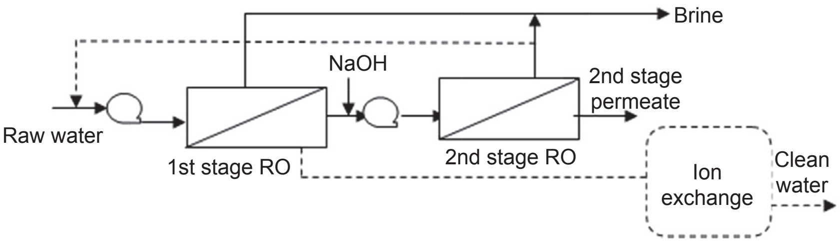

Figure 15.1 Two-stage RO system for boron removal (Bodzek & Konieczny, 2011a, 2011b). RO, reverse osmosis.

The removal of boron compounds from natural waters by means of RO is especially important because any of the conventional desalination methods (distillation or ED) are capable of reducing boron content to a permissible level. The retention of boron at low or neutral pH varies from 40% to 60%, which is insufficient to obtain a permissible level for drinking water, but also for seawater desalination or water disposed into the environment. On the other hand, high pH process conditions lead to fouling and scaling, which are mainly caused by the precipitation of calcium and magnesium compounds. Thus, RO permeate is alkalized to pH c. 9.5 and once more treated by RO or ion exchange (Figure 15.1) (Bick & Oron, 2005; Bodzek & Konieczny, 2011a, 2011b; Kołtuniewicz & Drioli, 2008). The cost of boron removal via the two-step process is high; usually multistep (3−4 steps) RO processes are applied (Kołtuniewicz & Drioli, 2008). Hence, second- and third-stage RO membranes are operated at lower concentrations and pressure. Currently, studies are focusing on developing and testing novel RO membranes that can be applied in a one-step process.

UF and MF can also be used to remove boron from water. An interesting solution is the hybrid process of sorption-membrane separation used in boron removal from seawater or the permeate after seawater desalination with RO. Boron is removed by ion-exchange resins (e.g., Dowex XUS 43,594, Dow Chemicals; Diaion CRB01, Mitsubishi) of very small grain size (20 μm) and after the sorption the resin is separated by means of MF. The small size of grains of resin causes the boron content to decrease after 2 min from 2 mg/L to 0.243−0.124 mg/L, depending on the dose of ion exchanger (0.25−1.0 g/L) (Dilek, Ozbelge, Bicak, & Yilmaz, 2002). Other studies have focused on removing boron from water solutions using PEUF, usually with poly(vinyl alcohol) (PVA) or other specially synthesized polymers (Dilek et al., 2002). The process consists of two stages: the complexation of boron with a polymer and the separation of complexes by a capillary UF membrane (Dilek et al., 2002). However, a decrease in the boron retention coefficient is observed during the process (starting from values close to 1) as the number of active centers of the chelating polymer decreases. The retention also depends on pH and boron and polymer concentrations in the feed.

Inorganic arsenic occurs in water in anionic forms as As(III) and As(V), and a lower-oxidation stage dominates in groundwater and a higher one in surface waters. At a pH close to neutral, As(III) occurs in the form of inert molecules H_3AsO_3 and As(V) as $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-}. The form of As(V) ions has a direct impact on the choice and effectiveness of the treatment method. To decrease arsenic content in drinking water, RO and NF membranes as well as a hybrid process of coagulation—MF/UF are applied (Bodzek & Konieczny, 2011a, 2011b; Shih, 2005). Reverse osmosis membranes, e.g., TFC-ULP (Koch), allow 99% of arsenic to be removed from groundwater (a decrease from 60 to 0.9 μg/L), whereas DK2540F membranes (Desal) retain 88—96% of the pollutant (Shih, 2005). The amount of As(III) removed is always lower than for As(V), and oxidizing conditions during the process are recommended (Pawlak, Zak, & Zabłocki, 2006). The pH and the content of dissolved organic matter have a great influence on arsenic removal. The rate of As(V) removal at pH 3 reaches 80%, whereas it can be up to 95% at pH 5—10 (NTR-729HF membrane). A higher removal of arsenic(V) (90%) is observed for waters with a lower organic matter content, whereas compared with a higher concentration of organics it is equal to 80% (Pawlak et al., 2006). Other laboratory and pilot research on arsenic removal using RO membranes has been performed (Bodzek & Konieczny, 2011a, 2011b). NF membranes can be also applied for As removal. For NF-70 FilmTec membrane, 97% removal of As(V) is obtained, and for NF-45 membrane it varies from 45% to 90% depending on the initial concentration of the pollutant in water (Nguyen, Bang, Cho, & Kim, 2009). In the case of As(III), as for RO, retention coefficients are much lower and decrease from 20% to 10% with an increase in the pollutant concentration in water. The rate of removal of As(V) with the use of NF-45 membrane significantly increases with an increase in pH (Shih, 2005), according to the difference in As ion hydration. An influence of pH in the range of 4—8 on the retention coefficient of As(III) was not observed, which indicates that the mechanism of arsenic removal using NF membranes is based on both sieving separation and electrostatic repulsion between ions and the charged membrane surface. Microfiltration and UF can be also used to remove arsenic from water, but mainly by means of integrated systems with coagulation (Han, Runnells, Zimbron, & Wickramasinghe, 2002; Shih, 2005). For example, from water with an As content equal to 40 μg/L, water containing less than 2 μg/L As can be obtained using ferric coagulants and membranes with a pore size of 0.22 and 1.22 μm (Shih, 2005). In the integrated process, As removal is caused by the adsorption of As on coagulation flocks and the separation of those flocks by the MF membrane. In such a case, the removal of As(III) is also less effective than that of As(V) and preliminary oxidation of As(III) to As(V) is often required.

15.2.1.2 Ion-exchange membrane processes

Donnan dialysis is a process that uses an ion-exchange membrane without applying an external electric potential difference across the membrane (Velizarov et al., 2004; Wisniewski, 2001). For anion removal, anion-exchange membranes are used whereas for cation removal, cation-exchange membranes are employed (Figure 15.2). Membranes separate two solutions, i.e., raw solution and stripping solution (concentrate) that differ in both composition and concentration. The type of operation such as DD requires the addition of a so-called driving counter-ion to the stripping solution (usually an NaCl solution of 0.1—1 M concentration is used), which is transported in the opposite direction of the target anion or cation to maintain electroneutrality

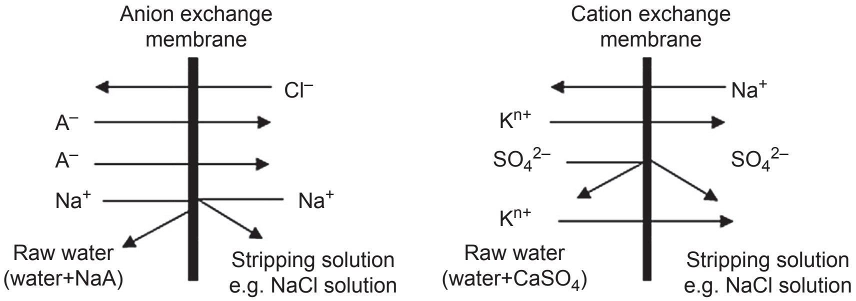

Figure 15.2 Scheme of Donnan dialysis process (A^-, target anion; K^{n+}, target cation) (Bodzek & Konieczny, 2011b).

(Figure 15.2) (Bodzek & Konieczny, 2011b; Wisniewski, 2001). The ions, which are permeable to the membrane, equilibrate between the two solutions until the Donnan equilibrium is obtained. Because the concentration differences and their ratios determine the Donnan equilibrium, DD allows the charged micropollutants to be transported against their concentration gradients, which is important for drinking water supplies because they usually contain only trace amounts of polluting ions. As a result of its properties, DD has received attention in the removal of inorganic ions from drinking water, especially nitrates (V) and fluorides, and some cations (Velizarov et al., 2004).

Because the mechanism of ion transport in DD is governed solely by the Donnan equilibrium principle, the ion fluxes achieved may be low for certain applications. In ED, the transport of ions is accelerated owing to an externally applied electric potential difference, which allows one to obtain higher anion fluxes than those in DD. In this process, anion-exchange and cation-exchange membranes are applied alternately, which allows solutions of varying concentration (diluate and concentrate) to be obtained (Bodzek & Konieczny, 2011b; Velizarov et al., 2004). The ED systems are usually operated in the so-called ED reversal (EDR) mode to prevent membrane fouling and scaling. Because most known toxic anions are monovalent, the use of monovalent anion permselective exchange membranes is especially attractive (Velizarov et al., 2004). The suitability of ED depends strongly on the ionic composition of contaminated water. Thus, the process appears to be less applicable to waters of very low salinity (conductivity less than 0.5 mS), for which DD can be a better solution. In cases in which low-molecular-weight non-charged compounds besides ion removal is necessary, pressure-driven membrane processes may be preferable. Successful applications of ED and EDR include the removal of various anions, e.g., nitrates (V), bromates (V), chlorates (VII), arsenic (V), boron, and fluorides as well as various heavy metals (Velizarov et al., 2004; Wisniewski, 2001). The brine discharge or treatment remains important for all of these separation processes.

The use of a monovalent anion permselective membrane in the ED process proved successful in a full-scale ED plant located in Austria, which was designed to remove nitrates (V) from groundwater (Velizarov et al., 2004; Wisniewski, 2001). The NO_3^- concentration in the raw water was 120 mg NO_3/L and the removal efficiency

(66%) was adjusted to obtain a product concentration of 40 mg NO_3/L at a desalination rate of c. 25%.

ED and EDR are also proposed to remove bromates from water (Bodzek & Konieczny, 2011a, 2011b; Wisniewski & Kliber, 2010). Studies on ED with anion-exchange membranes (Neosepta AMX) resulted in BrO_3^- removal efficiencies of 86–87%, and with the use of mono-anion-selective membranes (Neosepta ACS) up to 99%, at a current density of 20 A/m^2. The removal rates of other anions were from 80% (HCO_3^-) to 93% (NO_3^-) (Wisniewski & Kliber, 2010). This means that the ED of water with an initial concentration of BrO_3^- of 100 μg/L causes a decrease in the final concentration to approximately 1 μg/l, which is significantly below the limit value of drinking water (for BrO_3^-, 10 μg/L). The increase in power density for ED with standard anion-exchange membranes results in an increase in the anion transport rate of 36%.

Investigations were also carried out on chlorate (VII) ion removal by ED and EDR, and at high concentrations of silica (approximately 80 mg/L). Regardless of the presence of SiO_2 and its concentration, water recovery in the EDR installations was not affected. Pilot studies have shown that the removal of ClO_4^- varied in the range of 70–97% depending on the initial concentration of the anion and the number of steps in the configuration of the EDR system (Anonymous, 2008). During removal of chlorate (VII) ions using the EDR method, the retention coefficients of other anions with similar valence (e.g., nitrate) are also important.

ED can be applied to fluoride removal from water that contains a significant amount of this contaminant. The removal rate of F^- is often higher than that obtained for RO, and it increases with an increase in the electrical potential difference, temperature, and flow rate (Velizarov et al., 2004; Wisniewski, 2001). To minimize the precipitation of salts of bivalent ions (sulfates and carbonates) in the concentrate chambers, preliminary removal of bivalent ions is proposed using two-step ED with the application of various ED membranes in each step or by chemical methods followed by conventional ED (Bodzek & Konieczny, 2011b). The content of fluorides generally decreases from 3.0 to 0.63 mg/L for the first configuration and to 0.81 mg/L for the second one, which allows water of municipal quality to be obtained. The first method is preferred because of its simplicity and the elimination of the need to add other chemicals.

Similar to RO, electrodialytic removal of boron from water and wastewater requires a high pH because boric ions are transported through an anion-exchange membrane (Bick & Oron, 2005; Kabay et al., 2008). The main advantage of ED compared with RO is the lesser sensitivity of ion-exchange membranes to pH and fouling. High pH values also prevent the precipitation of $Mg(OH)_2$ and $CaCO_3$. However, even for such a high pH (9–10) chlorides are preferably transported and sulfates are removed in an extent similar to boron (Bick & Oron, 2005; Kabay et al., 2008). The low mobility of boric ions compared with others is the main disadvantage of ED because boron can be transported only after a significant decrease in other salt contents in diluate (Kabay et al., 2008). To omit high demineralization of the diluate, a monopolar membrane at alkali process conditions (pH 9–10) should be applied (Bick & Oron, 2005).

Studies on arsenic removal from water by ED have shown that it is possible to remove As with an efficiency exceeding 80% for As(V) and 50% for As(III) (Kartinen & Martin, 1995), with a water recovery of 85%. In other studies with EDR, a concentration of arsenic in eluate was decreased to 0.003 mg/L (its initial level was 0.021 mg/l), which corresponded to a retention coefficient of 86% (Bodzek & Konieczny, 2011b).

15.2.1.3 Membrane bioreactors

The main disadvantage of pressure-driven membrane processes and ED is the production of a concentrate highly loaded with anions. Thus, the use of MBRs to remove micropollutants from RO, NF, and ED concentrates as well as natural water and wastewaters is proposed. The concentration of pollutants can be decreased to a value corresponding to drinking water quality (Bodzek & Konieczny, 2011a, 2011b; Crespo et al., 2004; Velizarov et al., 2004, 2008).

The biological degradation of oxyanions (NO_3^-, ClO_4^-, and BrO_3^-) is based on their reduction to harmless substances (N_2, Cl^-, and Br^-) at anaerobic conditions, the presence of microorganisms (heterotrophic or autotrophic bacteria), and proper electron donors (ethanol, methanol, and acetates for heterotrophic conditions and sulfur compounds and hydrogen for autotrophic ones) (Bodzek & Konieczny, 2011a,b; Crespo et al., 2004; Velizarov et al.,2004). The kinetic of the reaction depends on the kind of microorganism and the biodegradation process conditions (pH and anion concentration) (Crespo et al., 2004). The advantage of autotrophic degradation is the lower production of excess sludge; however, the process runs slowly (Kołtuniewicz & Drioli, 2008). When heterotrophic process is applied, the removal of dissolved organic carbon (DOC) and biomass from treated water is required (Velizarov et al.,2004). Disadvantages of conventional biological anion biodegradation can be eliminated by applying an MBR, which ensures the total retention of biomass. The configuration of MBR processes can be arranged as a system with pressure-driven membrane modules (MF and UF) (Figure 15.3) (Bodzek & Konieczny, 2011a, 2011b) or as extractive MBRs (membrane contactors) (Figure 15.4) (Bodzek & Konieczny, 2011a, 2011b; Crespo et al., 2004).

In the case of an MBR with a pressure-driven membrane process, an MF or UF membrane may be placed inside or outside the bioreactor, because the retention of ions and low-molecular-mass compounds (electron donors and some metabolic by-products) by porous membranes is generally insufficient; therefore, either process modifications or water posttreatments are necessary. The solution is an extractive MBR (Figure 15.4) in which water with anions is supplied to the inside (lumen side) of hollow-fiber membranes and anions diffuse to the outside (shell side). There, existing microorganisms use anionic micropollutants as an electron donor for the reduction process (Bodzek & Konieczny, 2011a, 2011b). Under these conditions, both electron donor and biomass are separated from the water by a membrane.

Biological degradation of oxyanions may also be used to remove nitrates (V), bromates (V), and chlorates (VII). Studies have shown their full reduction to nitrogen, bromides, and chlorides by the same bacterial cultures that are used for nitrate (V) reduction (Wang, Lippincott, & Meng, 2008).

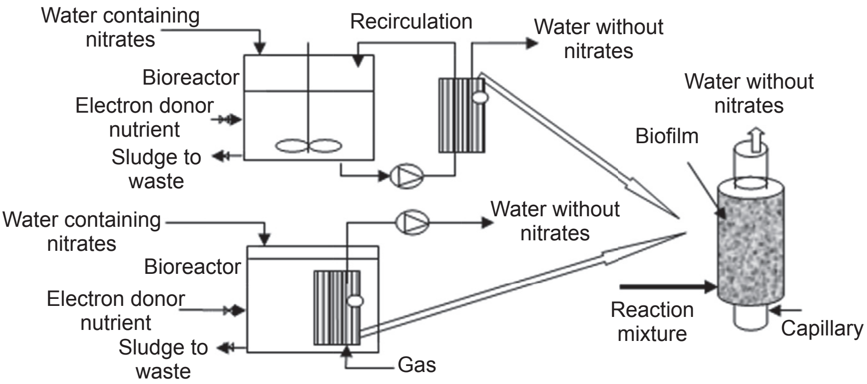

Figure 15.3 Membrane bioreactors with pressure-driven membrane module (Bodzek & Konieczny, 2011a, 2011b).

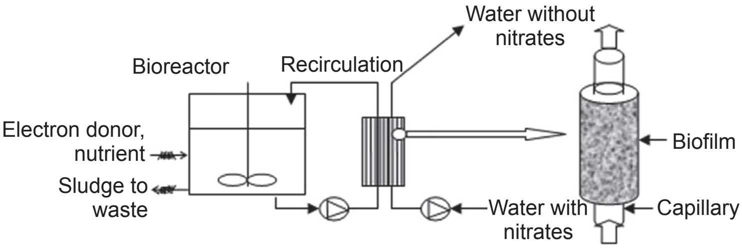

Figure 15.4 Extractive membrane bioreactor (Bodzek & Konieczny, 2011a, 2011b).

A new membrane bioprocess for the removal and bioconversion of ionic micropollutants from water streams is the ion-exchange MBR (IEMB) (Crespo et al., 2004; Velizarov et al., 2004). In this process, the ionic micropollutant is transported from the water stream through a nonporous ion-exchange membrane into a biological compartment. There, it is simultaneously converted into a harmless product by a suitable microbial culture in the presence of an adequate carbon source and other required nutrients. The mechanism of anion pollutant transport through the membrane is the same as in DD (Figure 15.5) (Bodzek & Konieczny, 2011a). The co-ions (cations) are excluded from the positively charged membrane and the target anion(s) transport is combined with its bioconversion. In addition, the bioconversion of the pollutant in the IEMB keeps its concentration at low levels, which guarantees an adequate driving force for transport.

This concept was first demonstrated in the example of synthetic waters prepared for the removal and bioconversion of nitrate to harmless nitrogen gas using a Neosepta ACS mono-anion permselective membrane and ethanol as the carbon source (Velizarov et al., 2004). Because of its very low diffusion coefficient (three orders of magnitude lower than that in water), carbon source penetration into the treated water was avoided by employing this nonporous type of membrane and the development of an ethanol-consuming biofilm on the membrane surface contacting

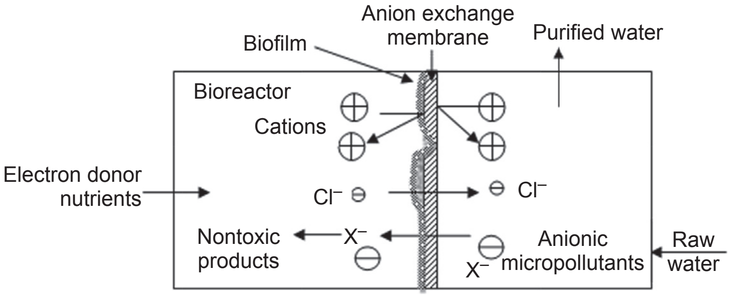

Figure 15.5 Schematic diagram of ion transport mechanism in the ion-exchange membrane bioreactor (Bodzek & Konieczny, 2011a).

the biocompartment. Chloride ions were used as major counterions in IEMB for oxyanion removal. Within the concentration relevant to nitrate polluted water (50–350 mg NO_3^-/L), complete denitrification was achieved without the accumulation of NO_3^- and NO_2^- ions in the biocompartment (Velizarov et al., 2004).

15.2.2 Heavy metals

Heavy metals are one of the most dangerous impurities present in natural waters and wastewaters. Because natural waters are the main source of drinking water, it is possible that heavy metals will appear in them. When the daily, monthly, or annual consumption of water is considered, the danger resulting from the presence of heavy metals in water is significant. Metals such as lead, mercury, selenium, iron, nickel, manganese, copper, cobalt, cadmium, zinc, and chromium are present in drinking water. The permissible concentration for only part of them is established in each country's regulations regarding tapwater. Except for iron, manganese, and aluminum in Polish regulations, permissible concentrations of the following metals are specified: antimony, 0.005 mg/L; arsenic, 0.010 mg/L; chromium, 0.050 mg/L; cadmium, 0.05 mg/L; nickel, 0.020 mg/L; copper, 2.0 mg/L; lead, 0.025 mg/L; mercury, 0.001 mg/L; selenium, 0.010 mg/L; and silver, 0.010 mg/L (Bodzek & Konieczny, 2011b). Conventional methods such as precipitation, extraction, and ion exchange have many shortcomings, especially with respect to the processing of large volumes of water containing a low concentration of metal ions. Nowadays, these contaminants are most frequently precipitated as hydrated metal oxides, hydroxides, or sulfides with the use of flocculation or coagulation. A major problem pertaining to the precipitation process involves the formation of substantial quantities of sludge containing metals (Bodzek, 1999). Often the concentration of metal ions in the filtrate after the final filtration process is still above the level of several milligrams per liter. Membrane techniques such as RO, NF, UF, and ED are more often applied to remove heavy metals from water solutions on an industrial scale (Bodzek, 2012).

15.2.2.1 Application of high-pressure membrane processes

Metal ions can be successfully removed from water solutions by means of RO or NF because the membranes applied in those processes are able to retain dissolved salts of molecular sizes as small as a few nanometers, as shown in a number of studies (Bakalár, Búgel, & Gajdošová, 2009; Mehiguene, Garba, Taha, Gondrexon, & Dorange, 1999; Qdais & Moussa, 2004).

The application of RO in the removal of heavy metals from solutions can be shown in the example of wastewater treatment in the electroplating industry. The wastewater consists mainly of effluent from product-washing processes after electroplating coating in electroplating baths. The concentration of metal ions in such wastewater ranges from 0.025 to 1 mg/L (Bodzek, 1999). Frequently electroplating effluents contain Cr, Cu, Cd, Zn, Ni, Pb, and Ag ions, and because the metal-coating technologies are based to a great extent on cyanide solutions, the presence of toxic cyanide anion is also important. The RO process allows the recovery of water at a very high purity level, which in many cases can be directly returned to the technological process without additional treatment. The concentrated solution (retentate) may be reused to fill up the electroplating bath (Bodzek, 1999). Figure 15.6 presents a typical diagram of the installation operating in a closed cycle applied to such a process (Bodzek, 1999; Bodzek & Konieczny, 2011b).

A series of investigations were conducted on the removal of heavy metals from aqueous solutions using RO technology. For example, Bakalár et al. (2009) presented the results of removing copper, nickel, and zinc using composite polyamide membrane TW30-1812-50 (Dow Filmtec). They determined the effect of the accompanying anions (co-ions), the concentration of cations, and the transmembrane pressure on the separation efficiency. In turn, Qdais and Moussa (2004) tested removing Cu^{2+} and Cd^{2+} ions by means of RO and NF. Results showed that the removal efficiency of individual heavy metals by RO was high and amounted to 98% for copper and 99% for cadmium, whereas for NF it was above 90%. In the case of a solution containing both metals, RO membranes reduced the concentration of ions from 500 to about 3 mg/L (removal rate of 99.4%), whereas the rejection efficiency of NF amounted to an average of 97%. These studies showed that NF was also an appropriate technique to remove heavy metals from wastewater to a level acceptable according to

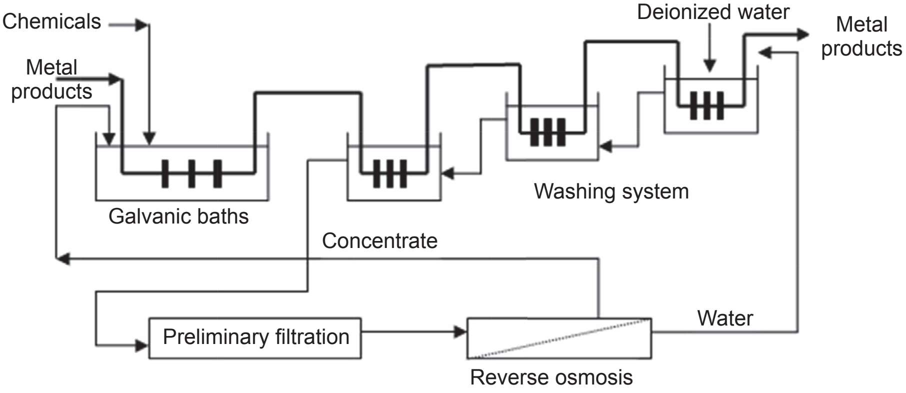

Figure 15.6 Diagram of electroplating process line integrated with reverse osmosis (Bodzek & Konieczny, 2011b).

environmental regulations. In addition, as with RO, it was possible to reuse permeate for rinsing purposes and to recycle the retentate containing heavy metals. Retention of the cations in the process strongly depends on the energy of hydration, the type and valence of co-ions passing through the NF membrane, and the applied pressure and pH. For example, the retention of Cu^{2+} and Cd^{2+} ions is greater for the higher co-ion valence and higher cation hydration energy (Mehiguene et al., 1999). The obtained retention coefficients of copper and cadmium sulfates are close to 100% independent of pressure. In the case of chlorides and nitrates, the retention rates increase with pressure to specific values that depend on the nature of the co-ions. Heavy metal retention during NF also strongly depends on the pH. In a highly acidic environment, a high concentration of hydrogen ions in solution causes gradual neutralization of the negative active centers on the membrane surface, so the impact of the membrane charge on cation and anion retention is significantly reduced. Under such conditions, nitrate and chloride ions easily pass through a membrane, and to maintain the electrostatic balance of the solution through the membrane protons also penetrate it. Therefore, copper and cadmium ions are retained in retentate.

15.2.2.2 Ion-exchange membrane processes

Electrodialysis is particularly useful and often applied to treat rinsing effluents and other wastewaters from electroplating plants (Bodzek, 1999). The diagram of installation is similar to Figure 15.6, but instead of RO, ED is applied. The retentate, which is a concentrated solution of metal ions, is used to fill up the electroplating bath, whereas the dialysate is returned to the washing installation. Hence, practically the entire quantity of water and salts present in washing effluents can be used (Bodzek, 1999). Recently, the application of ED to recover metals for electroplating with such metals as Au, Pt, Ni, Ag, Pd, Cd, Zn, and Sn/Pb from diluted electroplating wastewaters has gained attention (Bodzek, 1999). The solution of metal salt can be concentrated to a level corresponding to the components' content in the electroplating bath, e.g., for Ni from 1 to 60 g/L (Bodzek, 1999), which is much greater than with the application of RO. The principal disadvantage of ED is the inability to simultaneously remove the non-ionic substances (e.g., organic compounds) from the dilute stream, which can be done using RO.

15.2.2.3 Integrated low-pressure membrane processes

An interesting solution to removing heavy metals from aqueous solutions is the PEUF (Bodzek, Korus, & Loska, 1999; Korus, 2012). It combines UF with metal complexation using water-soluble polymers. The formed complexes are sufficiently large to be retained by a UF membrane. Permeate is deprived of metal ions and retentate can undergo regeneration to recover both the metal and polymer.

The process was applied to deactivate radioactive liquid waste containing metal ions, i.e., cesium, cobalt, strontium, antimony, and technetium isotopes, the major components of radioactive wastewater, and to separate the lanthanides (^{140}La, ^{152}Eu, and ^{169}Y) (Zakrzewska-Trznadel, 2003). A significant reduction in permeate radioactivity was observed.

Mavrov, Nikolov, Islam, and Nikolova (1992) carried out investigations into the removal of Cu(II), Ni(II), and Co(II) ions from synthetic aqueous solutions with an initial metal concentration of 10^{-4} mol/L using the hybrid PEUF method with polyacrylonitrile membranes (UF-25-PAN) (cutoff of 25 kDa). Polyvinyl alcohol (50,000 Da) and polyethyleneimine (PEI) (30,000−40,000 Da) were used as complexing agents. The optimal concentration of PEI was two to six times higher compared with the stoichiometric concentration and retention rates of formed complexes, which ranged within 85−99%. The highest retention rate was obtained for PVA complexes (97−99%) at a ratio of metal concentration to polymer concentration ranging from 1:4 to 1:8 (Mavrov et al., 1992).

Korus (2010, 2012) conducted studies on the removal of heavy metals (Ni, Cu, and Zn) from synthetic and galvanic wastewater by applying the hybrid complexation−UF process. Poly(vinyl alcohol) (50,000 Da), PEI (30,000−40,000 Da), polyacrylic acid, and sodium polyacrylate as complexing agents were used in connection with polysulfone and polyamide membranes. The efficiency reached 85−97% for polyamide membrane, depending on the polymer to the metal ratio, pH, and kind of metal. A high removal efficiency of zinc and nickel ions (97−99%) was obtained for polysulfone membrane. The decomplexing process enabled metal to be recovered from the concentrated solution to an extent suitable for its reuse.

Sodium poly(styrene sulfonate), a water-soluble anionic polymer with strong cation-exchange groups, was used as a complexing agent for lead ion complexing (Korus, 2010). The high rate of metal removal (85−99%) depended on the ratio of metals to polymer, the pH of the solution, and the operating UF conditions obtained for the polysulfone membrane. It was possible to obtain the retentate with a concentration of Pb 20 times higher than the concentration of the feed solution, which contained 50 mg Pb/L. The main process parameters were a fivefold excess of polymer in relation to metal as well as a pH of 6 and a pressure of 0.1 MPa. The decomplexation−UF process involved breaking the polymer−metal bond and allowed it to recover 85% of metal, whereas diafiltration conducted with a sufficient volume of water enabled five- to 15-fold reduction of the concentration of metal remaining in retentate, so the recovery and reuse of the polymer were possible.

The use of membrane separation combined with the biological removal of metals from a solution (MBRs) is of a great interest. Wastewaters with a high load of metals usually contain compounds that may be toxic for microorganisms or inhibit their growth; they often have a high salinity or pH. Therefore, it is often impossible to carry out conventional biological removal of metals from wastewater owing to the inactivation of microorganisms. The solution may be extractive MBRs with sulfate-reducing bacteria (EMBR-SRB), which eliminate these restrictions because of the physical separation of biomass from effluents (Figure 15.7) (Bodzek & Konieczny, 2011b; Mack, Burgess, & Duncan, 2004). Membranes, which are usually made of silicone polymers, perform two functions: they separate two water phases and enable H_2S transport from the phase containing biomass to wastewater, where the precipitation of metal sulfide(s) takes place. Study of zinc removal from synthetic wastewater using EMBR-SRB MBRs showed that the reaction rate between H_2S and Zn ions was high owing to the large concentration gradient of H_2S on both sides of the membrane. When the

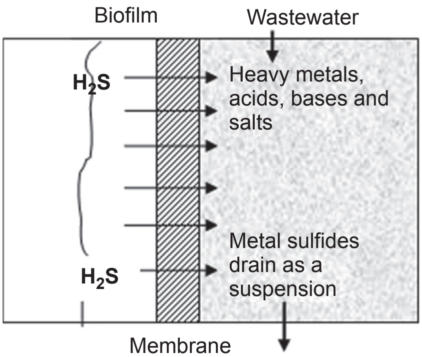

Figure 15.7 Scheme of bioreactor with sulfate-reducing bacteria: EMBR SRB (Bodzek & Konieczny, 2011b).

pH of the biological mixture decreased, the quantity of nondissociated H_2S grew, increasing its concentration gradient. More than 90% removal of Zn ions from solutions containing 250 mg/L of this metal was obtained. The transport rate of H_2S also depends on the membrane thickness. On the side of wastewater, a thin layer of zinc sulfide formed on the membrane surface, constituting significant resistance to H_2S transport. This problem can be solved by changing the hydrodynamic conditions of the water stream or using pulse flow.

15.2.3 Removal of chromium

A separate discussion on chromium is associated with the fact that in the natural environment chromium most commonly occurs in the third oxidation state as cation (Cr^{+3}) and sixth, Cr(VI), in the form of anions. Chromium (VI) is a strong oxidant easily reduced to Cr(III) (Jacukowicz-Sobala, 2009). Chromium (III), which is naturally present in the environment, is an essential nutrient, whereas chromium (VI) is formed in industrial processes and enters the environment as anthropogenic pollution. Chromium (VI) and chromium (III) compounds are widely used in many industries because of the durability of the metal and its aesthetic effects. One can mention the galvanic industry; the production of dyes and pigments, and textile and leather articles; tanneries and wood maintenance. That is why chromium compounds are increasingly found in wastewaters, groundwater, or soil. Chromium (VI) compounds are soluble in water, and at pH 1−6 they appear as $HCrO_4^-$ and $Cr_2O_7^{2-}$ ions, whereas at pH > 6 CrO_4^{2-} ions are formed. The influence of chromium compounds on living organisms depends on the oxidation state of chromium, the solubility, and the method of entry into the body. Chromium (III) is trace element essential to the proper functioning of plants, animals, and humans (Bodzek & Konieczny, 2011b), whereas Cr(VI) is highly toxic to living organisms, so their permissible concentration in drinking water amounts to 0.05 mg/L, including 3 μg/L for Cr(VI). The traditional way to remove and recover chromium salts from contaminated water and wastewater is to reduce Cr(VI) to Cr(III) and then precipitate Cr(III) hydroxide, and in the final stages filter the suspension

(Owlad, Aroua, Daud, & Baroutian, 2009). For Cr(III) the reduction stage is omitted. For chromium removal several other methods are also proposed, such as adsorption and biosorption, ion exchange (used on an industrial scale), solvent extraction, and electrochemical methods (Owlad et al., 2009). Membrane processes, both high-pressure and low-pressure membrane processes enhanced with surfactants and polymers, are very important to the recovery and disposal of chromium (Bodzek & Konieczny, 2011b; Kołtuniewicz & Drioli, 2008; Owlad et al., 2009). Application has also been found for liquid membranes and processes based on ion-exchange membranes, including ED, EDI, and membrane electrolysis (Bodzek, 2012).

Reverse osmosis and NF permit the direct separation of chromium compounds from the solutions and find practical application in this respect (Bodzek, 2012; Kołtuniewicz & Drioli, 2008; Owlad et al., 2009). To remove Cr(III) and Cr(VI), both inorganic membranes and polymer membranes can be used. Studies carried out on Cr(VI) removal from water involved RO using Osmonics membranes Sepa-S type and membranes made of cellulose acetate (CA) (Bodzek et al., 2011; Kołtuniewicz & Drioli, 2008; Owlad et al., 2009). It was found that the CA membranes retained 96% of Cr(VI) ions, whereas Osmonics membranes retained 80–96%, depending on the membrane compactness (Bodzek & Konieczny, 2011a). Application of RO for the treatment of chromium tanning wastewater is limited by chloride and sulfate ion concentration. High concentrations require the use of high transmembrane pressure. This causes removal of chromium to become economically justifiable only if the salt concentration does not exceed 5 g/L, and the chromium concentration 1 g/L. However, to treat galvanic wastewater with a concentration of chromium amounting to 2 g/L, the RO process can be successfully applied (Bodzek, 2012). In this case, permeate with a concentration of 0.0017 mg Cr/L, suitable for reuse, can be obtained, as well as concentrated chromic acid anhydride (concentration of Cr, 5 g/L) (Jacukowicz-Sobala, 2009).

It seems that NF is a better solution for the removal of chromium from water (tannery and galvanic wastewaters). The obtained filtrate is then without chromium, but it contains a significant amount of salt that can be used to prepare etching baths. As for the retentate, a concentrated solution of chromium, after further concentration hydroxide is precipitated, and then dehydrated sludge is dissolved in sulfuric acid. The resulting solution can be used directly in the process of tanning (Religa & Gawroński, 2006). For NF, the retention coefficient of Cr increases with an increase in pH but the effect is more pronounced for membranes with lower separation capacity (e.g., from 47% to 94.5% for Osmonics membranes) compared with more compact membranes (e.g., from 84% to 99.7% for Osmonics membranes) (Hafiane, Lemordant, & Dhahbi, 2000). The dependence of the retention coefficient on the concentration of Cr in feed was also observed for NF membranes (Hafiane et al., 2000), but the range of the effect also depended on the pH. In an acidic solution at higher concentrations of Cr in feed, a higher retention was found, whereas at pH 6.5–11 the nature of this relationship was the opposite, i.e., lower retention was obtained for higher concentrations of Cr. This phenomenon is important because Cr(VI) changes its ionic form with a change in pH. In the highly acidic environment, Cr(VI) occurs in the form of no dissociated chromic acid (H_2CrO_4) and when the pH is changed to 6.5, $HCrO_4^-$ ions are formed, the concentration of which increases with an increase in the parameter. A further increasing in pH above 7 causes the formation of CrO_4^{2-} ions, the concentration of which also depends on pH. $Cr_2O_7^{2-}$ ions are also present in the solution and their concentration depends on the initial concentration of the contaminant in the feed and pH. This ion is usually dominant at high concentrations of Cr and in a strongly acidic environment (pH 1−7) but its concentration decreases with an increase in pH (Bodzek & Konieczny, 2011a, 2011b; Hafiane et al., 2000).

Characteristics of membranes used in UF and MF processes do not allow chromium ions to be retained directly in the retentate. That is why low-pressure membrane processes are used to remove Cr in an integrated process. In this respect, the following possibilities can be identified (Bodzek, 2012; Kołtuniewicz & Drioli, 2008; Owlad et al., 2009):

- Preliminary MF/UF before further treatment with conventional or membrane processes
- Modification of UF membranes to reduce pore size or ion-exchange properties
- Polymer-enhanced UF or surfactant/micellar-enhanced UF (MEUF).

The first method was used in the initial stages of tanning and galvanic wastewater treatment. Microfiltration/UF removes suspended solids, fats, and emulsions from the aqueous phase (without added chemicals), which makes it easier and improves the performance of subsequent purification/process separation (Religa & Gawroński, 2006). The main methods of introducing the charge on the surface and inside the pores of UF membranes are sulfonation of polysulfone membranes and the introduction of amino and carboxylic groups. Modification of UF membranes extends their separation property by giving them ion-exchange properties (Bryjak, 2001). Polymer-enhanced UF or MEUF allows separation of metal ions, including chromium. Polymer-enhanced UF has been successfully applied to remove chromate (VI) from groundwater using complexing agents such as 1-hexa-decylopiridine chloride, sodium polyacrylate, poly(dimethyldiallylammonium) chloride, chitosan, and pectin (Bodzek & Konieczny, 2011b). Polyethylenimine (PEI) is used for the concentration and recovery of chromium (III).

Electrochemical separation techniques are an alternative method of removing chromium from the water environment. This toxic metal is present in various streams produced by a number of industrial processes, which also contain other substances (mainly metals) that should be separated from chromium. Therefore, electrochemical technology is more flexible than other membrane techniques and is applied to recover chromic acid (VI) from the bath coating metal parts (a large concentration of chromium) or as a method of disposal and recovery of chromium from wastewater derived from washing these elements. In most cases, among others in the plating industry, so-called three-compartment electro-electrodialysis (EED) is applied. It is based on electrolysis reactions running on electrodes and the ED process (Bodzek & Konieczny, 2011b; Frenzel, Holdik, Stamatialis, Pourcelly, & Wessling, 2005) (Figure 15.8). It can simultaneously manage three different tasks: removal of impurities, chromic acid recovery, and purification of rinse water. The treated solution feeds the center chamber of the device, which is separated from the anolite chamber by the anion-exchange membrane and from the catolite chamber by the cation-exchange membrane

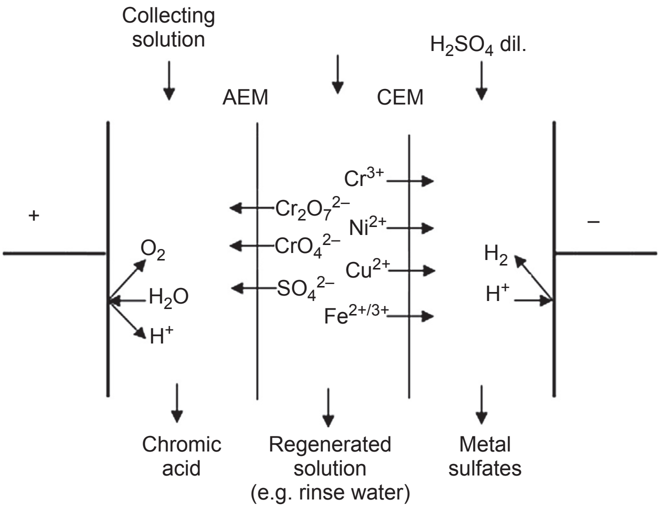

Figure 15.8 Principles of three-compartment electro-electrodialysis for chromic (Bodzek & Konieczny, 2011b) acid recovery. AEM, anion-exchange membrane; CEM, cation-exchange membrane.

(Frenzel et al., 2005). The anolite chamber is supplied with water whereas the catolite chamber is supplied with sulfuric acid. Chromium (VI) ions migrate to the anolite, where they form chromic acid (VI) with protons formed on the anode. In turn, metal cations permeate to catolite chamber, where sulfuric acid neutralizes the hydroxide ions formed on the cathode, so in this part of the device, soluble metal sulfates (VI) are formed.

Both the ED and EDI processes can be applied to remove and separate metal ions and their mixtures, including chromium. In ED, the electrical resistance in dialysate chambers increases in time as the ions are removed from the diluted solution to the concentrate chamber, which causes higher energy consumption and decreases the efficiency of the process. One solution to this problem is the EDI process, in which the dilute solution chamber is filled with an ion-exchange resin (Bodzek & Konieczny, 2011b). The applied voltage improves the migration of ions to the respective electrodes and thus to concentrated stream and causes water dissociation into H^+ and OH^- ions, which regenerate the ion-exchange resin. Alvarado, Ramirez, and Rodríguez-Torres (2009) assessed the feasibility of EDI and ED continuous processes for the removal of chromium (VI) from synthetic solutions at pH 5. The ED/EDI installation consisted of electrodes and two acrylic separation plates between which an anion-exchange membrane manufactured by Neosepta was placed (Figure 15.9) (Alvarado et al., 2009; Bodzek & Konieczny, 2011b).

Two cation-exchange membranes by the same producer separated the electrodes from the separation plates. In this way, two chambers with diluate and concentrated solution were formed. Synthetic wastewater containing 100 mg/L Cr(VI) was treated. During the EDI process, a chamber with diluted solution was filled with a mixed

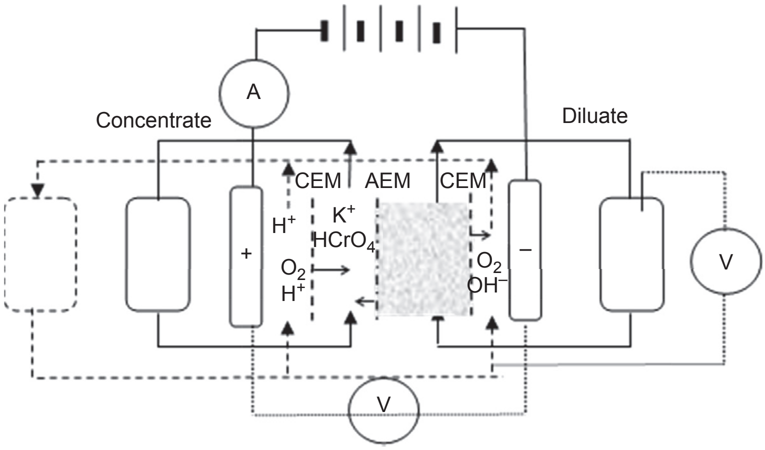

Figure 15.9 Diagram of apparatus for electrodialysis/electrodeionization processes. AEM, anion-exchange membrane; CEM, cation-exchange membrane (Bodzek & Konieczny, 2011b).

ion-exchange resin. In the ED process, the removal of Cr amounted to 98% during 6.25 h at an energy consumption of approximately 1.2 kWh/m^3 and at a maximum limited current (I_{lim}) of 85%. In the EDI process with the use of a mixed bed at the same I_{lim}, 99.8% removal of Cr(VI) was reached within 1.3 h (energy consumption = 0.167 kWh/m^3).

15.3 Removal of microorganisms and NOM

15.3.1 Removal of dispersed substances and microorganisms by low-pressure membrane processes

The turbidity of water is caused by the presence of suspended mineral and organic molecules of different sizes (colloids and coarse and fine suspensions). Usually, MF or UF is applied to decrease water turbidity to the level below 1 nephelometric turbidity unit (NTU), i.e., the value that corresponds to regulations for drinking water. Only several studies discussed in the literature focused on turbidity removal by means of membrane processes, although it is proven that the use of those techniques enables the production of water with a turbidity below 1 NTU from water with an initial turbidity of 100 NTU and greater (Taylor & Wiesner, 2000). It is accepted that UF and MF can also be used for water clarification (Bodzek & Konieczny, 2005). The study of application of a UF Aquasource membrane (France) revealed that from waters of different turbidity ranging from 0.1 to 11.5–24.8 NTU, drinking water of a turbidity of 0.03–0.04 NTU could be obtained (Taylor & Wiesner, 2000). The publication (Anonymous, 2005) summarizes the results of a series of studies carried out on membrane filtration in 1989–2001, which showed that the use of MF and UF allowed for maximum removal of turbidity regardless of raw water turbidity, the kind of membrane, and

Table 15.1 **Turbidity and NOM removal using membrane techniques**

Process	Pressure, kPa	Turbidity removal, %	NOM removal, %	Water wastage, %
Microfiltration	<100	>97	<2	5–10
Ultrafiltration	<100	>99	<10	10–15
Nanofiltration	<500	>99	>90	15–30

Note: NOM, natural organic matter.

its producer, as well as the application of precoagulation. The average value of the filtrate turbidity was 0.097 NTU at a standard deviation of 0.06 for 72 measurements. Similar results were obtained for various membrane modules during studies in the United States, France, and other countries (Taylor & Wiesner, 2000). Sometimes, when turbidity is caused by colloidal fraction, membrane filtration is preceded by coagulation to obtain flocks of a greater size (Bodzek & Konieczny, 2005). Reverse osmosis and NF also can eliminate these types of impurities and organic admixtures, but those processes are not applied because of the fouling phenomenon. Table 15.1 summarizes the percent removal of turbidity and NOM by various membrane techniques (Bodzek, 2013).

Water and wastewater that contain microorganisms, i.e., viruses, bacteria, and protozoa (fungi, algae, snails, worms, and Crustacea) may have many negative health effects (Anonymous, 2005; Taylor & Wiesner, 2000). Polish regulations regarding the quality of drinking water establish the maximum permissible content of *Escherichia coli* and *Enterococcus*, and, as additional requirements, the amount of *Coli* bacteria group, the total number of microorganisms, and the amount of *Clostridium perfringens* (Bodzek & Konieczny, 2005). Water contamination can occur at its source, at the site of its intake or treatment, and directly in the water supply system. Various methods can be applied to water disinfection, each of which has some advantages and disadvantages. Sand filters remove 99–99.9% of bacteriophages, whereas commercial water treatment devices based on ultraviolet (UV) and ozonation do not guarantee the removal of all pathogenic microorganisms. Chlorination causes the formation of trihalomethanes (THMs) and is ineffective in the case of microorganisms associated with suspension. Some microorganisms (e.g., *Cryptosporidium*) are resistant to its action (Taylor & Wiesner, 2000).

Membrane filtration (MF and UF) may significantly improve the disinfection process, because it almost completely eliminates viruses, bacteria, and protozoa. The size of viruses varies from 20 to 80 nm, whereas the pore size of UF membranes is less than 10 nm. Thus, at least theoretically the elimination of microorganisms is possible. On the other hand, bacteria (0.5–10 μm), cysts, and oocytes (3–15 μm) are larger, and thus they can be totally eliminated during MF (Bodzek & Konieczny, 2005; Taylor & Wiesner, 2000). A comparison of the pore sizes of UF and MF membranes with the size of microorganisms indicates that the UF process can be successfully used for water

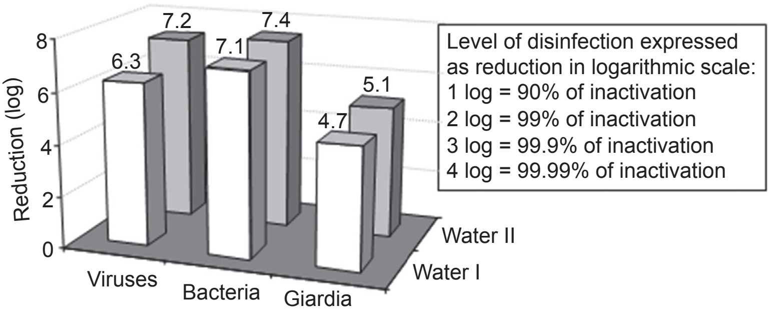

Figure 15.10 Removal of microorganisms using UF (Bodzek & Konieczny, 2010). UF, ultrafiltration

disinfection (Bodzek & Konieczny, 2005). Figure 15.10 shows the rates of removal of viruses, bacteria, and protozoa for different UF membranes (Bodzek & Konieczny, 2010; Taylor & Wiesner, 2000). The obtained retention for all types of microorganisms was greater than 4 log, i.e., 99.99%.

However, it has been shown in practice that UF membranes are not always able to eliminate bacteria and viruses completely from water. This is mainly connected to imperfections in membranes and membrane modules and the secondary growth of bacteria in water after its passage through a membrane. In commercial membranes, a discontinuous skin layer through which microorganism can pass takes place. In addition, the design of the modules often requires the raw stream to be sealed off from the permeate stream, which is not always appropriate. The most efficient disinfection is obtained using capillary modules, in which isolation of raw water from permeate is easier than in the spiral-wound and hollow-fiber modules (Bodzek & Konieczny, 2005). Furthermore, cells of microorganisms could penetrate membrane pores with diameters much smaller than the dimensions of the cells themselves, owing to pressure deformation with the filtration of intracellular fluid, but tonus of the cellular membrane remains unchanged (Figure 15.11) (Bodzek, 2013; Bodzek & Konieczny, 2010;

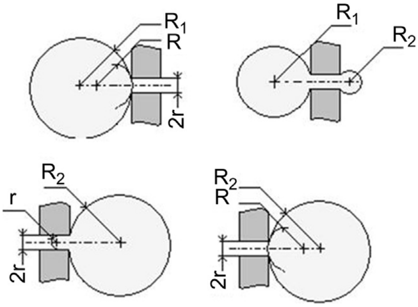

Figure 15.11 Deformation of *Cryptosporidium parvum* in the microfiltration process (Bodzek, 2013; Bodzek & Konieczny, 2010).

Sosnowski, Suchecka, & Piątkiewicz, 2004). In addition, it was demonstrated that the shape of microorganisms could be a key factor determining the efficiency of bacteria removal via a membrane. For example, bacteria or viruses of a slim, elongated shape were removed to a greater extent than ones of more compact shape (Bodzek, 2013).

15.3.2 Natural organic matter

NOM present in aqueous ecosystems is the mixture of many compounds characterized by various chemical structure and properties. Fulvic acids soluble in water ($MW \leq 2000$ Da), more hydrophobic humic acids ($MW \leq 2000-5000$ Da), and insoluble humic fraction (humins) of bituminous character are part of NOM (Bodzek, 2013; Domany, Galambos, Vatai, & Bekassy-Molnar, 2002). Humic substances usually appear in water as dissolved compounds, colloids, and non-dissolved admixtures; usually, the appearance of a given form strongly depends on the water pH. The dissolved NOM fraction in natural water is equal to c. 80–90% of the total NOM content. Humic substances cause intensive coloration of water from brown to black. In addition, complexation reactions of humic substances with heavy metals or adsorption of toxic organic substances creates many health hazards. Humic substances are also disinfection by-product (DBP) precursors (Domany et al., 2002). These are the main reasons for the need to remove NOM from water.

The elimination of NOM is one of the most important processes in water treatment technology. The main advantage of applying membrane techniques in water treatment is to remove DBP precursors including part of NOM (Taylor & Wiesner, 2000; Wilf, 2010). As one of the most popular disinfection methods, chlorination results in the formation of adsorbable organic halides (AOX) including THMs, halogenated acetic acids, halogenated aldehydes and ketones, halogenated acetonitriles, amines, and other DBPs (Bodzek, 2013; Bodzek & Konieczny, 2005). The introduction of pressure-driven membrane processes to water treatment allows the formation of DBP to be controlled as semipermeable membranes retain NOM including DBP precursors (Van der Bruggen & Vandecasteele, 2003). The removal of NOM also decreases the amount of chlorine required for disinfection, which results in a reduction of the biological activity of water in the distribution system (Bodzek, 2013; Bodzek & Konieczny, 2005). According to a very wide molecular size distribution of NOM (from c. 1 nm to c. 0.45 μm), the effectiveness of its removal depends on properties of the applied membranes (Bodzek, 2013). Table 15.2 compares the effectiveness of NF, UF, and MF processes in NOM content control in natural waters (Bodzek, 2013; Bodzek & Konieczny, 2010).

15.3.2.1 Application of RO and NF

By introducing NF or RO systems to water treatment, one can directly control formation of the DBP because semipermeable membranes retain NOM, including the precursors of DBP. Nanofiltration membranes are particularly important for removing NOM and DBP precursors because they are an effective barrier against organic compounds if their molecular weight (particle diameter) is greater than the cutoff of the membrane.

Table 15.2 **Comparative assessment of MF, UF, and NF processes for NOM removal**

Parameters	MF	UF	NF
NOM removal	<10%	0% ± 30%	>80%
Removal of suspensions and colloids	20% ± 40%	70% ± 90%	>95%
DBP removal	No	50% THM; 32% HAA	>80%
Requirements for cleaning	Required back-washing	Cyclical cleaning required	Cyclical cleaning required
Performance problems	Moderate fouling	Fouling	Fouling, clogging
Pretreatment	In-line coagulation or other process	In-line coagulation or other process	No

Note: MF, microfiltration; UF, Ultrafiltration; NF, nanofiltration; NOM, natural organic matter; HAA, haloacetic acids; THM, trihalomethane; DBP, disinfection by-product.

Nanofiltration membranes are able to retain 90% of DBP precursors from natural waters because they have a cutoff of 200–500 Da (e.g., Filmtec NF-50 and NF-70) (Bodzek, 2013; Taylor & Wiesner, 2000; Thorsen, 1999; Van der Bruggen & Vandecasteele, 2003). The obtained permeate is high-quality drinking water with a low amount of DBP and a small risk of secondary bacteria growth after chlorination, which precedes water distribution to the network. The results of removing DBP precursors are given in Table 15.3 (Bodzek, 2013; Bodzek & Konieczny, 2010; Taylor & Wiesner, 2000). High removal rates of DBP precursors are obtained for both surface and groundwater. However, because of greater fouling mainly caused by the high content of colloids and suspensions, surface waters are more difficult to clean using membrane methods. As a consequence, to keep appropriate membrane flux, more advanced pretreatment or a combination of NF and low-pressure membrane techniques is required.

Long-term research on DBP precursor content in Flagler Beach, Florida (groundwater), and Punta Gorda, Florida (surface water), treatment stations compared the effectiveness of groundwater and surface water purification using RO and NF (Taylor & Wiesner, 2000). Although satisfactory levels of THM precursor removal were achieved, permeate flux was low for surface water and the system required adequate regeneration. A pilot study of water treatment from Florida River using NF showed a 95% reduction in THM precursor content (Siddiqui, Amy, Ryan, & Odem, 2000). In addition, RO membranes (cutoff of 100 Da) were significantly more effective in removing THM precursors (98%) than NF ones with a cutoff of 400 Da (96%) (Siddiqui et al., 2000).

Table 15.3 **Natural organic matter (NOM) removal by nanofiltration (NF) (NF-50 and NF-70 membranes from Filmtec)**

Water type	Pretreatment	Raw water	Purified water	Removal, %
		NOM content, μg/L		
Ground	Antiscalant	961	28–32	97
	Preliminary filtration	961	31–39	96–97
Surface	Preliminary filtration	157–182	55–84	49–70
Ground	Preliminary filtration	259	39	85
Ground	Preliminary filtration	120	6	95
Surface	Preliminary filtration	40–460	NA	30–90

Note: NA, data not available.

Amy, Alleman, and Cluff (1990) conducted laboratory-, pilot-, and full-scale studies of the NF treatment of water from the Colorado River. A relatively low reduction in the content of THM precursors (65–70%) was associated with their small molecular weight (a significant amount of compounds of a molecular weight < 500 Da). Tan and Amy (1991) compared ozonation and NF used in color and DBP precursor removal and found that membranes were much more effective. Laine, Clark, and Mallevialle (1990) and Jacangelo, Aieta, Carns, Cummings, & Mallevialle (1989) proposed the use of UF/MF as water pretreatment before NF and observed that MF membranes with a high cutoff (e.g., 100,000 Da) were effective only in removing fine particles of suspended solids in the range of 0.05–2 mm, whereas UF membranes with a lower cutoff (e.g., 10,000–50,000 Da) caused the retention of a certain group of DBP precursors.

15.3.2.2 Microfiltration and UF

Aside from for NF and RO processes, low pressure-driven membrane filtration is also widely used in water treatment (Thorsen, 1999). Ultrafiltration and MF membranes effectively remove colloids and ionic and non-ionic organic compounds of sizes that correspond to the nominal molecular weight cutoff of UF or MF membranes. Thus, single-step UF/MF can be directly used to remove greater fractions of NOM from water, including part of high-molecular-weight DBP precursors, whereas medium- and low-molecular-weight compounds can be eliminated in integrated systems (Bodzek, 2013; Thorsen, 1999). To eliminate humic substances from water, direct UF with modules equipped with dense membranes (e.g., c. 1000 Da) or hybrid

Table 15.4 Characterization of NOM removal processes using UF/MF

Process	Direct UF/MF	UF/MF-PAC process
Diameter of membrane pores, nm	1–5	10–100
Transmembrane pressure, MPa	0.2–0.8	0.1–0.4
Permeate flux, L/m^2 h	15–25	50–200
Removal of NOM	Partial (10–20%)	60–80%
Removal of particles, bacteria, and viruses	Yes	Yes

Note: UF, Ultrafiltration; MF, microfiltration; NOM, natural organic matter; PAC, powdered activated carbon.

systems of UF or MF with coagulation, activated carbon adsorption, or oxidation (ozonation or photocatalysis) can be applied (Bodzek, 2013).

For the application of powdered activated carbon (PAC), the removal rate depends on the concentration of DOC, the concentration of an adsorbate on the surface of an adsorbent and adsorbent dose, pH, temperature, and contact time. For direct UF/MF removal of DOC, precursors of AOX, including precursors of THM and haloacetic acids (HAA), do not exceed 20%. On the other hand, retention obtained for combination with activated carbon increases to values between 7% and 82% for DOC; 20–85% for AOX precursors, including 0–97% for THM precursors; and 26–81% for HAA precursors (Bodzek, 2013; Bodzek & Konieczny, 2010) (Table 15.4). Hybrid systems are effective in view of the extended contact time and a greater concentration of adsorbent in a membrane system.

Results on the efficiency of hybrid systems using coagulation and MF/UF (aluminum and iron (III) coagulants) indicate the removal rates between 12% and 83% for DOC, 30% and 88% for THM precursors, 39% and 92% for HAA precursors, and 20% and 85% for precursors of AOX (Anonymous, 2005). Retention rates are a function of the dose and type of coagulant, pH, temperature, and time and speed for mixing the reaction mixture. Organic pollutants are adsorbed onto coagulation flocks, and these in turn are retained by the MF/UF membrane. In the coagulation–sedimentation–UF/MF (ceramic membrane and capillary) integrated process, removal of organic compounds was approximately 90% (DOC and UV$_{254}$) in the first stage of the purification process, whereas in the second it increased almost to 100% (Bodzek & Konieczny, 2005). In coagulation–membrane filtration, the removal of organic compounds increases, among other things, because of the increased retention time of flocks in the reaction system (Anonymous, 2005). Membrane flux observed in an integrated system also increased with reference to single-step UF. This was according to the removal of organic compounds, and thus the intensity of NOM fouling reduction, but it depended on the coagulation mode used in the integrated system (Bodzek & Konieczny, 2005; Konieczny, Bodzek, & Rajca, 2006). Processes conducted with coagulation and sedimentation exhibit relative permeability values close to unity, but in the case of in-line hybrid processes, relative permeability amounts to

0.83–0.89 for ceramic membranes and 0.74–0.78 for capillary ones (Bodzek & Konieczny, 2005; Konieczny et al., 2006). This is caused by a reduction in the fouling substance penetration of the membrane pores, and the creation of a filter cake characterized by much greater porosity and smaller hydraulic resistance compared with one formed during direct UF/MF. Such a process increases the lifetime of membranes and reduces the frequency of back-washing and chemical cleaning.

Recently, an ion-exchange–UF/MF integrated process was proposed for NOM removal, especially with the use of magnetic ion-exchange (MIEX®) resin, (Kabsch-Korbutowicz, Biłyk, and Mołczan 2006; Rajca, 2012). The effectiveness of NOM removal from water with the ion-exchange process is 30–90% (Kabsch-Korbutowicz et al., 2006) and depends on the properties of water and the mode of process conduction. Application of MIEX® resins before UF/MF allows the filtration cycle to be extended and water with better parameters than in the case of direct membrane filtration to be obtained. However, fine resin particles present in the water could cause the membrane surface to be blocked. Therefore, an integrated process, i.e., the use of ion exchange as water pretreatment before MF/UF, is a more useful solution (Kabsch-Korbutowicz et al., 2006). Interesting comparative studies conducted by Kabsch-Korbutowicz et al. (2006) showed the superiority of an ion-exchange–UF over a coagulation–UF system.

The problem with the membrane filtration of surface water and groundwater is a drop in permeate flux caused by membrane fouling, especially in the case of MF/UF membranes (Laine, Campos, Baudin, & Janex, 2002). It is known that NOM, and in particular its hydrophobic fraction, is the primary substance that causes fouling (Bodzek, 2013). A symptom of this phenomenon is the formation of a brown gel on the membrane surface, which can cause a decrease in flux by up to 75% over 2000 h of operation (Bodzek, 2013). To determine the role of natural organic substances and their properties in membrane fouling, many studies have been carried out (Bodzek, Płatkowska, Rajca, & Komosiński, 2008). However, their results are often contradictory, possibly because of the number of factors affecting this phenomenon. Fouling depends on the characteristics of both filtered water and the membrane used. Adsorptive properties connected with membrane hydrophobicity, pore sizes, cutoff, surface charge, performance, or surface roughness have a significant impact on fouling. In the case of water properties, the ionic strength of the solution is important: in particular, the content of calcium cations, which affects the solubility of organic substances and influences the distribution of NOM molecular weight, type of organic matter, and pH of the water.

15.4 Organic micropollutant removal

The following organic micropollutants can be found in water and wastewater (Bodzek, 2013):

1. DBPs
2. EACs and endocrine-disrupting compounds (EDCs)
3. PhACs

Both secondary DBPs and residues of pharmaceuticals in the aquatic environment may exhibit properties of compounds with estrogenic biological activity. Organic micropollutants have strong carcinogenic and mutagenic properties. The presence of NOM in water, especially humic substances, may change the chemical properties of micropollutants and contribute to their migration to a significant distance. It has been shown that humic substances can hydrophobically bind water additives through covalent bonds, hydrogen bonds, and van der Waals forces (Nawrocki, 2005). They can also increase the water solubility of nonpolar compounds, cause hydrolysis of some pesticides, photodegrade organic substances, and restrict the bioaccessibility of aquatic organisms (Nawrocki, 2005). These properties significantly depend on the form of the organic micropollutants, i.e., whether they are a free state or are adsorbed onto other substances. The removal of micropollutants during water treatment is usually performed using activated carbon sorption or advanced oxidation processes (AOPs). The first method is economically unattractive when the amount of NOM in water is high, whereas for AOPs the possibility exists of forming by-products of undefined biological activity (Bodzek, 2013). This results in the need to develop new separation processes, among which pressure-driven membrane processes seem to be a good solution. In addition, they can be performed as independent processes as well as be a part of integrated/hybrid systems with coagulation or sorption on active carbon, or in MBRs (Bodzek, 2013; Bodzek & Konieczny, 2005).

15.4.1 Oxidation and DBPs

Disinfection and oxidation by-products constitute a group of undesirable substances formed as a result of the reaction of disinfectants and other strong oxidants with water pollutants and admixtures. Table 15.5 shows the number of DBPs, among which the most important are THMs and HHAs (Bodzek, 2013).

Reverse osmosis and NF are most often applied to remove THMs, halogenated acetic acids, and other halogenated hydrocarbons from water. In Poland, permissible concentrations of THMs in water are established as follows: total THM, <100 μg/L, chloroform, 30 μg/L, and bromodichloromethane, 15 μg/L (Bodzek et al., 2011).

Table 15.5 Organic water disinfection and oxidation by-products of contaminants and impurities present in natural waters

Disinfectant	Organic by-products
Chlorine	Trihalomethanes, haloacetic acids, halocetonitriles, haloaldehydes, haloketones, halopicrates, nitroso-dimethylamine, 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (MX)
Chlorine dioxide	Aldehydes, carboxylic acids
Ozone	Aldehydes, carboxylic acids, aldo- and ketoacids

Table 15.6 **Retention coefficients of THMs for RO and NF**

Osmonics membranes	Concentration in raw water, (μg/L)	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$
NF-MQ16	10−100	83−87	88.5−96.5	90.5	92
RO-SS10	10−100	67−81	65−81	57−65	61−80

Note: NF, nanofiltration; RO, reverse osmosis; THMs, trihalomethanes.

A study in which RO and NF Osmonics membranes (SS10 and MQ16) were applied for the removal of THMs revealed that the retention depended on the membrane capacity; i.e., the higher permeate flux, the lower retention coefficient (Bodzek, 2013; Waniek, Bodzek, & Konieczny, 2002) (Table 15.6). The increase in molecular weight of the halogenated compound resulted in an increase of the retention coefficient according to the following series: $CHCl_3 < CHBrCl_2 < CHBr_3 < CHBr_2Cl$. The removal rate of chloroform varied from 67% to 87%, bromodichloromethane from 65% to 96.5%, dibromochloromethane from 57% to 90.5%, and tribromomethane from 61% to 92% depending on the type of membrane applied (Waniek et al., 2002). Another study investigating the effectiveness of removing THMs by means of NF with the use of NF200 and DS5 Osmonics membranes (Bodzek, 2013; Uyak, Koyuncu, Oktem, Cakmakci, & Toroz, 2008) (Figure 15.12) showed that the operating pressure did not affect THM retention, whereas the initial concentration of THM had a noticeable influence on capacity and retention. The NF200 membrane removed THM more effectively than the DS5 membrane. The most effectively removed compound was dibromochloromethane, which resulted from the higher molecular weight of bromine and in the greater size of the molecule.

NF is also suggested for the removal of halogenated acetic acids (chloro-, dichloro-, and trichloroacetic acid; and bromo- and dibromoacetic acid) from water (Chalatip, Chawalit, & Nopawan, 2009). The high reduction in HAA content compared with an open negatively charged sulfonated polysulfone NTR7410 membrane and a neutral NTR729HF polyvinyl alcohol membrane (all membranes by Nitto Denco Corp., Japan) was found for dense negatively charged ES10 aromatic polyamide membranes. Effective separation was caused by repulsion forces (Donnan effect) and a sieving effect. The ES10 membrane removed HAAs in 90−100% even at the low operating pressure of 0.1 MPa, and the change in linear velocity did not influence membrane performance (Chalatip et al., 2009). The increase in the concentration of acids resulted in a decrease in the removal rate in all investigated membranes according to the greater concentration polarization effect, which was the driving force for HAA anion diffusion through the membrane.

There are also studies on the removal of HAAs from water in bioreactors with immobilized enzymatic UF membranes (Kowalska, Dudziak, & Bohdziewicz, 2011). Enzymes isolated from strains of bacteria from activated sludge were used in the immobilization process. Trials have shown that after 8 h of degradation 37% of

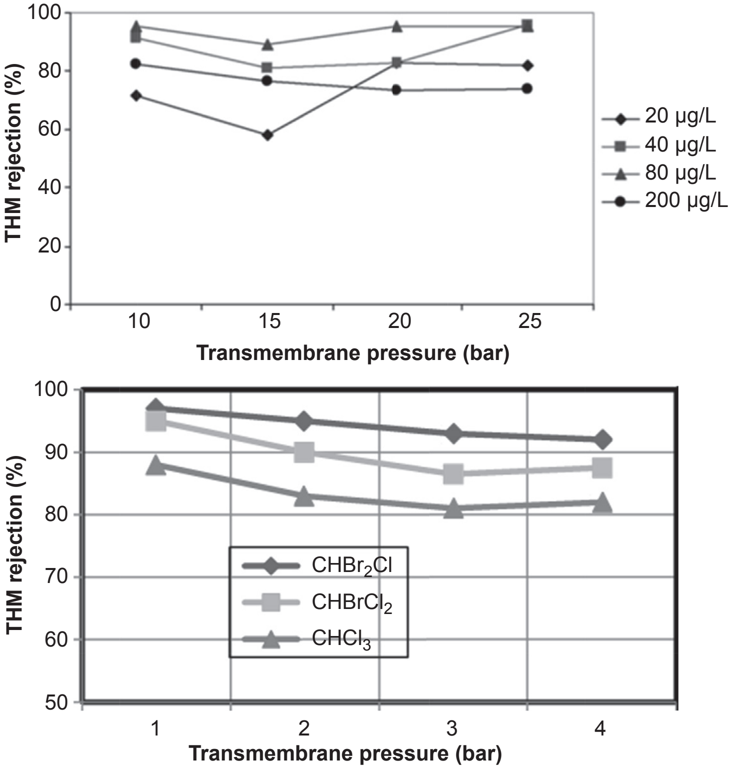

Figure 15.12 Influence of pressure, concentration, and type of THM on retention coefficients of THMs in the NF process (Bodzek, 2013). THM, trihalomethane; NF, nanofiltration.

monochloroacetic acid, 35% of monobromoacetic acid, and 48.4% of dichloroacetic acid were removed (Kowalska et al., 2011).

Studies suggest that NF is the best available technology for removing THMs and HAAs from water.

15.4.2 Endocrine-active/disrupting compounds

Recent investigations focus especially on EACs as groups of micropollutants that appear more often in natural waters and wastewaters, even ones biologically purified (Biłyk & Nowak-Piechota, 2004). According to the definition, those are chemicals that may interfere directly or indirectly with the endocrine system and affect target organs or tissues. Depending on the dose of EAC and the destination physiology, this effect may (but not necessarily) have a side effect. In the case of negative consequences for the health of the organism, its progeny or (sub)population compounds are classified, according to the definition of the International Program on Chemical Safety, as EDCs (Bodzek, 2013). These behave similarly to natural (17β-estradiol, estriol, and estrone) and synthetic estrogens (ethinylestradiol and diethylstilbestrol), and in the body may mimic endogenous estrogens (produced within the body), antagonize the action of estrogens, and disturb the synthesis of estrogen receptors and the metabolism of endogenous hormones (Bodzek, 2013). The EDC group includes endogenic hormones, natural organic compounds produced by fungi (including toxins, i.e., mycoestrogenes) and plants (phytoestrogenes), and a wide range of anthropogenic micropollutants, among which the most important are:

1. Polycyclic aromatic hydrocarbons
2. Surfactants
3. Plant protection products (pesticides, herbicides, and insecticides)
4. Phthalates
5. Halo-organic compounds including dioxins, furans, and polychlorinated biphenyls
6. Phenol compounds (alkylphenols and bisphenols)

Major sources of EDCs for humans are both food and drinking water; pollution is introduced into them by chemicals in rain, landfill leachate, and industrial wastewater. Endocrine-disrupting compounds are present in natural waters in concentrations ranging from nanograms per liter to micrograms per liter.

Phytoestrogens are found in plants and are used for therapeutic and cosmetic purposes. The most important are these compounds are genistein, daidzein, formononetin, biochanin, glicitein, puerarin, coumestrol, and equol as a metabolite of daidzein. Their chemical structure is similar to 17β-estradiol, and therefore they have estrogenic activity. These compounds enter water bodies as a result of the decomposition of plants into wastewaters. Research has focused on removing *phytoestrogens* in water treatment processes, including membrane filtration. Removal of biochanin, daidzein, genistein, and coumestrol in RO amounted to 97%, 69%, 92%, and 86%, respectively, and for NF 86%, 68%, 71%, and 72%, respectively (Dudziak and Bodzek, 2010a, 2010b). During membrane filtration of water also containing NOM and inorganic compounds (salts of calcium, sodium, and bicarbonates), the relative permeability of the membranes was less than unity, which confirmed the existence of fouling or scaling phenomena.

Mycoestrogens are natural organic compounds that contaminate grain crops; when washed by rain, they can contaminate ground and surface waters. They are toxic and reveal estrogenic activity. The presence of mycoestrogens in the aquatic environment creates a need to remove them in water treatment processes. Dudziak (2011) studied the efficiency of removing selected mycoestrogens from water in coagulation, sorption on activated carbon, and NF. Coagulation removed 34% of mycoestrogens, sorption with PAC gave >80%, whereas NF gave from 70% to 88%, depending on the type of compound tested. Integration of NF with sorption or coagulation improved the removal of mycoestrogens.

One of the main anthropogenic pollutants present in drinking water sources is **polycyclic aromatic hydrocarbons** (PAHs). These pollutants are harmful to human health because most are carcinogenic, e.g., benzo(a)phyrene, so their permissible concentration in drinking water cannot exceed 0.010 μg/L; the total amount of benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, and ideno(1,2,3-cd)pyrene may be only 0.1 mg/L. Table 15.7 shows results obtained during studies focused on removing

Table 15.7 Comparison of retention coefficients of PAHs removed during RO and NF (membranes from Osmonics, USA)

PAH name	Concentration in raw water, ng/L	Retention coefficient (%)			
		RO-SS10	NF-SF10	NF-MQ16	UF HP-09
Fluorantene	50	39.6	45.9	89.9	66−88.6
Benzo(b)fluorantene	60	64.4	97.8	85.9	
Benzo(a)pirene	50	62.8	96.4	99.2	
Benzo(g,h,i)perylene	70	96.8	91.1	93.3	

Note: PAH, polycyclic aromatic hydrocarbons; NF, nanofiltration; RO, reverse osmosis.

PAHs by means of RO and NF at similar compound concentrations (Bodzek, 2013; Bodzek & Konieczny, 2010; Luks-Betlej, Bodzek, & Waniek, 2001). The most effective membrane used during the studies was MQ16 (the retention coefficient of PAHs was in the range of 85.9% to 99%, independent of the molecular weight of the compound). For other membranes, the retention coefficient increased with an increase in the molecular weight of the removed compound. Ultrafiltration membranes used in the research removed xenobiotics to a high level even though the molecular weights of these compounds were smaller than the cutoff and the radius of the UF membrane pores (Bodzek, 2013; Luks-Betlej et al., 2001). The likely cause of this phenomenon was the adsorption of PAHs onto the surface of the UF membranes (Bodzek, 2013).

Surface active agents (SAAs) are a specific group of anthropogenic water pollutants: in particular, detergents, complexing and bleaching substances, inhibitors, stabilizers, optical whiteners, and others. They affect wastewater treatment plant performance mainly because of the toxic action on activated sludge, the formation of foam, the simulation of solubility of many hazardous substances, etc. The usefulness of conventional methods (coagulation, foaming, sorption, ion exchange, and oxidation) is limited because of the variety of chemical structures of SAAs and their changes in concentration. Pressure-driven membrane techniques are alternative methods for removal of SAAs from water, whereas the effectiveness and type of process depend on the concentration of the SAA (Bodzek, 2013). When the concentration is below critical micelle concentration (cmc), the application of NF membranes, eventually RO, is proposed. It was shown that NF membrane Desal 5K eliminated SAAs in 90–96% when the concentration was below cmc, whereas for a concentration higher than the cmc the removal rate varied from 92% to 99% (Kowalska, 2008). However, when the concentration of the pollutant in water is greater than cmc, UF can be used, even though the cutoff of applied membranes is greater than the molecular weight of the eliminated compounds. Membranes with a cutoff of 5000–30,000 Da are able to remove SAAs in the range of 30 to >90%, depending on membrane compactness and the type of membrane material (Kowalska, 2008). An important parameter in determining the effectiveness of the method is the concentration of the SAAs; initially, the retention ratio decreases with an increase in concentration, and then above the cmc the retention starts to increase (Bodzek, 2013). Hybrid methods are also proposed to remove anionic SAAs, e.g., integrated UF and ion exchange with an MIEX® and other anionic resins (Kowalska, 2010). Application of MIEX® resin in the amount of 20 cm^3/L of solution at a contact time of 20 min removed 95% of the contaminant; polyetherosulfone membranes of various densities were used (Kowalska, 2010).

Plant protection products (pesticides, herbicides, and insecticides), which belong to xenoestrogenes, appear in surface and ground waters. Pesticides are a group of artificially synthesized substances used to fight pests and improve agricultural production. However, they are generally toxic to living organisms and difficult to degrade, because toxic agents have persistent bioaccumulative effects. The use of pesticides also constitutes a risk for water quality in agricultural areas because these components may pass through the soil and subsoil and pollute natural surface waters. Regulations defining the quality of drinking water establish permissible concentrations of particular compounds

Table 15.8 **Pesticide removal in RO and NF (data published from 1967 to 2001)**

Membrane process (membrane)	Compound	Retention (%)
RO−cellulosic membrane	DDT	99.9
RO−cellulosic membrane	DDT	99.9
RO−TFC (aromatic polyamide)	DDT	99.5
NF (NF−270, PVD1, PZ, SU−610)	Simazine	66−94
	Atrazine	79−99
	Diuron	45−92
	Other	38−100
NF (CA−50, BQ−01, Desal 5−DK, NTC−20, NTC−60, PVD−1, NTR−7250)	Simazine, atrazine	0−80
	Diuron	5−90
	Other	5−96
RO and i NF (20 types of membranes studied)	Symazine	14−95
	Atrazine	41−99
	Diuron	15−83
	Other	0−99
NF (SF−10, ST−10)	Atrazine	25−67

Note: NF, nanofiltration; RO, reverse osmosis.

or their sum at levels at 0.1 and 0.5 μg/L. These are substances with low molecular weight; thus, they can be effectively removed from water (above 90%) during NF or by integrated systems with low pressure-driven membrane processes (MF or NF) and activated carbon adsorption (powdered or granulated) (Taylor & Wiesner, 2000). Since the 1990s in many European countries, including Poland, studies have been performed on removing pesticides from natural waters using NF (Bodzek, 2013; Bodzek & Konieczny, 2005; Taylor & Wiesner, 2000); several pilot-scale and industrial installations are already working. Table 15.8 presents data from the literature on removing selected pesticides from water by means of RO and NF (Bodzek, 2013; Bodzek & Konieczny, 2005; Taylor & Wiesner, 2000). Nanofiltration membranes eliminate pesticides with a molecular weight above 190 Da to an amount below the limit of detection; generally, the retention coefficient varies from 50% to 100%, depending on the molecular weight and the concentration of pesticides in water as well as on the presence of organic and inorganic compounds (Bodzek, 2013; Taylor & Wiesner, 2000). The formation of complexes of organic matter, especially humic acids, with molecules of pesticides causes an increase in the retention of those compounds (Bodzek, 2013; Zhang, Van der Bruggen, Chen, Braeken, & Vandecasteele, 2004). However, the presence of inorganic substances decreases the negative zeta potential of a membrane and causes the destruction of complexes of pesticides with humic acids resulting in the release of micropollutants, which finally leads to a decrease in retention (Taylor & Wiesner, 2000). In France, near Paris, a pilot installation is operating with a capacity of 2,800 m^3/d based on Filmtec membranes (NF-70 and NF-200B), which are characterized by the high removal of atrazine and simazine up to 90% and 85% (concentration in treated water drops from 1−2 g/L to 0.1 g/L) (Mallavialle, Odendaal, & Wiesner, 1996). In the course of the study, an increase in the retention rate of pesticides with an increase in organic carbon content in the raw water was found.

Research on applying UF to the separation of atrazine from water solutions has been carried out by several scientists (Majewska-Nowak, Kabsch-Korbutowicz, & Dodź, 2001; Sarkar, Venkateswralu, Nageswara, Bhattacharjee, & Kale, 2007). The efficiency of the process depends on the type of membrane material and membrane compactness. The best separation properties are exhibited by membranes with a cutoff of about 1−2 kDa (retention rate of about 60%) (Majewska-Nowak et al., 2001). An increase in efficiency up to 85−95% can be obtained during UF in the presence of NOM and/or cationic polyelectrolyte. Hybrid systems combining coagulation, adsorption on activated carbon, and NF are often used in pesticide removal (Sarkar et al., 2007). For example, 98−99% removal of isoproturon (herbicide) was obtained in the process of sorption, and introduction of NF to the process protected treated water against pesticide intrusion, even for the exhaustion sorption bed.

The presence of **phthalates** in the environment is caused by the massive production of plastics, mainly polyvinylchloride, in which they are used as plasticizers. Because of their negative effects on living organisms, the concentration of phthalates in different parts of the environment should be controlled, especially in water. Polish regulations establish the permissible concentration of di-*n*-butyl phthalate at 20 μg/L. A surprisingly high retention of phthalates was observed during both RO and NF processes (initial concentration, 40 μg/L) (Table 15.9) (Bodzek & Konieczny, 2010; Bodzek, Dudziak, & Luks−Betlej, 2004). Retention rates achieved for diethyl phthalate, di-*n*-butyl, and di-2-ethylhexyl were very high and were from 89.7% (UF) to 99.9% (RO and NF). Results obtained during the removal of phthalates with a molecular weight of 222−391 Da revealed that the molecular weight of a compound did not influence the effectiveness of removal.

Phenolic xenoestrogenes (octylphenol, nonylphenol, bisphenol A, and bisphenol F) can be removed from water by means of NF. Both the retention coefficient and the rate of adsorption of xenoestrogenes strongly depend on the type of compound that is removed (Table 15.10) as well as on the type of membrane (Bodzek, 2013). During the membrane filtration of water containing a mixture of xenoestrogenes, changes in volumetric permeate flux (Jv) were not observed, and relative volume permeate flux (α) was close to 1. High retention of octylphenol and nonylphenol in the range of 61% to 73% was observed for SF-10 and DS-5-DK membranes, whereas for bisphenol A DS-5-DK (69%) and MQ-16 (75%), the membranes were more efficient (Dudziak & Bodzek, 2008). With an increase in the concentration of xenoestrogenes in filtered water, a decrease in their retention was observed as a result of the progressive saturation of the membrane surface with these compounds. Nanofiltration

Table 15.9 **Removal of phthalates with RO, NF, and UF (membranes from Osmonics, USA)**

Phthalates	Molecular weight, Da	Concentration in raw water, μg/L	Process (membrane) RO (DS–3–SE)	NF (DS–5–DK)
			Retention coefficient, %	
Diethyl phthalate	222.2	40	95.1	99.9
Di–*n*–butyl phthalate	278.3		95.1	99.9
2-ethylhexyl phthalate	390.6		99.9	99.9

Note: RO, reverse osmosis; NF, nanofiltration.

separation is often accompanied by the phenomenon of adsorption, which greatly affects the elimination of pollutants and is directly correlated with their retention. This may impede separation and cause the release of adsorbed organic micropollutants in the course of the NF. For UF membranes with concentrated compounds in deionized water at a level of 40 μg/L, the removal of bisphenol F, bisphenol A, 4-*tert*-octylophenol, and 4-nonylphenol for GM membranes was 19%, 67%, 28%, and 52%, respectively, whereas for the more compact DS-GE membrane it was 72%, 56%, 88%, and 100%, respectively (Dudziak & Bodzek, 2008). A clear impact of the presence and concentration of the NOM and the presence of inorganic salts, as well as substances causing concentration polarization on the retention of xenoestrogens, was found. During filtration in the presence of macromolecular substances, the relative permeability of membranes (α) was significantly less than unity, which confirmed the existence of the fouling phenomenon.

A large amount of toxic **halogenated aromatic hydrocarbons**, including chlorobenzenes and **polychlobiphenyls** (PCBs), **chlorophenols**, and **dioxins** (polychlorodibenzo-*p*-dioxins and dibenzofurans), is introduced into the environment. These compounds are insoluble in water. They are characterized by high thermal, chemical, and biochemical stability and are harmful to humans when they are deposited in adipose tissue. They damage the liver and kidneys and interfere with the action of the human enzyme system. Polychlobiphenyls, chlorobenzenes, and chlorophenols are used in various industries and enter the environment via wastewater from the chemical industry, through the production of plastics and dyes, from petroleum plants and plants producing plant protection substances, and others. Effective methods of removing chloro-organic compounds from industrial wastewater include thermocatalytic oxidation; stripping with air, inert gas, or steam; solvent extraction; and adsorption on activated carbon or synthetic resins (Żarczyński, Stopczyk, Zaborowski, Gorzka, & Kaźmierczak, 2010). They can be removed from wastewater using a conventional activated sludge

Table 15.10 Comparison of retention coefficients and degrees of adsorption of phenolic xenoestrogens and relative permeate flux of investigated NF membranes (Osmonics)

	Nanofiltration membrane			
	SF−10	**DS−5−DK**	**MQ−16**	**DS−51−HL**
Compound	**Retention/adsorption, %**			
4−*tert*−octylphenol	71.8/52.2	72.7/51.4	47.0/17.9	48.0/19.5
4−nonylphenol	60.5/68.0	70.3/68.0	50.0/52.5	43.5/57.3
Bisphenol A	45.8/52.5	68.8/69.3	75.0/75.0	60.7/33.4
Bisphenol F	−	75−78	−	−
Relative permeate flux, α	0.92	0.99	0.99	0.98

process; however, the presence of suspended solids in the effluent significantly reduces the removal rate. Thus, a better solution is the application of MBRs, in which MF or UF modules are applied instead of secondary settlers (Bolzonella, Fatone, Pavan, & Cecchi, 2010). This ensures the complete removal of suspended solids and extended retention times in bioreactors, which contributes to the high removal of halogenated aromatic hydrocarbons from wastewaters. Examples include the removal of chloro-dibenzo-*p*-dioxin, which was 61–99%, and chloro-dibenzo-*p*-furans, which was 91.5–99.5%, depending on the type of dioxin and the concentration of biomass in the bioreactor (Bolzonella et al., 2010). In the case of natural waters, in which the concentration of the halogenated aromatic hydrocarbons is low, one can use adsorption on activated carbon or other sorbents and photochemical oxidation with TiO_2. In the latter case, for the photocatalyst separation membrane filtration is often used. In addition to the removal of this group of compounds, NF and RO are proposed, so one can get over 99.5% of them removed. Hydrophobic pervaporation with the use of polydimethylsiloxane membranes can also be used. It revealed a high removal rate of contaminants that increased with increasing vapor pressure, and therefore did not depend on the molecular weight of xenobiotics. The studies covered both PCBs and polychlorinated dioxins (Yoon, Koyanagi, Asano, Hara, & Higuchi, 2002).

The appearance of compounds that affect hormone production processes in living organisms is often observed in surface waters. Among these compounds, **natural** and **synthetic hormones** are specified. Natural estrogens (17β-estradiol, estrone, and estriol) are present in the environment as a result of their natural excretion by animals and people. Recently, an increase in concentration of synthetic hormone (α-ethinylestradiol, mestranol, and diethylstilbestrol) resulting from the discharge of large amounts of expired pharmaceuticals from households and from wastewater and hospital waste as well as from pharmaceutical plants has been observed. It was shown that this type of pollutant could be eliminated from water by means of membrane processes (Bodzek & Dudziak, 2006). Considering the relatively low molecular weight of those pollutants, dense membranes (RO or NF) must be applied. Reverse osmosis membranes totally eliminate particular hormones; retention coefficients obtained for NF and UF membranes were lower (Bodzek & Dudziak, 2006). For natural estrogens the concentration of micropollutants (10–1000 ng/L) does not affect the effectiveness of separation, whereas for synthetic estrogens an increase in concentration causes an increase in retention (Bodzek & Dudziak, 2006). Separation of hormones by means of NF and UF strongly depends on the hydrophobicity and molecular weight of a compound. Natural hormones, i.e., estrone, estriol, and estradiol, are removed less efficiently compared with their synthetic equivalents, ethinylestradiol and mestranol (greater hydrophobicity) (Table 15.11) (Bodzek, 2013; Bodzek & Konieczny, 2010). In addition, instead of single-process elimination of hormones from water, a hybrid system of coagulation and NF could be used (Bodzek & Dudziak, 2006). Membrane bioreactors are also proposed for the removal of hormones from wastewaters. The effectiveness of operating an MBR pilot installation (polyvinylidene difluoride membrane with a pore diameter of 0.1 and 0.2 μm) was studied, comparing the obtained results with the conventional installation working on a full-scale basis (Zuehlke, Duennbier, Lesjean, Gnirss, & Buisson, 2006). The ability to remove a

Table 15.11 Retention of synthetic and natural hormones in pressure-driven membrane processes (concentration in water, 1 μg/L) (membranes from Osmonics, USA)

Process (membrane)	Hormones(estrogens)					
	Natural			Synthetic		
	Estrone	17β−estradiol	Estriol	Mestranol	17α−ethynyl Estradiol	Diethyl Stilbestrol
	Retention coefficient, %					
UF (DSGM)	36.8	35.3	28.1	68.5	55.3	70.1
NF (DS−5−DK)	63.0	76.7	71.1	100	90.4	86.1
RO (DS−3−SE)	100	100	100	100	100	100

Note: RO, reverse osmosis; NF, nanofiltration; UF, Ultrafiltration.

selected group of estrogenous hormones (estradiol, estrone, and ethinyl estradiol) was monitored. More than 90% of natural hormones (estradiol and estrone) and approximately 80% of synthetic ones (ethinylestradiol) were removed with conventional treatment. In the case of MBR, estradiol and estrone were removed in 99%, and ethinylestradiol in 95%.

15.4.3 Pharmaceutically active compounds

One of the most important and specific anthropogenic groups of substances affecting the environment are compounds called pharmaceutical and personal care products (PPCPs). This group includes compounds with pharmaceutical activity as well as substances used by people to maintain personal hygiene (Heberer & Feldmann, 2008). Pharmaceutical and personal care products significantly affect wastewaters and other aquatic environments (surface water and groundwater, which constitute a source of drinking water). Main sources of aqueous environment pollution by pharmaceuticals are households and hospitals, as well as diagnostic units, pharmaceutical plants, and livestock farms. Medicines used by sick people do not totally metabolize and are removed in urea and feces, finally reaching wastewater treatment plants. The occurrence of pharmaceutically active compounds and personal care products and their biologically active metabolites in water can generate serious genetic mutations and encourage the formation of drug-resistant bacteria cultures. They may lead to a situation in which the human body will be resistant to the action of the drugs. These chemicals can also accumulate in the tissues of organisms, which poses a threat to health and even life. Therefore, increasing numbers of countries around the world have introduced monitoring of these compounds in water and their impact on ecosystems and the aquatic environment (Heberer & Feldmann, 2008).

Studies on the comparative efficiency of removing drugs in wastewater treatment plants have shown that biological methods are not always sufficient (Bodzek, 2013). Methods to remove medicines from water and wastewater are advanced oxidation, activated carbon adsorption on granulated beds, membrane processes such as NF and RO (Snyder et al., 2007), and in the case of wastewater treatment, MBRs (Clara et al., 2005; Heberer & Feldmann, 2008).

The first results of studies performed at municipal wastewater treatment plants, during which MBRs equipped with MF or UF modules were used, revealed that the removal of trace amounts of pollutants was comparable to conventional treatment methods (Clara et al., 2005). These results attest to the fact that MF and UF membranes are too open to remove biologically nondegradable micropollutants in wastewater treatment plants. On the other hand, the higher age of activated sludge and elongated contact time achieved in MBR improves biological degradation and the removal of PhACs and EDCs. Membrane bioreactors with immersed modules have been checked for the removal of selected pharmaceuticals (clofibric acid, diclofenac, ibuprofen, ketoprofen, mefenamic acid, and naproxen) (Kimura, Hara, & Watanabe, 2005). In the experiments, high rates of removal of ketoprofen and naproxen for MBR have been observed, which were not been found with a conventional treatment system. Removal rates of phenazone, propyphenazone, and formylamino-antipyrine were also less in conventional installation (15%) than with MBR (60–70%) (Zuehlke et al., 2006). Also, the effectiveness of removing pharmaceuticals using MBR depended on the structure of the PhAC molecules, e.g., the number of aromatic rings. A higher removal rate of pharmaceutical substances was observed under low pH conditions, owing to their adsorption on activated sludge flocks (Zuehlke et al., 2006).

In most cases, installations that use MBR to treat wastewater improved the efficiency of organic micropollutant removal compared with conventional wastewater treatment plants. This was because of the extension of retention time and increasing age of the biomass, but also because of the increase in its concentration and the adsorption ability of micropollutants on the much larger flocks of activated sludge. Thus, they were retained during filtration through MF/UF membranes, even though these micropollutants were often several hundred times smaller than the pores of the membranes. Radjenovic, Petrovoc, and Barcelo (2009) observed significant improvement in the efficiency of removing regulators of lipids and cholesterol, statin drugs (gemfibrozil, bezafibrate, clofibric, acid and pravastatin), β-blockers (atenolol and metoprolol), antibiotics (ofloxacin and erythromycin), and some painkillers and anti-inflammatory drugs in MBRs. Data from the literature indicate a high and stable rate of removal of clofibric acid and diclofenac in plants equipped with MBR. The efficiency of removal for clofibric acid usually amounted to 50–70%, and for diclofenac, 51% (Radjenović et al., 2009) during conventional wastewater treatment. Other data indicate a low removal of diclofenac in typical wastewater treatment plants (10–30%). This illustrates how inconsistently the data are presented in the literature and confirms the need to conduct further research on the removal of pharmaceutical residues from wastewater (Radjenović et al., 2009).

Two-month performance monitoring was carried out in MBRs to examine the long-term stability of the system and the effect of retention time on the efficiency of removing residues of pharmaceuticals from treated wastewater (Barceló, Petrovic, & Radjenovic, 2009). In general, the pharmaceuticals were removed to a higher extent by MBR than by a conventional wastewater treatment process. In some cases, the removal efficiency was similar and equally high for both cases (e.g., ibuprofen, naproxen, acetaminophen, paroxetine, and hydrochlorothiazide). Carbamazepine was not removed by the installation with MBR or by the wastewater treatment plant. Nevertheless, wastewater coming from the MBR was characterized by low Chemical oxygen demand (COD) and total organic carbon (TOC) values and a small content of ammonium nitrogen and total suspended solids. The results of monitoring summarized in Table 15.12 (Barceló et al., 2009; Bodzek, 2013) show a distinct advantage of MBRs over the processes in typical wastewater treatment plants. Membrane bioreactors enable the much more effective removal of residues of pharmaceuticals and other micropollutants. For many PPCPs, the removal rate obtained by MBR is virtually 100%. Thus, the use of bioreactors results in treated wastewater of a very high quality, so that the load of pollutants introduced into surface waters is less than that for wastewaters coming from conventional treatment plants.

High-pressure membrane technology, i.e., NF and RO, used to purify wastewater and natural waters along with other pollutants, can also be used to remove residues of PPCPs (Heberer & Feldmann, 2008; Yoon, Westerhoff, Snyder, Wert, & Yoon,

Table 15.12 **Efficiency of removal of pharmaceuticals in installation with MBR, as well as in conventional wastewater treatment plant**

Pharmaceutical	Efficiency of removal with MBR, %	Efficiency of removal in conventional wastewater treatment plant, %
Naproxen	99.3	85.1
Ketoprofen	91.9	51.5
Ibuprofen	99.8	82.5
Diclofenac	87.4	50.1
Indomethacin	46.6	23.4
Acetaminophen	99.6	98.4
Mefenamowy acid	74.8	29.4
Propyfenazon	64.6	42.7
Ranitidine	95.0	42.2
Carbamazepine	No elimination	No elimination
Paroxetine	89.7	90.6
Ofloxacin	94	23.8
Sulfamethoxazole	60.5	55.6
Erythromycin	67.3	23.8
Atenolol	65.5	No elimination
Metoprolol	58.7	No elimination
Hydrochlorothiazide	66.3	76.3
Glibenclamide	47.3	44.5
Gemfibrozil	89.6	38.8
Bezafibrate	95.8	48.4
Klofibric acid	71.8	27.7
Pravastatin	90.8	61.8

Note: MBR, membrane bioreactor.

2007). The NF membrane exhibited relatively low retention (40%) for polar PhACs, low volatile, and low hydrophobicity. In the case of polar organic compounds, retention significantly depended on the dipole moment and pH (Kimura, Toshima, Amy, & Watanabe, 2004). Test results showed that negatively charged and ionic compounds such as the analgesic diclofenac could be removed in more than 90% regardless of other physicochemical properties, mainly according to electrostatic repulsion.

Retention of other ionized drugs exceeded 95% for NF membranes 90, XLE, and TFC-HR; for the NF-200 membrane it was about 90% (Xu et al., 2005). For neutral compounds, retention takes place according to molecular exclusion and adsorption. For example, the neutrally charged antipyretic drug phenacetin or anti-inflammatory and anti-rheumatic drug ibuprofen show a lower retention rate (for phenacetin only more than 20%) because they are significantly adsorbed onto membranes with relatively high hydrophobicity (Nghiem, Schäfer, & Elimelech, 2005). On the other hand, another neutral antipyretic medicament, piramidon, is always retained by more than 70%, which suggests that its retention is affected by other phenomena. In addition, the retention of pharmaceuticals in RO and NF is affected by the membrane material (Kimura et al., 2004). For example, polyamide membranes had higher efficiency (57–91%) than CA membranes. In the case of polyamide membranes, the molecular weight of the compound could be used as a retention trend indicator (separation based on molecular sieving), whereas the polarity predicted the retention of individual compounds in the case of CA membranes. Retention of pharmaceuticals also depends on the concentration (Kimura et al., 2004). Experiments conducted at a concentration of 100 ng/l resulted in significantly lower retention (14–72% for NF and 50–80% for RO) compared with tests at a higher concentration, which amounted to 100 μg/l (19–93% for NF and 71–95% for RO). One can therefore conclude that the retention of pharmaceuticals by a compact NF membrane is dominated by the spherical exclusion (size) mechanism, whereas electrostatic repulsion and spherical exclusion govern the retention of ionized pharmaceuticals in the case of an open NF membrane. The United States evaluated the conventional drinking water treatment processes under typical water treatment plant conditions for the removal of antibiotics (carbadox, sulfachlorpyridazine, sulfamethoxazole, sulfamerazine, sulfamethazine, sulfathiazole, and trimethoprim) (Adams, Wang, & Meyer, 2002). They showed a very high efficiency of RO in removing all antibiotics.

Table 15.13 **Concentration of pharmaceuticals in water of Teltow Canal and in permeate after one step of RO**

Compounds	Average concentration in raw water, ng/L	Average concentration in permeate, ng/L	Retention coefficient, %
AMDOPH	290	<1	>99
Caffeine	429	<1	>99
Clofibric acid	155	<1	>99
Diclofenac	330	<1	>99
Ketoprofen	17	<1	>99
Naproxen	38	<1	>99
Propyfenazon	177	<1	>99

Note: AMDOPH, 1-Acetyl-1-methyl-2-dimethyl-oxamoyl-2-phenylhydrazide.

Table 15.14 **Average concentration of pharmaceuticals in biologically treated wastewater and permeate after treatment with two-stage RO system**

Compound	Concentration, ng/L		Retention coefficient, %		
	Raw water	Permeate	After preliminary filtration and UF	After first RO stage	After second RO stage
AMDOPH	811	<1	32	>99.9	>99.9
Bezafibrate	257	<5	7	96.0	>99.9
Carbamazepine	2282	<1	13	>99.9	>99.9
Clofibric acid	178	<1	20	>99.4	>99.4
Diclofenac	869	<1	44	>99.9	>99.9
Fenofibric acid	705	<1	22	97.0	>99.9
Gemfibrozil	16	<1	38	>93.3	>99.3
Ibuprofen	87	<1	12	98.5	>98.9
Indomethacin	46	<1	0	92.0	>97.8
Ketoprofen	99	<1	20	>99.0	>99.0
Naproxen	224	<1	0	98.2	>99.5
Oxazepam	153	<5	0	>99.3	>99.3
Primidone	734	<1	0	>99.9	>99.9
Propyphenazone	309	<1	46	99.3	>99.7

Note: AMDOPH, 1-Acetyl-1-methyl-2-dimethyl-oxamoyl-2-phenylhydrazide; RO, reverse osmosis; UF, Ultrafiltration.

Pressure-driven membrane processes (MF, UF, NF, and RO) were also tested to remove EDCs and PPCPs on a pilot scale and in industrial installations (Snyder et al., 2007; Heberer & Feldmann, 2008).

Snyder et al. (2007) performed pilot- and industrial-scale tests with MF, UF, NF, and RO for the removal of EDCs and PPCPs from crude municipal wastewater with leachates after the first, second, and third treatment stages and saline groundwater into which specified micropollutants were introduced. The study revealed that only some compounds were removed during MF and UF, whereas for NF and RO significant retention of all investigated compounds was observed. However, several compounds such as iopromide and pentoxifylline were detected in permeate in trace concentrations.

Heberrer and Feldmann (2008) performed a wide pilot study of PhAC removal using a mobile installation for water treatment equipped with RO modules normally used during natural disasters or military operations. The substrate of the study was water from Teltow Channel (Berlin) and treated wastewater from the Ruhleben municipal wastewater treatment plant (Berlin). The prototypic three-stage installation with a capacity equal to 10,000 L/h included duplex bag filters with a particle separation less than 0.5 μm, UF, and RO; RO could be performed as a one- or two-stage process. The presence of PhAC in treated water from Teltow Channel was not observed (Table 15.13) (Bodzek, 2013; Bodzek & Konieczny, 2010), whereas in RO permeate obtained during treated wastewater treatment the amount of pharmaceutical was below 10 ng/l for both one- and two-stage configurations (Table 15.14) (Bodzek, 2013; Bodzek & Konieczny, 2010).

15.5 Conclusions

Properly selected, membrane processes such as RO, NF, UF, and MF in hybrid systems, DD, ED, and MBRs can be used to remove micropollutants from natural waters and wastewaters.

High-pressure membrane techniques, i.e., RO and NF, can be used for direct removal of inorganic and organic micropollutants, while low-pressure (MF and UF) can be used in integrated systems, first of all into coagulation and adsorption and in MBR as well as after complexion with polymers or surfactants.

Processes with ion-exchange membranes are suitable for micropollutants with an electrical charge. Because of this, they are used in many large-scale applications including the separation of ions, desalination, and removal of ionic species.

15.6 Final remarks

A number of inorganic and organic micropollutants have been found in potentially harmful concentrations in numerous water sources. The maximum permissible level of these compounds in drinking water set by the WHO and a number of countries is very low (in the range of micrograms per liter to a few milligrams per liter); thus, most of them can be referred to as charged micropollutants. Several common treatment technologies that are currently used to remove contaminants from natural water supplies represent serious exploitation problems.

The use of membranes (NF, RO, and ED) to treat water sources containing anionic and metal micropollutants for drinking and industrial purposes can provide more or less selective removal of the target pollutants, especially when the separation of monovalent and multivalent ions is desired. In NF, it can be obtained by both ion size and charge exclusion effects, whereas in ED it results from the use of ion-exchange membranes with mono-anion permselectivity. Nanofiltration and, to some extent, RO are also suitable for removing organic micropollutants from water and wastewaters. The most important among them are DBPs, pharmaceutical active compounds, and EDCs, which have high biological activity. In the first case, volatile THMs and nonvolatile compounds, mainly HAAs, are formed. For this last groups of compounds, special attention in natural waters is paid to PAHs and surface-active substances, chlorinated pesticides, phthalates, alkylphenols, polychlorinated biphenyls, hormones, synthetic pharmaceuticals, and other chemicals and substances produced by humans and disposed into the environment.

The application of MF and UF in inorganic and organic micropollutant removal is possible in integrated systems through coagulation, adsorption, complexion with polymers or surfactants, and biological reactions. In the last case, three major membrane bioprocesses have been developed: pressure-driven MBRs, biological membrane contactors, and IEMBs. The problem with operating low-pressure-driven membrane processes is membrane fouling.

Drinking water containing biologically active substances, i.e., viruses, bacteria, protozoa, and other microorganisms, is a significant health threat. Ultrafiltration and MF can help improve the process of disinfecting water using traditional methods because membranes are barriers to microorganisms. Viruses can be retained by UF membranes, whereas bacteria and protozoa need UF and MF membranes.

To remove NOM, it is possible to successfully use either direct NF or integrated systems combining UF or MF with coagulation, adsorption on activated carbon, and even oxidation. NOM and some other anthropogenic organic pollutants can be precursors of DBPs, which is why it is very important to remove NOM from water.

List of acronyms

AOP Advanced oxidation process
AOX Adsorbable organic halides
cmc Critical micelle concentration
COD Chemical oxygen demand
DBP Disinfection by-product
DD Donnan dialysis
DOC Dissolved organic carbon
EAC Endocrine active compounds
ED Electrodialysis
EDC Endocrine-disrupting compounds
EDI Electrodeionization

EDR Electrodialysis reversal
EED Electro-electrodialysis
EMBR-SRB Extractive membrane bioreactors with sulfate-reducing bacteria
EU European Union
HAA Haloacetic acid
IEMB Ion-exchange membrane bioreactor
MBR Membrane bioreactor
MCR Membrane coagulation reactor
MEUF Micellar enhanced ultrafiltration
MF Microfiltration
NF Nanofiltration
NOM Natural organic matter
NTU Nephelometric turbidity unit
PAC Powdered activated carbon
PAH Polycyclic aromatic hydrocarbon
PCB Polychlorobiphenyl
PEI Polyethyleneimine
PEUF Polymer-enhanced ultrafiltration
PhAC Pharmaceutical active compound
PPCP Pharmaceutical and personal care product
PVA Poly(vinyl alcohol)
RO Reverse osmosis
SAA Surface active agent
THM Trihalomethane
TOC Total organic carbon
UF Ultrafiltration
WHO World Health Organization

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Membrane technologies for water treatment and reuse in the gas and petrochemical industries

16

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16.1 Introduction

Petrochemicals can be defined as a large group of chemicals derived from natural gas and petroleum and further used for a variety of chemical purposes, which are extremely important in modern civilization. Nevertheless, like most production activities, petroleum oil and gas production and further processing processes such as extraction and refining are responsible for generating a huge volume of wastewater to be discharged into the environment. Because environmental policy is increasingly severe, water contaminated with petroleum derivatives and processing additives should be treated to separate these derivatives from water before it can return to the environment.

Wastewater generated in the petrochemical industry is a mixture of organic and inorganic materials containing many different chemical compositions, depending on the complexity of the refinery, the existing processes, and the type of petroleum oil and gas employed. The effluents are mainly produced by extraction and physical separation processes such as atmospheric and vacuum distillation, deparaffinization, and de-asphalting, and also by processes involving chemical conversions by isomerization, alkylation, etherification, catalytic reform, etc. Therefore, wastewater composition is qualitatively similar to petroleum oil and/or gas production.

The major compounds of the wastewater include: (1) oil compounds; (2) dissolved formation minerals; (3) production chemical compounds; and (4) production solids (including formation solids, corrosion and scale products, bacteria, waxes, and asphaltenes). Among pollutants present in effluents from petrochemical industries at higher concentrations, oil—water emulsions stand out. Besides oil—water emulsions, specific chemical concentrations of wastewaters vary considerably with the geographical location and refining processes. Table 16.1 lists chemical compositions of typical wastewaters from petrochemical and gas production (Hansen & Davies, 1994; Li & Lee, 2009).

Oil is a mixture of hydrocarbons such as benzene, toluene, ethylbenzene, and xylene; naphthalene, phenanthrene, dibenzothiophene; polyaromatic hydrocarbons; and phenols. Oil—water mixtures are generated at different production stages. Because the solubility of oil in water is generally very low, most of the oil is dispersed in water. Oil in these wastewater streams may exist in three forms: free oil (separate oil globules of sufficient size that they can rise as a result of buoyancy force, generally larger than

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Table 16.1 Typical wastewater composition from petrochemical and gas production

Component	Oil wastewater (mg/L)	Gas wastewater (mg/L)
Organic composition		
Aliphatic, C_2-C_5	1	1
Aliphatic, $>C_5$	5	10
Fatty acids, C_2-C_5	300	150
Benzene	8	25
Naphthalenes	1.5	1.5
Phenols	5	5
Inorganic composition		
HCO_3^-	1538.1	5870.3
H_2S	22.5	65
Cl^-	130,636	2389.5
SO_4^{2-}	4594.1	24.1
Na^+	80421.2	4169.3
K^+	398.6	35
Mg^+	894.1	19
Ca^+	4395.5	11
Sr^+	88.9	63
Fe^{2+}	65.3	0.65

150 μm), dispersed oil (20−150 μm), and emulsified oil, which has droplets typically less than 20 μm. Stable oily emulsion is a dispersed system in which the phases are immiscible or partially miscible liquids and difficult to be flocculated. Wastewater in petrochemical industry is currently treated by activated sludge process with pretreatment of oil−water separation. However, de-emulsifying these effluents with conventional processes including chemical dispersion breakup, gravity settling, centrifugation, air flotation, fibrous or packed-bed coalescence, and biological degradation is often not economically feasible, might cause secondary pollution, does not have appropriate efficiency with regard to separation, or produces large amounts of mud that also need treatment (Almeida Neto, Silva, Valenzuela-Díaz, & Rodrigues, 2006).

Furthermore, with regard to the significant matter of environmental concern, many countries have implemented stringent regulatory standards for discharging these wastewaters. According to United States Environmental Protection Agency (USEPA) regulations, the daily maximum limit of "oil and grease" for petroleum oil and gas production wastewater is 42 mg/L and the monthly average limit is 29 mg/L (USEPA).

Besides, the increasing need to reuse treated water has generated interest in treating petrochemical wastewater with the advanced physical, membrane-based separation process.

16.2 Membrane technologies for water treatment and reuse in the gas and petrochemical industries

Generally, membranes are defined essentially as a barrier in the form of thin synthetic organic or inorganic films, selectively separating fluid from its components and restricting transport of various chemicals. The membrane pressure-driven process relies on the pore size of the membrane to separate oily droplets according to their pore sizes. Membrane processes including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) are increasingly being applied to treat oily wastewater (wastewater containing oil) (Bhave & Fleming, 1988; Daiminger, Nitsch, Plucinski, & Hoffmann, 1995). Microfiltration is mainly for the separation of suspended particles, UF for macromolecules, RO for dissolved and ionic components, and NF for multivalent ions rather than for univalent ions. Among these processes, UF is especially useful for stable emulsions, particularly water-soluble oily wastes in wastewaters from the gas and petrochemical industries.

The membrane unit is usually operated in a semi-batch recycle as shown in Figure 16.1. The oil—water emulsion is fed into the separation tank at the same rate as treated permeate is withdrawn, therefore maintaining a constant level in the tank. The retentate containing the oil is recycled to the process tank and allowed to concentrate only when the oil concentration reaches a set level. Generally, the final concentrate volume is only 3—5% of the initial volume of oily wastewater fed into the

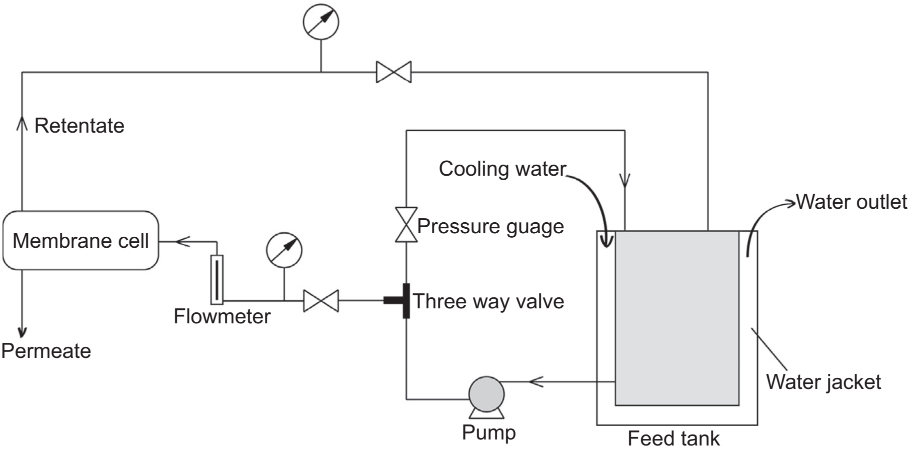

Figure 16.1 Schematic setup of membrane treatment of wastewaters from petrochemical and gas production.

separation tank. The recovered oil can be collected as a by-product or be further treated using other oxidation technologies.

Membranes have many advantages over traditional techniques (Makki, Al-Alawy, Al-Hassani, & Rashad, 2011): (1) They are more widely applicable across a wide range of industries; (2) the quality of the treated water is more uniform regardless of influent variations; (3) no extra chemicals are added; (4) membranes can be used in-process to allow recycling of selected waste streams within a plant; (5) concentrates up to 40−70% oil can be obtained by UF or MF; (6) the membrane equipment has a smaller space requirement and offers a simple, easy-to-operate, low-maintenance process option; and (7) energy costs are lower compared with thermal treatments.

Membrane processes also have the following limitations: (1) Scale-up is almost linear above a certain size, and therefore the capital costs for large effluent volumes can be high; and (2) polymeric membranes experience fouling and degradation during use, which can increase operating costs significantly.

Despite these disadvantages, membrane separation is gaining wider acceptance because it consistently produces effluents of acceptable discharge quality and it is perceived to be a simple process from an operational viewpoint. Therefore, compounded with other methods, membranes are a commercial success for oily wastewater treatment, with more than 3000 polymeric UF/MF installations and over 75 inorganic/ceramic units worldwide (Bilstad & Espedal, 1996; Ciarapica & Giacchetta, 2003; He & Jiang, 2008; Lee & Frankiewicz, 2005; Li, Yan, Xiang, & Hong, 2006).

16.3 Integrating membrane processes into existing treatment infrastructure

Currently, wastewaters from gas and petroleum oil industries are generally treated based on biodegradation by oxidation (and to a lesser extent, reduction) worldwide. Retrofitting such facilities with an entirely new approach not based on oxidation is rarely possible. Generally, process integrations integrated with more advanced physicochemical technologies are accepted to be able to improve the sustainability of old treatment facilities, and are typically necessary to minimize the overall environmental impact. Among these technologies, membrane processes are thought to be ideal candidates for process integration because membrane technologies can be easily integrated into the total treatment systems combining several processes. The term “integrated membrane system” (IMS) frequently refers to water treatment systems that incorporate membranes. An IMS can be defined either as a system that integrates two or more membrane processes or a system combining a membrane process with other treatment processes. It is claimed that IMS has significant advantages for the treatment of wastewater streams containing oily substances, halogenated organics, or organic solvent (Scott, 1995). Integrated membrane systems have gained increasing importance in treating oily wastewaters, combined with a chemical or biological process or a conventional unit operation such as distillation, or absorption. An IMS with two or more separation processes is most frequently employed to treat wastewater from the gas and petrochemical industries to meet severe emission standards and reduce cost.

16.3.1 Permeate flux and concentration polarization

The capital and operational costs of membrane systems depend directly on membrane permeate flux. Consequently, the permeate flux is the central consideration in designing a membrane process for water treatment and reuse in the gas and petrochemical industries.

Generally, if the concentration of the emulsified oil droplet and pressure are below a certain limit, the permeate flux is directly proportional to the trans-membrane pressure, which can be described as:

$$J_w^0 = \frac{\Delta P}{\eta_0 R_m} \tag{16.1}$$

where J_w^0 is the permeate flux of pure water, ΔP is the trans-membrane pressure, R_m the intrinsic resistance of the clean membrane, and η_0 is the water viscosity.

During the membrane process, the oil droplets accumulate on the membrane surface and a concentration difference between the membrane surface and bulk solution is formed, resulting in oil droplets diffusing into the bulk solution backward and in increasing hydraulic resistance to permeate flow until a balance is obtained, concentration polarization. The concentration polarization layer results in an additional osmotic pressure; therefore, the effective driving force of membrane process as well as the filtration flux and solute rejection are reduced correspondingly. Consequently, the permeate flux declines in time and the following is the differential equation of mass transfer for steady state:

$$J_w \frac{\mathrm{d}C}{\mathrm{d}x} - D\frac{\mathrm{d}^2C}{\mathrm{d}x^2} = 0 \tag{16.2}$$

Integrating Eqn (16.2) gives the following equation:

$$J_w C - D\frac{\mathrm{d}C}{\mathrm{d}x} = C_1 \tag{16.3}$$

where D is the diffusion coefficient of oil droplets, $J_w C$ is the solute flux onto membrane, and $D\frac{\mathrm{d}C}{\mathrm{d}x}$ is the solute diffusion flux in the backward direction. The integral constant C_1 is equal to the oil droplet permeate flux, which is a constant at steady state.

By integrating Eqn (16.3) we can obtain the following equation:

$$J_w = \frac{D}{\delta}\ln\frac{C_m - C_f}{C_b - C_f} \tag{16.4}$$

where C_b is the oil droplet concentration in the bulk solution of feed, C_m is the oil droplet concentration at the membrane surface, C_f is the oil droplet concentration in the permeate, and δ is the thickness of the boundary layer (polarization layer).

Increasing pressure can improve permeate flux of water, and the oil droplet concentration at the membrane surface also goes up, leading to more severe concentration polarization and higher flux of the solute diffusion backward to the bulk solution.

16.3.2 Membrane fouling

Besides concentration polarization, another major challenge confronting membrane applications in water treatment and reuse in the gas and petrochemical industries is membrane fouling. Concentration polarization decreases the driving force of flux across the membrane, which is completely reversible and could be reduced by modifying the flow over the membrane (Asatekin, Kang, Elimelech, & Mayes, 2007). However, membrane treatment of oily wastewater is economically limited by one factor: loss of membrane flux owing to severe fouling. Flux is often reduced by one to two orders of magnitude, severely affecting the economic viability of membrane treatment of petrochemical industry wastewaters (Asatekin & Mayes, 2009).

As soon as the upper surface of the membrane comes into contact with the wastewater, contaminants such as oil droplets and colloid particles adsorb at the membrane surface because of physiochemical interactions. It is widely accepted that there are two mechanisms of membrane fouling: pore blocking, which is responsible for the initial sharp drop from the flux of pure water filtration; and cake formation, which is the reason for long-term gradual flux decline (Song, 1998). The fundamental cause of membrane fouling is the nonequilibrium operation, in which the applied pressure is much higher than the critical pressure that can be absorbed by the concentration polarization layer. In such an operation, the membrane pores will be quickly blocked and a cake layer will form to absorb the excessive pressure.

There are four models of fouling that are categorized according to different blockage mechanisms, as follows (Kim & DiGiano, 2009): complete (solute particles reach open pores of the membrane and block and seal the pore entrances completely), standard (solute particles enter the pores and are adsorbed or trapped inside the pore walls), intermediate pore blocking (solute particles occupy a fraction of the pore entrance, leading to a reduction in the permeate flux without totally sealing the pores), and cake filtration (particle diameters are larger than those of the membrane pores so the particles do not enter the pores.). Hermia developed an empirical model to identify the fouling mechanism by analysis of the characteristic curve (Hermia, 1982):

$$\frac{\mathrm{d}^2 t}{\mathrm{d}V^2} = \beta\left(\frac{\mathrm{d}t}{\mathrm{d}V}\right)^n \tag{16.5}$$

where V is the cumulative volume of filtrate, t is the time of operation, and β is a constant.

The volumetric permeate flux can be expressed as:

$$J_w = \frac{1}{A}\frac{\mathrm{d}V}{\mathrm{d}t} \tag{16.6}$$

Therefore, the governing equation of the flux decline with time could be obtained by substituting and integrating Eqn (16.6):

$$J_w = \frac{1}{A}\frac{\mathrm{d}J_w}{\mathrm{d}t} = -\alpha J_w^{3-n} \tag{16.7}$$

where α is a constant. The value of n depends on the blockage mechanism: $n = 2$ for complete pore blocking, $n = 1.5$ for standard pore blocking, $n = 1$ for intermediate pore blocking, and $n = 0$ for cake formation.

16.4 Improving process design, operation, monitoring, and control

16.4.1 Design considerations

Efforts have been made to improve permeate flux including:

1. *Membrane modification*. The separation behavior is strongly influenced by the membrane materials (Hamza, Pham, Matsuura, & Santerre, 1997), and the surface properties of the membrane have a critical role in the determination of fouling resistance. The widely accepted fact is that surface hydrophilic membrane is employed to treat an oily emulsion because the hydrophobic membranes are easily fouled owing to adsorption of oily substances in water on and in the pores of the membranes (Nakatsuka, Nakate, & Miyano, 1996). To achieve this goal, membrane material can be modified or functionalized by (Ochoa, Masuelli, & Marchese, 2003; Ulbricht, 2006): (1) synthesis of new surface hydrophilic polymers; (2) hydrophilic functionalization of polymeric membranes; (3) preparation of homogenous or heterogenous hydrophilic blends starting from different polymeric materials or particles from organic or inorganic origin. Recently, polyvinyl alcohol, cellulose acetate, and ceramic—polymeric composite membranes are being used for oil—water emulsions separation because of their antifouling properties (Mittal, Jana, & Mohanty, 2011).
2. *Pulsed flow*. The process of transporting oil droplets through a membrane boundary in a steady flow field is related to the classic Graetz problem that analyzes the concentration profile of a steadily flowing fluid that undergoes a step change on the boundary. Superimposing an oscillating flow to the steady flow will alter the flow profiles and thus alter the concentration and mass transfer of the system. The oscillations and unsteady flows can be obtained by introducing pulsations into the feed or filtrate channels, which can enhance shear at the membrane surface to decrease concentration polarization. Although pulsed flow decreases the effective operating time and results in a loss of permeate to the feed stream, filtration performance was greatly improved in both tubular and flat-sheet membrane systems (Howell, Field, & Wu, 1993; Wu, Howell, & Field, 1993); in another case, flux improvement of up to 300% was found when using periodically spaced, donut-shaped baffles in UF tubes together with pulsed flows, with an oscillation frequency up to 2.5 Hz (Finnigan & Howell, 1989).
3. *Improving mass transfer by turbulence promoters*. Insertion of static turbulence promoters is a method for increasing shear stress at the membrane surface and is an effective technique

for reducing concentration polarization and membrane fouling. Flux enhancement and flux control under laminar flow conditions can be achieved by generating well-defined secondary-flow structures by using baffles; this is successful only when the radial velocities are high, which leads to high Reynolds numbers and the flow becomes turbulent. Bellhouse (1997) described designs of tubular membranes into which were placed concentric screw thread inserts, which had a clearance with the tubular membranes to permit substantial leakage flow in the resulting annular gap. The shape of the helical screw thread was semicircular, to permit approximately 50% of the flow to pass along the helical path, with a corkscrew vortex superimposed on the path to create radial mixing in the flow field (Wakeman & Williams, 2002). Different shapes of static turbulence promoters, such as static rods, spiral wire, metal grills, and disc and donut-shaped inserts, have been extensively constructed and placed concentrically inside membrane tubes during MF and UF with or without superimposing the pulsating flow (Gupta, Howell, Wu, & Field, 1995; Holdich & Zhang, 1992). However, pressure loss induced by the insertion of the static turbulence promoter increased energy consumption and might cause significant variation in trans-membrane pressure along the membrane length.

4. *Rotating/vibrating membranes*. In classical cross-flow filtration, the shear stress at the membrane surface is increased by applying a tangential flow. Therefore, the shear stress and feed flow rate are interrelated because a higher shear stress implies a higher flow rate and subsequently higher energy consumption as a result of the pressure drop. In rotating filters, the shear stress is independent of the flow rate because it relies on the speed of membrane rotation. A high-shear stress can be developed at the membrane surface by rotating the surface at high speed, rather than pumping feed across the surface at a high cross-flow velocity (Wroński, Molga, & Rudniak, 1989). This rotating membrane—high-shear (dynamic) filtration can be implemented by rotating either the membrane or a baffle near the membrane. The magnitude of the shear stress can be varied independently of overpressure of the slurry in the filter by varying the rotational speed of the rotating element. Generally, there are two types (Serra, Wiesner, & Laîné, 1999): rotating cylinders or rotating disks. Rotating cylinders referred to as annular membranes consist of two concentric cylinders separated by a small gap, which take advantage of Taylor vortices when one of those cylinders is rotating. The latter consist of two axial disks and take advantage of radial flow in the vicinity of the rotating disk to reduce particle deposition on the membrane as well as the centrifugal force and shear stress exerting on particles deposited on the membrane surface to drive them back into the bulk liquid.
5. *Incorporating force fields such as electric or ultrasonic*. The use of additional forces to aid filtration has gained increasing attention in recent years. Application of an electric field to improve the efficiency of pressure-driven filtration processes, called electro-filtration, has been practiced for a long time. Besides the bulk flow tangential to the membrane in cross-flow filtration, there also exists a convective flow into the porous surface, leading to oil droplets being transported laterally toward the membrane. By applying a direct current electric field gradient to give oil droplets electrophoretic velocity, the convective flow could be counterbalanced to a greater or lesser extent, which might reduce membrane fouling and enhance filtrate flux. Two different configurations have been reported for electro-filtration. An electric field can be applied across the membrane with one electrode on either side of the membrane or the electric field may be applied between the membrane and another electrode. In both cases, the performance of the membrane process is primarily improved owing to electrophoresis. For electro-filtration to be successful, a voltage higher than some critical value must be applied (Henry, Lawler, & Kuo, 1977; Wakeman, 1982). The critical voltage gradient defines the voltage gradient at which the net particle migration toward the membrane is zero.

The electrophoretic velocity (v) gained by an oil droplet could be obtained using the Henry formula as follows:

$$v = \frac{2\varepsilon_0 D_d \xi E}{3\mu} \tag{16.8}$$

where ε_0 is the permittivity of a vacuum, D_d is the dielectric constant, ξ is the zeta potential, E is the electric field gradient, and μ is the fluid viscosity.

Huotari, Huisman, and Trägårdh (1999a), Huotari, Trägårdh, and Huisman (1999b) reported the effect of an electric field in the filtration of an oil emulsion, in which the limiting fluxes for low flow rate increased significantly using an electric field. The limiting flux increase was affected by the electrophoretic mobility of the oil droplets and the applied electric field strength. In this work, the permeate quality also improved significantly and membranes with large pore sizes could be employed when the electric field was present.

The passage of ultrasound waves through a suspension can cause many phenomena, including particle dispersion, viscosity reduction, changes in particle surface properties, and cavitation (Kost & Langer, 1988). Generally, ultrasound is characterized by an ability to transmit substantial amounts of mechanical power through small mechanical movements. The passing of ultrasonic waves of a suitably high intensity through liquid media is accomplished by phenomena such as cavitation, radiation pressure, and acoustic streaming. Cavitational mechanisms are considered important in detaching particles from the membrane surface, whereas turbulence associated with ultrasound has a role in transporting of particles away from the surface after detachment.

Previous works demonstrate that higher particle concentrations produce greater attenuation of the sound waves as they pass through the cross-flow suspension owing to increased acoustic impedance (Wakeman & Tarleton, 1991; Yunus & Jones, 1995). The degree of attenuation varies with different feed particles and processing conditions, and is believed to be the controlling parameter for ultrasonic field efficiency. Besides, wastewater viscosity is a limiting factor as ultrasound is applied. When viscosity goes up, the flux enhancement decreases and no flux enhancements are found when the liquid viscosity is about 4 cp. Experimental results showed that an ultrasound cleaning technique was applied to remove fouling of UF and MF membranes by cross-flow filtration (Chai, Kobayashi, & Fujii, 1998). For each polymeric membrane made of polysulfone, polyacrylonitrile, and polyvinylidene fluoride, cleaning experiments were performed with three kinds of methods: sonication, water cleaning, and water cleaning under sonication. Results showed that water cleaning under sonication was an effective method for the recovery of permeate flux.

16.4.2 Wastewater pretreatment

Pretreatment of wastewaters for the gas and petrochemical industries is an effective option to enhance permeate flux and prevent membrane fouling; therefore, the use of innovative pretreatment can significantly reduce the treatment cost. This technique is commonly used either to remove particles that may cause clogging in the membrane pores or to prevent particles or macromolecules from reaching and depositing onto the membrane surface, or to reduce the total oil emulsion load by breaking it. Traditional methods for separating oil emulsion can be classified as physical, chemical, or combined.

Physical processes usually include prefiltration or centrifugation to remove suspended and colloidal solids that may plug the module or blind the membrane, and mechanical emulsion breaking based on the phenomenon of gravity (Adewumi, Erb, & Watson, 1992; Knudsen et al., 2004). The efficiency of these methods mainly depend on the size of the oil droplets as well as the difference in density between water and oil. Another physical pretreatment method breaks the oil emulsion thermally by heating the wastewater, leading to a significant increase in the oil droplet size (Aptel & Clifton, 1986). This process requires a large amount of energy, which makes it economically unfeasible.

Chemical methods are most widely used in treating oily wastewater, which are usually directed toward destabilizing the dispersed oil droplets or destroying emulsifying agents. Chemical methods are primarily based on neutralizing detergents (emulsion's stabilizers), resulting in the acceleration of a separation process owing to the coalescence effect, and a change in solution pH so that molecular or colloidal foulants will be far from their isoelectric point, thereby reducing the tendency to form a gel layer. Chemical methods include precipitation, coagulation, or flocculation or the use of proprietary antiscalants or disinfectants (Garbutt, 1997, 1999). Currently, ferric and aluminum salts are the most widely used agents for demulsification. The process usually consists of rapidly mixing the chemicals with the wastewater followed by flocculation and flotation or settling. The work has been reported for the application of membrane technology for oily emulsion stabilized by anionic surfactants (Belkacem, Matamoros, Cabassud, Aurelle, & Cotteret, 1995). By adding a reactive salt ($CaCl_2$) at a very low concentration in the feed solution, the permeate flux increased significantly. The UF membrane behaved as efficient surface coalescer when the agent was added, which reduced polarization layer resistance.

16.4.3 Operation optimization

Optimizing the operation conditions may involve maintaining a high cross-flow velocity, limiting trans-membrane pressure, manipulating wastewater temperature, and periodical hydraulic, chemical, and/or mechanical cleaning, etc.

Pumping the feed at higher flow rates into the membrane can lead to increased shear on the membrane surface, which will reduce concentration polarization and cake formation in commercial membrane modules in the same way turbulence promoters do. Whereas steady flows often require cross-flow velocities in the turbulent regime, unsteady flows can be effective in both the laminar (as, for example, Taylor and Dean vortex flows) and the turbulent regimes (Gekas & Hallström, 1987). These fluid instabilities could disturb foulants (Chung, Brewster, & Belfort, 1993; Winzeler, 1990) and induce fluid mixing at the membrane—solution interface (Jeffree, Peakock, Sobey, & Bellhouse, 1981). Fluid instabilities could substantially increase mass transfer of solutes away from the membrane; therefore, the performance of membrane processes can be improved when unsteady fluid instabilities are superimposed on cross-flow velocity (Thomas, 1973; Winzeler & Belfort, 1993).

High cross-flow velocity reduces cake formation and polarization in membrane processes, but the pressure drop on the feed side is generally high whereas the permeate side is often at or close to atmospheric pressure, which means that the trans-membrane pressure at the feed end of the membrane is greater than at the retentate discharge end, causing more cake formation (the extent of compaction depends on the properties of the feed) at the feed end. Besides, high pressure might induce other problems into oil-in-water emulsion by membrane technology when some surfactants are present in emulsion. It has been reported that for water—oil—surfactant emulsions, high trans-membrane pressure results in an increase in the permeability of the surfactant without a commensurate increase in the permeability of the water or oil (Sweet, 1990).

Temperature is another important factor in cross-flow UF of oily emulsions. The separation efficiency and membrane fouling depend on the oily droplet size distribution, which correlates strongly to the varying temperature. With properly chosen membrane materials and pore sizes, by manipulating the emulsion temperature below the cloud point of the least soluble component, it is also possible to remove finely dispersed contaminant oils selectively without simultaneously losing active components from adequately formulated fluids (Misra & Skold, 1999).

After a certain period of use, the membrane should be cleaned mechanically, hydraulically, or chemically. Cleaning-in-place procedures are generally recommended to rejuvenate fouled membranes because they commonly involve shorter downtimes than cleaning-out-of-place. It is common practice to pump permeate back through the membrane periodically, which is achieved by applying pressure on the permeate side of the membrane with the help of an automatic time switch or a microprocessor. Permeated water is then forced in the reverse direction through the membrane, thereby lifting off the boundary layer and washing it out of the membrane surface. The permeate flux could be significantly improved and the concentration polarization and membrane fouling could be effectively controlled by periodic back-flushing. Short pulses (about 0.1 s or shorter) are particularly useful for oily wastewater with colloidal suspensions.

Besides periodic hydraulic cleaning and mechanical cleaning, chemical cleaning is also commonly employed. Cleaning solutions are prepared with cleaning agents and are usually circulated with a pressure somewhat lower than that of normal filtration to prevent deeper foulant penetration into the membrane. The selection of cleaning agent is determined by factors such as the foulant type and the compatibility of the membrane with the solution. A temporary adverse effect on the membrane rejection is commonly observed after using many cleaning agents, which can be attributable to membrane swelling during contact with the cleaning solution (Jonsson & Johansen, 1989). Kim, Sun, Chen, Wiley, and Fane (1993) investigated the relationships between membrane fouling and cleaning in terms of flow conditions, trans-membrane pressure, pH, membrane properties, and cleaning agents using a stirred batch-cell and aqueous albumin solution. Currently, for a better cleaning effect, combined processes, i.e., chemical agents with physical procedures, are widely employed, which include pretreatment, pulsating gas, back-washing, adding chemicals in opposite direction, flushing the feed at high pressure, and combining mechanical devices with chemical cleaners.

16.5 Energy consumption of membrane operations in the gas and petrochemical industries

Although the membrane technology is widely accepted as a reliable way to treat wastewater with specific requirements, the high operating energy consumption is one of the main constraints preventing it from increasing deployment in gas and petrochemical industries. Generally, the total cost of membrane process for wastewater treatment consists of pretreatment of original wastewater influents, capital cost (typically including membrane, pump, and basic construction expenses), equipment maintenance, operating expenses, and oily wastewater concentrate disposal cost.

The Oslo/Paris Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR Commission) proposed a method for evaluating wastewater treatment costs in the gas and petrochemical industries. Capital cost and operating expenses were estimated based on market conformity. The method was based on three model situations:

1. Small gas installation (based on 26 gas installations with small water discharges)
2. Large gas installations (based on 27 gas installations with larger water discharges)
3. Petroleum oil installations (based on seven oil installations)

Because of the high pressure required to overcome the trans-membrane osmotic pressure, the operating expenses, mainly energy consumption, are the major part and can reach as high as 45% of the total cost (Busch & Mickols, 2004; Manth, Gabor, & Oklejas, 2003). Currently, the energy consumption of membrane process has been estimated using a phenomenological approach, which does not explicitly consider the membrane properties and operating parameters. Qi, Wang, Xu, Wang, and Wang (2012) proposed a method to theoretically calculate the energy consumption described below. According to the mass balance law, the mass of oil in the feed solution equals the mass of oil in the retentate effluent plus that in the permeate, which can be expressed as:

$$Q_f\overline{C_f} = Q_p\overline{C_p} + Q_b\overline{C_b} \tag{16.9}$$

where Q_f represents the inflow rate, Q_p is the permeate flow rate, and Q_b is the volumetric retentate outflow rate. $\overline{C_f}$, $\overline{C_p}$, and $\overline{C_b}$ are the average oil concentrations of influent, permeate, and retentate effluent, respectively.

The osmotic pressure difference at the exit of membrane module (i.e., $\Delta\pi_{a,exit}$) is therefore approximated by

$$\Delta\pi_{\text{exit}} = \Delta\pi_{m,\text{exit}} + \Delta\pi_{a,\text{exit}} = \frac{\pi_0\overline{R_t}}{1 - Y\overline{R_t}} + \Delta\pi_{a,\text{exit}} \tag{16.10}$$

where π_0 is the osmotic pressure of oily wastewater, $\Delta\pi_m$ is the osmotic pressure difference without concentration polarization, $\Delta\pi_a$ is the osmotic pressure difference with concentration polarization, R_t is the observed rejection, and Y is the target recovery rate.

The pressure of wastewater to the treatment system should be higher than the osmotic pressure difference at the exit of membrane module, in which ΔP is the applied pressure and ΔP_f is the pressure drop:

$$\Delta P - \Delta P_f \geq \Delta\pi_{\text{exit}} = \frac{\pi_0 \overline{R_t}}{1 - Y\overline{R_t}} + \Delta\pi_{a,\text{exit}} \tag{16.11}$$

Here, the average rejection is defined as:

$$\overline{R_t} = \int_0^L R_t \mathrm{d}x / L \tag{16.12}$$

Equation (16.12) is the thermodynamic limit for the cross-flow filtration process. It is shown that $\Delta\pi_{\text{exit}}$ would increase rapidly at high target recovery rates and so is the required applied pressure. The partial recovery rate Y_x is defined as:

$$Y_x = Y \int_0^x j(x)\mathrm{d}x \Bigg/ \int_0^L j(x)\mathrm{d}x \tag{16.13}$$

Finally, the rate of pump work or operating energy consumption of membrane process is normally calculated by:

$$W = \frac{Q \times \Delta P}{\eta} \tag{16.14}$$

Here, Q is the flow rate of pump and η is the efficiency of pump.

16.6 Conclusions

Wastewater from the gas and petrochemical industries is widely treated via an activated sludge process with oil—water separation. Increasingly tightened environmental regulations and the growing need to reuse treated water have generated interest in the treatment of these wastewaters by the membrane process. Integrated membrane systems combined with different treatment technologies can help maximize water recovery, achieve high water quality for water reuse, and minimize life cycle costs. Consequently, it is clear that in the near future the use of membranes will grow substantially for wastewater treatment from the gas and petrochemical industries.

16.7 Future trends

For the gas and petrochemical industries, the most significant waste stream is water. For each barrel of oil produced, 3−10 barrels of wastewater are generated. If properly treated, about 95% of the water can be reinjected to enhance oil recovery. However, the fraction remaining is considerable; consequently, using cost-effective and efficient technology to reduce contaminants for water reuse or for discharge constitutes a challenge for gas and petrochemical companies.

To treat wastewater from the gas and petrochemical industries, a suitable strategy for the membrane process depends on the following major criteria:

1. Source of wastewater and concentration of pollutants
2. Final requirements for discharge, recycle, or reuse.

Developing a fouling-resistant membrane will always be the core consideration for this application.

Nomenclature

A	Membrane area (m^2)
C	Solute concentration (M/L)
C_1	Integral constant, equal to the oil droplet permeate flux (L/m^2 h)
C_b	Oil droplet concentration in the bulk solution of feed (vol. %)
C_f	Oil droplet concentration in permeate (vol. %)
C_m	Oil droplet concentration at the membrane surface (vol. %)
$\overline{C_b}$	Dimensionless form of average oil concentration of retentate effluent
$\overline{C_f}$	Dimensionless form of average oil concentration of influent
$\overline{C_p}$	Dimensionless form of average oil concentration of permeate
D	Diffusion coefficient of oil droplets (m^2/s)
D_d	Dielectric constant
E	Electric field gradient (V/m)
J_w^0	Permeate flux of pure water (L/m^2 h)
J_w	Permeate flux of waste water (L/m^2 h)
n	Constant
ΔP	Applied pressure (bar)
ΔP_f	Pressure drop (bar)
Q	Flow rate of pump (m^3/s)
$\mathrm{Q_b}$	Volumetric retentate outflow rate (m^3/s)
$\mathrm{Q_f}$	Inflow rate (m^3/s)
R_m	Intrinsic resistance of the clean membrane (L/m)
R_t	Observed rejection (%)
$\overline{R_t}$	Average rejection (%)
t	Time of operation (s)
v	Electrophoretic velocity (μm/s)
V	Cumulative volume of filtrate (L)
W	Rate of pump work (KW/h)

Y	Target recovery rate (%)
Y_x	Partial recovery rate (%)

Greek symbols

α	Constant
β	Constant
δ	Thickness of boundary layer (polarization layer) (m)
ε_0	Permittivity of vacuum (C^2/J m)
η	Efficiency of pump
η_0	Water viscosity (Ns/m^2)
μ	Fluid viscosity (Pa.s)
ξ	Zeta potential (mV)
π_0	Osmotic pressure of oily wastewater (bar)
$\Delta\pi_a$	Osmotic pressure difference with concentration polarization (bar)
$\Delta\pi_m$	Osmotic pressure difference without concentration polarization (bar)

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Membrane technologies for water treatment and reuse in the textile industry

17

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17.1 Introduction

The textile industry is one of the largest consumers of water and chemicals for wet processing of textiles (Banat, Nigam, Singh, & Marchant, 1996). This has led to increasing environmental concerns; thus, control of water pollution is an important issue. Here we will review some aspects related to the treatment of textile wastewater with special emphasis on membrane processes.

Textile processing is complex and includes sizing where various types of water-soluble polymers, also called textile sizing agents, such as modified starch, polyvinyl alcohol, carboxymethyl cellulose and acrylates are used to increase the strength of the yarn for weaving, scouring (e.g., detergent treatment), bleaching, mercerizing (where sodium hydroxide is added to provide lustrous appearance and strength to cotton), carbonizing (adding acid followed by baking and thereby removing (carbonized) impurities from wool, dyeing and finishing). Consequently wastewater pollutants arise both from raw fabrics and a wide range of additives used to produce the finished product. In textile wastewater treatment, one therefore has to deal with pollutants spanning a wide range including nonbiodegradable highly persistent organics and pesticides used in speciality textiles such as insect-proof fabrics.

Organic matter represents the main emission load for textile wastewater, which suggests treatment based on biological processes. However, the introduction of effective and sustainable water recycling techniques in this branch of production is often prevented by recalcitrant organic compounds and remaining dyes. Because of the poor biodegradability and sometimes even toxicity of the textile wastewater components, advanced treatment technologies are necessary. Especially if reuse of treated wastewater is the objective, extensive removal of organic contents as well as almost complete decolourization is required.

Industrial wastewater streams can vary greatly in their composition within a plant, and even during the same process over short periods of time. For wastewater treatment to be practical in this situation, wide processing latitude is required, to accommodate inherent variability. The textile industry provides examples of this variability in batch processes such as dyeing, printing, finishing and washing, as well as frequent changes

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in product runs. In addition to this variability in water content, many production process reactions are incomplete, leaving varying amounts of residue chemicals in the processed water.

When dyeing/printing textiles, water serves two purposes: First, it ensures the transmission of the colour onto the fibre; second, it washes out excess amounts of dyes from the treated fabrics. Of all dyed/printed textile fibres, cellulose fibres stands out as the most prominent, and more than 50% of production is dyed/printed with a special class of dyes, the so-called reactive dyes. Over 80,000 tons of reactive dyes are produced and consumed each year, which makes it possible to estimate the total pollution caused by their use (Allegre, Moulin, Maisseu, & Charbit, 2006). They are adsorptive to the cellulose fibres, and the hydrolysed dyestuff requires large amounts of water, preferably at high temperatures, to be properly washed out. Unfortunately, this class of dyes is also the most unfavourable from an ecological point of view, because the effluents produced are heavily coloured and contain high concentrations of salt and exhibit high biochemical oxygen demand (BOD) and chemical oxygen demand (COD) values (Allegre et al., 2006).

17.2 Textile wastewater

A detailed source analysis of coloured wastewater released by a dye/printing house indicated that 15–30% of the applied dyestuff is released into the wastewater. The main portion, corresponding to 50–80% of this amount, results from the washing/rinsing stages and thus has been diluted to average concentrations of 1–2 g/l (Bechtold & Turcanu, 2004). Wastewater containing reactive dyes is considered problematic because it is removed less efficiently compared with other dye classes in which wastewater can be processed by activated sludge sewage treatment (Pierce, 1994). Moreover, fixation of the reactive dyes on the textile fabric is low, 70% on average, compared with other dye classes (over 90% on average).

In addition to reactive dyes, the textile industries are dominated by the use of direct dyes, acid/basic dyes, and disperse dyes, depending on the material to be processed. Thus, for example, for polyester disperse dyes are most common, whereas for blended fabrics a mixture of reactive dyes and acid dyes is typically used. For polyester and nylon mixtures, disperse dyes and acid dyes are blended. For nylon alone a mixture of reactive dyes, disperse dyes and acid dyes is used. See Table 17.1 for a list of common dyes found in textile wastewater.

A particular problematic group of dyes is constituted by the so-called azo dyes (containing $-N{=}N-$ bonds) because they and their metabolites may be mutagens and carcinogens (Chang et al., 2001; Pandey, Singh, & Lyengar, 2007; Żyła, Sójka-Ledakowicz, Stelmach, & Ledakowicz, 2006). Azo dyes commonly used in the textile industry include reactive, acid and direct dyes (You & Teng, 2009). They are aromatic compounds that make up the largest and most diverse group of synthetic dyes found in the wastewaters of dye = using industries such as textile, paper printing, food and cosmetic industries.

Table 17.1 **Examples of dye components in textile wastewater**

Dye class	C.I. name	Commercial name
Reactive	Reactive Red 120	Suncion Red H-E3B
	Reactive Blue 160	Sunicon Blue H-ERN
	Reactive Yellow 84	Sunicon Yellow H-Z4RN
Acid	Acid Red 57	Nylosan Red E-BL
	Acid Blue 72	Nylosan Blue E-GL
	Acid Yellow 256	Nylosan Yellow E-2RL
Disperse	Disperse Red 60	PALANIL Red FD-BFY
	Disperse Blue 56	DZANIX Blue E-R
	Disperse Yellow 54	PALANIL Yellow 3GZ

C.I.: Colour Index International is a reference database jointly maintained by the Society of Dyers and Colourists and the American Association of Textile Chemists and Colourists.
Source: Partially adapted from Choi et al. (2003).

17.3 Treatment of textile wastewater

These wastewater streams are usually collected together and, after eventual pH adjustment, sent to communal wastewater treatment plants. Methods for wastewater treatment have to focus on the cleaning of wastewater streams originating from individual textile processes. In practice, realization of this process is difficult. Suitable technologies for the treatment of individual streams are used only when the dyeing process is well-defined and/or when a wastewater stream contains materials that can be separated out and reused in the finishing processes. When treating textile wastewater for reuse by the industry, colour removal as well reduction in total suspended solids (TSS), BOD, COD and nonbiodegradable substances must be addressed in the primary treatment stage.

Therefore, advanced treatment processes are required to improve the quality of the treated wastewater up to reuse criteria (Feng, Xu, Li, You, & Zhen, 2010). Many treatment methods for textile wastewater have been investigated, including: (1) treatment using lime and alum. This method generates large quantities of hazardous sludge and is generally ineffective in removing colour, TSS, BOD and COD; (2) biological treatment with aeration to reduce BOD and COD levels; (3) chlorination that successfully removes colour (e.g., as sodium hypochloride [NaOC])-based attack of dye molecule amino bonds). Although this method reduces BOD and COD, it produces chloro-organic compounds that are potentially carcinogenic and therefore not eco-friendly; (4) ozonation with or without ultraviolet irradiation; and (5) sorption using H_2O_2—Fe(II) salt and cucurbituril. Other methods include adsorption (e.g., via activated carbon, peat, wood chips, fly ash and silica gels), ion exchange (for cationic and anionic dyes), irradiation electron beams (combined with oxygenation) and electrokinetic coagulation (using added ferrous sulphate or ferric chloride); see (Robinson, Mcmullan, Marchant, & Nigam, 2001) for a review of chemical and physical treatments.

Because of their complex chemical structure, dyes are generally resistant to fading on exposure to light, water and many chemicals. When decolourization of water polluted with organic colorants occurs, it takes place by reduction of $-C{=}C-$ and $-N{=}N-$ bonds and heterocyclic/aromatic rings (Slokar & Le Marechal, 1998). The azo ($-N{=}N-$) bonds (as well as sulfonic ($-SO_3$) groups) are electron-withdrawing groups and this generates electron deficiency within the molecule, making the compound less susceptible to oxidative catabolism by bacteria (You & Teng, 2009).

Consequently decolouration of textile dye effluent is not normally observed when the textile wastewater is treated aerobically by municipal sewerage systems (Chang et al., 2001; Pandey et al., 2007; Żyłła et al., 2006). Therefore anaerobic systems have been used to cleave azo bonds in the treatment of textile wastewater (Dos Santos, Cervantes, & Van Lier, 2007; O'neill, Hawkes, Hawkes, Esteves, & Wilcox, 1999), and many bacterial groups possess enzymes (i.e., azo-reductases) capable of disrupting the azo bonds under anaerobic conditions (Żyłła et al., 2006). The anaerobic degradation product is colourless aromatic amines that are carcinogenic, but these aromatic amines can then be readily degraded via aerobic digestion by nonspecific enzymes through hydroxylation and ring opening of the aromatic compounds (Sponza & Işik, 2005). Mineralization of the azo dyes is complete when the aromatic amines have been biodegraded to carbon dioxide (CO_2), water (H_2O), and ammonia (NH_3) (Sponza & Işik, 2005; Van Der Zee & Villaverde, 2005). Thus, for complete mineralization of azo dyes, a combination of reductive (anaerobic) and oxidative (aerobic) steps are required (Dafale et al., 2010; Kodam & Gawai, 2006; Kodam, Soojhawon, Lokhande, & Gawai, 2005).

Recently membrane bioreactor (MBR) technology has attracted interest for wastewater treatment (Badani, Ait-Amar, Si-Salah, Brik, & Fuchs, 2005; Banat et al., 1996; Brik, Schoeberl, Chamam, Braun, & Fuchs, 2006; Pierce, Lloyd, & Guthrie, 2003). Conventional MBR is operated at aerobic conditions and therefore is not suitable for dye degradation. However, anoxic or anaerobic MBR for dye wastewater treatment has been investigated and shows some potential; for a review on MBR-based textile wastewater treatment, see Simonic (2013). However, it has also been reported that the anoxic phase or low dissolved oxygen (DO) conditions ($DO < 0.3$ mg/l) have a negative effect on membrane permeability in the MBR process because low oxygen concentration leads to poorer flocculated activated sludge (Kang & Lee, 2004). Also, biofouling is a major issue of concern in MBR processes because colony buildup on the membrane surface decreases water permeability (Lewandowski, 2004).

A physical method gaining increasing general interest for wastewater treatment is direct membrane separation because this can be used to recycle valuable components (and energy) as well as lower overall operating costs by lowering the volume of wastewater to be delivered to the wastewater treatment plant. Membrane techniques, characterized by their ability to clarify, concentrate and continuously separate, are therefore potentially interesting for textile wastewater effluent treatment including potential recycling of dyes.

17.3.1 Membrane filtration in textile wastewater treatment

Processes using membranes provide possibilities for separating hydrolysed dyestuffs and auxiliaries, thus simultaneously reducing coloration. Over the past few years, technical and economical improvements have made treatment of wastewater by membrane systems increasingly advantageous over conventional treatment processes (Porter, 1999; Rozzi et al., 1999; Sojka-Ledakowicz, Koprowski, Machnowski, & Knudsen, 1998). The most notable outcome of the membrane treatment is the superior quality of the produced water, which is attained by adding fewer chemicals, over conventional water treatment processes. In addition, membrane plants can be much smaller than conventional wastewater treatment plants because of the modular configuration of the membranes and the possible elimination of other processes (e.g., clarification). Traditional membrane processes studied in textile wastewater treatment include the use of ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) membranes in which the selection of membrane technologies for textile effluent relies on costs based on the balance between water flux and solute retention.

Ultrafiltration membranes have been successfully applied in many industries, but they have not been as widely accepted by the textile industry because they do not remove low-molecular-weight dyes. There are examples of micelle-enhanced use of UF membranes for dye removal (Ahmad & Puasa, 2007; Zaghbani, Hafiane, & Dhahbi, 2007), but in general the rejection range from 30% to 90% makes the direct use of UF membranes impossible and further filtration is required by either RO or NF membranes. In RO, problems with fouling are present that result in low fluxes owing to the dense polymeric membrane used and poor separation. Reverse osmosis also becomes less effective when osmotic pressure, caused by high salt concentration in the feed wastewater, becomes too high to obtain a reasonable transmembrane permeate flux without applying excess transmembrane hydraulic pressure. In this situation NF provides a possible alternative, maintaining high dye rejections albeit with the cost of lower rejection of electrolytes.

Nanofiltration membranes have been used to recover salt from used dyeing baths (Erswell, Brouchaert, & Buckley, 1988; Gonzálvez-Zafrilla, Sanz-Escribano, Lora-García, & León Hidalgo, 2008; Petrinic, Andersen, ŠOstar-Turk, & Le Marechal, 2007; He et al., 2009; Koyuncu, 2003; Koyuncu, Kural, & Topacik, 2001), where the principle is that electrolytes will pass through the membrane as the dyes are rejected. However, this principle requires the use of sufficiently small electrolytes. For example Na_2SO_4, which often is used as electrolyte, is rejected by the NF membrane, limiting the feasibility of this approach. Also standard electrolytes (such as NaCl) are not high-value products. An NF process for the treatment of mixed waste streams from the reactive dyeing process has been developed using this principle (Rautenbach & Mellies, 1994) in which the retentate is further treated in a wet oxidation process. The effective desalination of the retentate by the NF membrane is desired because this diminishes electrolyte corrosion in the wet oxidation. Nanofiltration-based dye retention can be effective and retentions up to 99% with a permeate flux of 64 l/m^2 h have been obtained (Tegtmeyer, 1993).

Reverse osmosis membranes have also been used in textile wastewater treatment (Suksaroj, Héran, Allègre, & Persin, 2005). One example of this used a combination of RO membranes designed for brackish and seawater desalination (Treffry-Goatley, Buckley, & Groves, 1983). Thus, the brackish water RO membrane is used in the first stage and the seawater RO membrane is used in the second stage. In this way the retentate is recycled in the second stage to obtain high water recovery and the cross-flow velocity is kept high to minimise membrane fouling. Using this two-stage RO process, water recovery is 85–95% with a mean permeate flux of 15 l/m^2 h.

In a comparative study (Bonomo, 1992), pilot plant tests with UF, NF and RO treatment of wastewater from washing processes subsequent to reactive dyeing processes are described. Ultrafiltration membrane treatment leaves the permeate stream colourized whereas NF membrane treatment results in efficient permeate decolourization with a flux of 70 l/m^2 h at 10 bar. The RO membrane both decolourizes and desalinates the waste stream. Interestingly, the reactive dyes retention was somewhat lower than in the NF process despite the use of the denser RO membrane. Severe membrane fouling was observed when the waste stream contained dispersed dyes together with reactive dyes, which illustrates the important issue of membrane fouling when treating complex wastewaters.

To elucidate fouling effects, synthetic waste streams mimicking actual waste streams can be analysed (Fritsch, 1993). This approach would in principle make it possible to relate the permeate flux decline to certain components or a combination of component presents in the actual waste stream. One could thus make a list of no-go components in dyeing and washing if the resulting wastewater is to be treated efficiently by membrane filtration processes. In general, pressure-driven processes such as UF, NF and RO are all prone to fouling typically caused by the presence of natural organic matter (NOM) (Li & Elimelech, 2004) and biofouling (Vrouwenvelder & Van Der Kooij, 2001). With textile wastewater as a membrane feed stream this issue becomes particularly important and it is therefore necessary to address this issue. This can be done in principle by making no-go list of components (i.e., components with strong fouling propensity). Another more general strategy is to consider alternatives to pressure-driven processes.

17.3.2 Osmotic-based wastewater reduction and potential dye recovery

In contrast to pressure-driven processes, FO is less prone to fouling and FO-based systems are attracting increasing interest in water treatment/engineering applications for a wide variety of aqueous solutions (Achilli, Cath, Marchand, & Childress, 2009; Cath, Childress, & Elimelech, 2006; Coday, Yaffe, Xu, & Cath, 2014; Cornelissen et al., 2008; Holloway, Childress, Dennett, & Cath, 2007; Klaysom, Cath, Depuydt, & Vankelecom, 2013; Teoh et al., 2008). Thus, FO has been used to treat industrial wastewaters (at bench-scale), to concentrate landfill leachate at pilot- and full-scale

(Beaudry, Herron, & Peterson, 1999; York & Beaudry, 1999) and to treat liquid foods in the food industry at bench-scale (Dova, Petrotos, & Lazarides, 2007a,b; Petrotos, Lazarides, Wolf, Behsnilian, & Spiess, 2001). Forward osmosis is also being evaluated for reclaiming wastewater for potable reuse in life support systems (at demonstration-scale), for desalinating seawater and for purifying water in emergency relief situations; for a detailed review, see Cath et al. (2006). Although, no scientific reports on direct FO in the textile wastewater treatment have appeared so far, Catalyx Inc of Anaheim, California, have reported an FO-based system for recycling difficult-to-treat, high-BOD and high-COD carpet-dyeing wastewater (Atkinson, 2009). Thus, the FO technology can be seen as an addition to existing membrane processes such as UF, NF and RO, which are commonly used in textile wastewater treatment today.

For FO, there is no hydraulic pressure across the membrane. For RO, the applied hydraulic pressure must exceed the osmotic pressure and convectively drive the water from low to high water chemical potential. For pressure-assisted osmosis (PAO) hydraulic pressure is applied in the same direction as the water flow. For PRO, the hydraulic pressure retards the FO process but the effective hydraulic pressure is still less than the osmotic pressure. In all cases the osmotic pressure difference across the membrane can be approximated as the difference in osmotic pressure of each solution. In ideal solutions the osmotic pressure π can be determined from the Morse equation: $\pi = \mathrm{iMRT}$, where i is the van't Hoff factor, M is the molarity, R is the gas constant and T is temperature. Figure 17.1 schematically shows the four processes: FO, RO, PAO and PRO.

Forward osmosis operates by concentrating a feed solution (FS) and diluting a highly concentrated aqueous solution – the draw solution (DS). The larger osmotic pressure of the DS compared with the FS constitutes the driving force for the separation process. Thus, FO is an osmotic concentration process that in principle can operate at zero hydrostatic pressure, providing a sustainable water treatment solution.

Forward osmosis is not implemented on a large scale for several reasons. There are at least three 'must-win' battles to successfully overcome before FO becomes a large-scale technology comparable with established technologies such as RO. First, a new type of membrane is needed that has to be very thin to minimise internal concentration polarization (Klaysom et al., 2013). Second, good DSs are needed; the most studied currently are ammonium bicarbonate–based DSs (Mccutcheon, Mcginnis, & Elimelech, 2006) and their use poses several problems including unfavourable interactions with known (conventional) membrane materials. Third, a new system solution, an FO membrane, cannot simply replace an RO membrane in conventional membrane modules (Gruber et al., 2011, 2012). Until good FO membranes and DSs are available for major industrial applications, no system provider is likely to begin designing new FO-based systems.

Recently a cellulose triacetate (CTA) FO membrane with an embedded support screen stabilizing a dense rejection layer (10–20 μm thick) and thin-film composite (TFC) membranes were commercialized by Hydration Technologies Inc (HTI). So far, the use of these membranes has focused on low-volume nutrient drink production (Salter, 2006). Thus, a concentrated nutrient solution with a high osmotic pressure is used as DS where unsafe water as FS is purified through the FO membrane with a salt

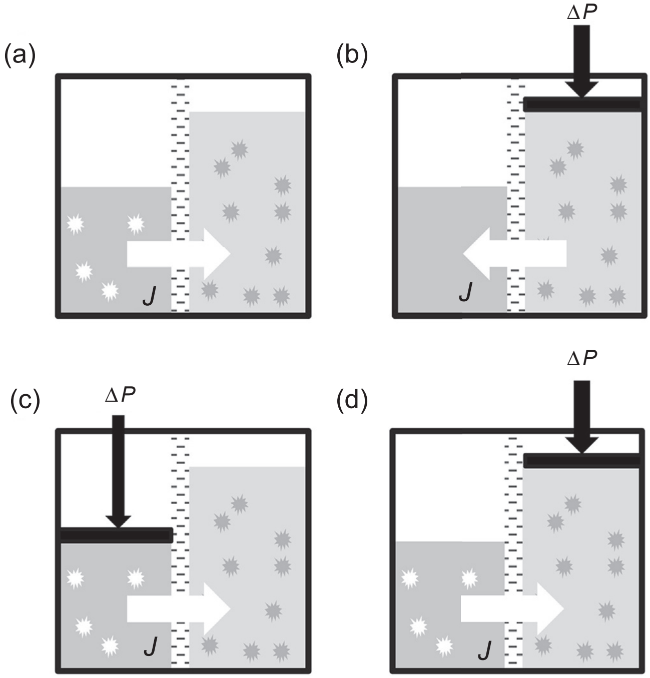

Figure 17.1 Osmotic processes. Water flux (J) versus hydraulic pressure (ΔP) in (a) forward osmosis (FO), (b) reverse osmosis (RO), (c) pressure-assisted osmosis (PAO) and (d) pressure-retarded osmosis (PRO).

rejection between 93% and 95%. However, when operated in a high-volume application setup, the HTI CTA membrane water flux is still low (< 6 l/m^2 h) although the HTI TFC membrane seemingly has a flux that is double that of the HTI CTA membrane. In comparison, for RO membranes water fluxes can reach 75 l/m^2 h although typical values are around 30 l/m^2 h (Xu, Peng, Tang, Shiang Fu, & Nie, 2010). However, water flux and solute retention have to be evaluated together when evaluating membrane performance.

One way to increase water flux across the membrane while preserving rejection of solutes is to enable facilitated water diffusion across the active layer. This has been studied intensively over the last few years where in particular the use of nature's own selective water channels – aquaporin proteins – have attracted considerable interest; for a review, see Tang, Zhao, Wang, Hélix-Nielsen and Fane (2013) and for a general review of the biomimetic approach to membrane technology, see Nielsen (2009). Aquaporins constitute a large family of membrane spanning proteins; for reviews, see Fu and Lu (2007), Gonen and Walz (2006) and Ludewig and Dynowski (2009). Much has been revealed about this class of proteins since the purification of a red blood cell membrane protein and subsequent heterologous expression of this protein revealing rapid water diffusion along osmotic gradients.

Recently, a design was developed in which vesicles are embedded in thin (200 nm) films deposited on a porous support (Zhao et al., 2012). Briefly, a microporous polysulfone substrate was soaked with an *m*-phenylene-diamine aqueous solution that contained aquaporin vesicles. The soaked substrate was subsequently exposed to trimesoyl chloride to form a three-dimensionally cross-linked polyamide layer in which the aquaporin vesicles are embedded. The resulting membranes are made in sheets up to 600 cm^2 and are sufficiently stable to allow normal handling and shipping procedures.

The resulting TFC membrane has been characterized in cross-flow RO and FO setups. Reverse osmosis membranes were tested under applied pressures up to 14 bar and benchmarked against commercially available RO membranes (Zhao et al., 2012). Compared with the control membranes (membranes with protein-free vesicles and membranes with protein vesicles in which the protein was mutated to an inactive form), the aquaporin TFC membranes achieved significantly higher water permeability ($\sim$4 l/m^2 h bar) with comparable NaCl rejection ($\sim$97%). Their permeability was $\sim$40% higher compared with a commercial brackish water RO membrane (Dow Filmtec BW30) and an order of magnitude higher compared with a seawater RO membrane (Dow Filmtec SW30HR). In FO the aquaporin membranes had greater than 90% rejection of urea with a water flux of 10 l/m^2 h with 2 M NaCl as draw solution. This clearly demonstrates the great potential of the aquaporin TFC membranes for industrial RO and FO applications; in 2014 the Danish Cleantech company Aquaporin A/S began commercializing membranes as aquaporin inside membranes (AIM™) based on this design.

Whether the FO membranes are to be used for wastewater volume reduction and/or recovery of dyes, a key question is whether the reactive dyes can be processed by the membranes. A simple test for this is to try and up-concentrate dyes using an FO membrane process. Because Nylosan dyes are acid dyes applicable for polyamide, we tested whether this class of dye can be processed using the aquaporin polyamide TFC design as described, without damaging the membrane.

Specifically we tested two different dyes, Nylosan Blue E-GL250 and Nylosan Red E-BL18, for up-concentration assays with FO AIM™ provided by Aquaporin A/S (see Figure 17.2). Fifty milligrams of the blue dye is solved in 100 ml milliQ water to generate a stock solution of 500 μm/ml. The stock solution is then diluted to encompass a dilution series from 200 to 5 μg/ml. A broad range wavelength scan from 200 to 800 nm is used to detect the optimal absorbing wavelength for the dye (620 nm for Nylosan Blue E-GL250 and 513 nm for Nylosan Red E-BL18). The optical density (OD) value is measured for the different concentrations and standard curves are plotted relating the OD value to the concentration.

Because of the osmotic gradient over the membrane, water from the dye solution will be extracted through the AIM membrane, resulting in up-concentration of the dye. The OD is then measured for the up-concentrated dye solution and the concentration is calculated from the standard curves. In a successful up-concentration experiment the up-concentration factor of the dye solution (light grey bars) follows the volume reduction factor (dark grey bars). In none of the experiments was dye detected in the draw solution. The results are summarized in Figure 17.2.

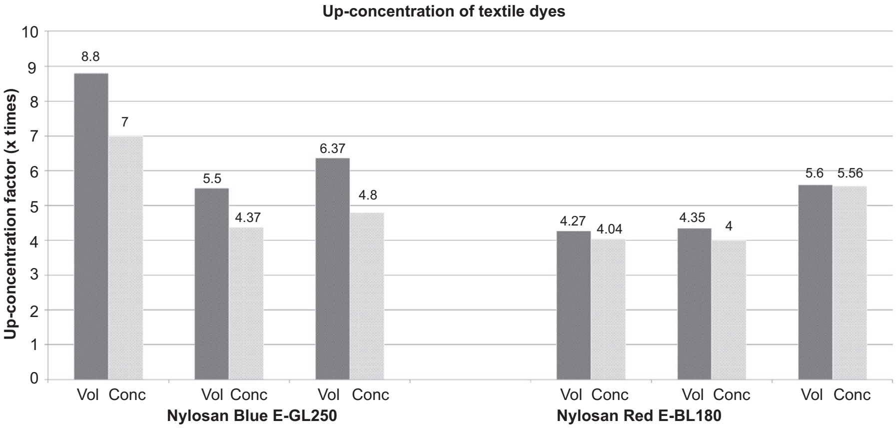

Figure 17.2 Experimental results for up-concentration of Nylosan Blue E-GL and Nylosan Red E-BL (n = 3 for each dye) with starting concentrations of 10 and 20 μg/ml, respectively. The up-concentration assay is carried with an FO membrane module. The dye solution to be up-concentrated is placed in the reservoir well of the upper part of the module while on the bottom part an osmotic draw solution (here, 1 M NaCl) is recirculated. The module is connected to a peristaltic pump by tubing to ensure the recirculation of the draw solution at 50 ml/min. The volume concentration factor (Vol) and concentration factor for the dye (Conc) reflect volume reduction and dye up-concentration factor, respectively.

17.4 Conclusions

In general, wastewater represents challenging feed streams to be treated by membrane separation. In particular, the large variability in composition and the presence of potentially reactive components makes textile industry wastewater a particularly difficult task for any remediation technology including membrane-based methods. To date, membrane technology for textile wastewater has been based on RO/NF/UF-based systems. Also, MBR technology has attracted considerable interest; however, the requirements for low oxygen and the general issue of biofouling present problems for bioreactors to function properly. Also, the large variation in water composition – even from the same textile process and plant – is a major obstacle in introducing MBR in textile wastewater treatment. Recent technological developments of FO membranes have opened up the possibility of using this technology in industrial processes and wastewater treatment. The inherent low fouling propensity of FO membranes makes them an intriguing supplement to existing remediation methods. Thus, FO can in principle be used to concentrate the wastewater – e.g., using seawater as a draw solution – thereby reducing the hydraulic load on the wastewater treatment plant – with diluted seawater being the discharged water stream. Forward osmosis may also be used in up-concentration of dyes directly, as exemplified by biomimetic aquaporin-based FO membranes.

List of abbreviations

AIM	Aquaporin inside membrane
BOD	Biological oxygen demand
CMC	Carboxymethyl cellulose
COD	Chemical oxygen demand
CTA	Cellulose triacetate
DO	Dissolved oxygen
DS	Draw solution
FO	Forward osmosis
FS	Feed solution
MBR	Membrane bioreactor
MPD	m-phenylene-diamine
NF	Nanofiltration
NOM	Natural organic matter
OD	Optical density
PAO	Pressure-assisted osmosis
PRO	Pressure-retarded osmosis
PVA	Polyvinyl alcohol
RO	Reverse osmosis
TFC	Thin-film composite
TMC	Trimesoyl chloride
TSS	Total suspended solids
UF	Ultrafiltration

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Membrane technologies for water treatment and reuse in the food and beverage industries

18

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18.1 Introduction

Water, raw materials, and energy are key resources used in the food-processing industry. In particular, water is used as ingredient, cleaning source, and conveyor of raw materials, and to sanitize plant machinery and areas. Subsequently, effluents from many agro-food industries are a hazard to the environment and require appropriate management approaches.

Wastewaters generated by different branches of the agro-food industry can be divided into two classes (on the basis of plant or animal origin) and seven subclasses (Table 18.1).

The characteristics and volume of these effluents vary with the products and production procedures. Typically, they contain macropollutants such as chemical oxygen demand (COD), biochemical oxygen demand (BOD), total suspended solids (TSS), fats, oils, and nutrients (nitrogen and phosphorous). In addition, some micropollutants including hormones, surfactants, antibiotics, and pesticides can be present. However, it is often difficult to predict the composition of food waste because of the seasonal nature of food processing and post-harvesting.

The main parameters of typical food waste are given in Table 18.2. On the basis of their composition, effluents from many agro-food industries produce negative effects when disposed into the environment and require appropriate management approaches. Consequently, extensive research has been devoted to coping with waste generated by agro-industries.

Technological innovations, including those in clean technologies and processes, aim to introduce into food-processing factories advanced wastewater treatment practices able to recycle spent process waters onsite and to reduce the amount of wastewater discharged into municipal sewage treatment plants. Another target of great interest is the reduction of water and wastewater from the manufacturing process (closed-loop/zero emission systems) and the reuse of treated waters in the food-processing industry.

In addition, food waste contains high—added value compounds (i.e., phenols, carotenoids, pectin, hemicelluloses, oligopeptides, lactose, proteins) that can be recovered

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Table 18.1 **Food waste and its origins**

Source	Waste origin	Type of waste
Plant	Cereals	Rice bran, wheat middling, wheat straw, wheat bran, oat mill waste, malt dust, brewery's spent grains
	Root and tubers	Potato peel, sugar beet molasses
	Oil crops and pulses	Sunflower seed, soybean oil waste, soybean wastewaters, olive pomace, olive mill wastewater
	Fruit and vegetables	Citrus peel, apple pomace, apple skin, peach pomace, apricot kernel, grape pomace, grape skin, wine lees, banana peel, tomato pomace, tomato skin
Animal	Meat products	Chicken by-products, slaughterhouse by-products, beef lung, bovine blood
	Fish and seafood	Fish leftovers, shrimp and crab shells, *surimi* wastewater
	Dairy products	Cheese whey

Source: Adapted from Galanakis (2012).

and recycled inside the food chain as functional additives in different products. To this purpose, conventional and emerging technologies offer interesting perspectives, taking into account the huge amounts of food-related materials discharged worldwide (Galanakis, 2012).

Conventional technologies for the treatment of food-processing wastewaters include: (1) physical and chemicophysical processes to remove suspended solids (screening systems, sedimentation, and dissolved air flotation); (2) biological treatment processes (anaerobic treatments, activated sludge processes, aerated lagoons, and land application) aimed at removing soluble pollutants; and (3) tertiary treatments including membrane processes or other chemicophysical processes such as precipitation, activated carbon, and chelation for the removal of specific pollutants or for improving water parameters (Bolzonella & Cecchi, 2007).

Membrane filtration processes offer interesting perspectives and key advantages over conventional technologies in the treatment of wastewaters from food-processing industries.

They can be combined with activated sludge processes to form membrane bioreactors (MBRs) to improve the capability of removing pollutants in biological treatment processes (Stephenson, Brindle, Judd, & Jefferson, 2000). In addition, pressure-driven membrane operations such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) can be used to treat high-strength wastewaters or at the end of conventional treatment systems to produce purified water for recycling or reuse and to recover valuable compounds (Moresi & Lo Presti, 2003; Muro, Riera, & del Carmen Diaz, 2012).

Table 18.2 Characteristics of agro-food wastewater

Industry	BOD (mg/L)	COD (mg/L)	TSS (mg/L)	Total phosphorus (mg/L)	Total nitrogen (mg/L)	References
Fruit juice	1580	3650	–	2.4	12	Noronha, Britz, Mavrov, Janke, and Chmiel (2002)
Fish and seafood				–	–	Cros, Lignot, Jaouen, and Bourseau (2006)
Fish trade activities	400–2200	500–4500	3–35	–	–	Vandanjon, Cros, Jaouen, Quéméneur, and Bourseau (2002)
Shrimp processing—thawing	650	1000	2	–	–	Walha et al. (2011)
Shrimp processing—cooking	2000–10,000	3000–20,000	200–1200	–	–	
Shrimp processing—rinsing	650	1300	7	–	–	

Continued

Table 18.2 Continued

Industry	BOD (mg/L)	COD (mg/L)	TSS (mg/L)	Total phosphorus (mg/L)	Total nitrogen (mg/L)	References
Tuna cooking juice	–	23,500	2100			
Food and beverage	–	1800–6600	1000–7300	–	–	Chmiel, Kaschek, Blöcher, Noronha, and Mavrov (2002) and Blöcher et al. (2002)
Food	680	880	2480	–	–	Katayon et al., 2004
Dairy	800–1000	1400–2500	1100–1600	–	–	Gotmare, Dhoble, and Pittule (2011)
Dairy	650–6250	400–15,500	250–2750	–	10–90	Passeggi, Lopez, and Borzacconi (2009)

Dairy	–	380–38,500	31–796	–	–	Vourch, Balannec, Chaufer, and Dorange (2008)
Poultry processing		858	1173	–	–	Lo, Cao, Argin-Soysal, Wang, & Hahm, (2005)
Winery						Valderrama et al. (2012)
Harvesting		13,448	1230	39.5	34.0	
Harvesting and vinasse	–	3887	662	6.5	–	
Vinasse	–	3400	271	7.5	41	
Process	–	2323	178	5.0	40.0	
Winery	–	4728	320	35	60	Bolzonella, Fatone, Pavan, and Cecchi (2010)
Steamed soybean wastewater	–	8400–8700	14,500–15,300	–	–	Matsubara, Iwasaki, Nakajima, Nabetani, and Nakao (1996)

This chapter gives an overview of membrane-based processes for water reuse and environmental control in the treatment of wastewaters from food-processing industries. Applications involving the use of pressure-driven membrane operations, electrodialysis (ED), and MBRs as well as a combination of membrane operations in hybrid systems in the treatment of waste from different agro-food productions are analyzed and discussed.

18.2 Wastewaters from food and beverage industry

In the food and beverage industries, exhausted waters generated from different operations (fruit processing, cleaning of tanks and pipes, and bottle washing) are mixed together before they are discharged into municipal sewage systems.

These wastewaters can be defined as high-strength wastewaters because of their high COD values and high content of biodegradable compounds such as nitrogen or phosphorous elements. They can be discharged into the environment after specific treatments to reduce polluting compounds according to standards defined by environment regulations.

The use of MBRs is a promising technology in treating high-strength wastewaters as an alternative to conventional activated sludge treatment. Fundamentals, configurations, and typical applications of MBR systems are analyzed and discussed in Chapter 6. As highlighted in this chapter, the best performance of MBR can be produced through optimizing operating parameters such as hydraulic retention time, solid retention time (SRT), mixed liquor suspended solids (MLSS), and transmembrane pressure (TMP). Pretreatment systems, physical and chemical cleaning, and biofouling reducers such as powdered activated carbon are all systems that can be used to reduce fouling phenomena, thus enhancing MBR performance (Katayon et al., 2004; Mutamim, Noor, Abu Hassan, & Olsson, 2012).

A hybrid process for the production of drinking water from spent process waters of fruit juice companies was developed by Blöcher et al. (2002) on an industrial scale after preliminary studies on a pilot scale (Noronha, Britz, Mavrov, Janke, & Chmiel, 2002). Spent waters from small and medium-sized enterprises were mixed in an equalization tank and clarified through a lamella clarifier to remove most solids. The clarified effluent was treated in an MBR equipped with immersed tubular MF membranes (pore size, 0.04 μm) in which the active biomass and other particulate matter were completely retained. Although the organic loading rate of the spent water varied widely (between 1800 and 6600 mg/L), COD and total organic carbon (TOC) were reduced by at least of 96% in this first step.

The MF permeate was then submitted to a two-step NF process with integrated ultraviolet (UV) disinfection. The first NF step was operated with spiral-wound membrane modules characterized by low rejection for sodium chloride (on average 55%), ensuring a reduction of dissolved organics up to 97%. The second filtration step was carried out using NF membrane modules with a rejection rate for sodium chloride higher than 90%. These membranes operated as desalting membranes with a low fouling index, reducing the salinity of the spent liquor more than 75%. The final COD of the treated water was below the detection limit and TOC did not exceed the limit value of 4 mg/L. Chemical and microbiological parameters of the final permeate were within the water quality standard of the German Drinking Water Act. The proposed process is illustrated in Figure 18.1. For a plant capacity of 5 m^3/h, the overall treatment cost for producing drinking water from spent process water was estimated to be about 2.5−3.0 €/m^3.

The presence of oils and fats in spent process waters generated in margarine production creates several problems when these waters are submitted to biological treatment (i.e., high costs for aeration and sludge disposal, flotation, and coating in the treatment plant and saponification of fats in the equalization tank). Treatment of these effluents with 0.2-μm ceramic MF membranes reduced the initial COD of 5000−10,000 mg/L below 250 mg/L. The produced permeate could be mixed with water of low and medium contamination and then submitted to biological treatment. A concentrated product was recovered from the MF retentate and reused for soap production after a skimming oil treatment (Chmiel, Kaschek, Blöcher, Noronha, & Mavrov, 2002).

The Kubota submerged anaerobic membrane biological reactor process, developed in the past decade by Kubota Membrane Technology (Hyogo, Japan), is an interesting application of anaerobic MBRs in food-processing factories. The process, also described in Chapter 6, consists of a solubilization tank and a mesophilic or thermophilic tank equipped with submerged membranes. These membranes retain methanogenic bacteria while methane fermentation inhibitors such as ammonia are allowed to pass in the permeate stream. The generated biogas can be used to heat water via boilers. Permeate and sludge can be further treated in aerobic treatment facilities (Kanai, Ferre, Wakahara, Yamamoto, & Moro, 2010). The process has been successfully implemented in food factory treatment plants, stillage treatment plants for *Shouchu* (a Japanese spirit made from sweet potato), and potato-processing sites.

Ng, Lin, Panchangam, Hong, and Yang (2011) compared the performance of a novel bio-entrapped membrane reactor (BEMR) packed with bio-ball carriers with that of a conventional MBR in the treatment of wastewater from a food and beverage−processing plant. The new reactor exhibited a longer SRT and lower MLSS compared with the conventional system. The BEMR produced also fewer soluble microbial products than the conventional system (34−48% less protein and 16−29% less carbohydrate) owing to slow-growing microorganisms with long SRT. Finally, the new BEMR was able to operate at a constant permeate flux requiring less frequent chemical cleanings, with consequent economic benefits.

The technical feasibility of recovering and concentrating tartaric acid by ED from fruit juice processing wastewater was assessed by Andrés, Riera, and Alvarez (1997). In particular, the ED treatment of synthetic solutions simulating ionic exchange regeneration waters obtained in grape juice processing increased five times the initial ion tartrate concentration (from 1 to 10 kg/m^3 up to 53.2 kg/m^3). The energy consumption was estimated to be about 5×10^3 kJ/kg tartaric acid. The purified acid can be reused for food and pharmaceutical applications.

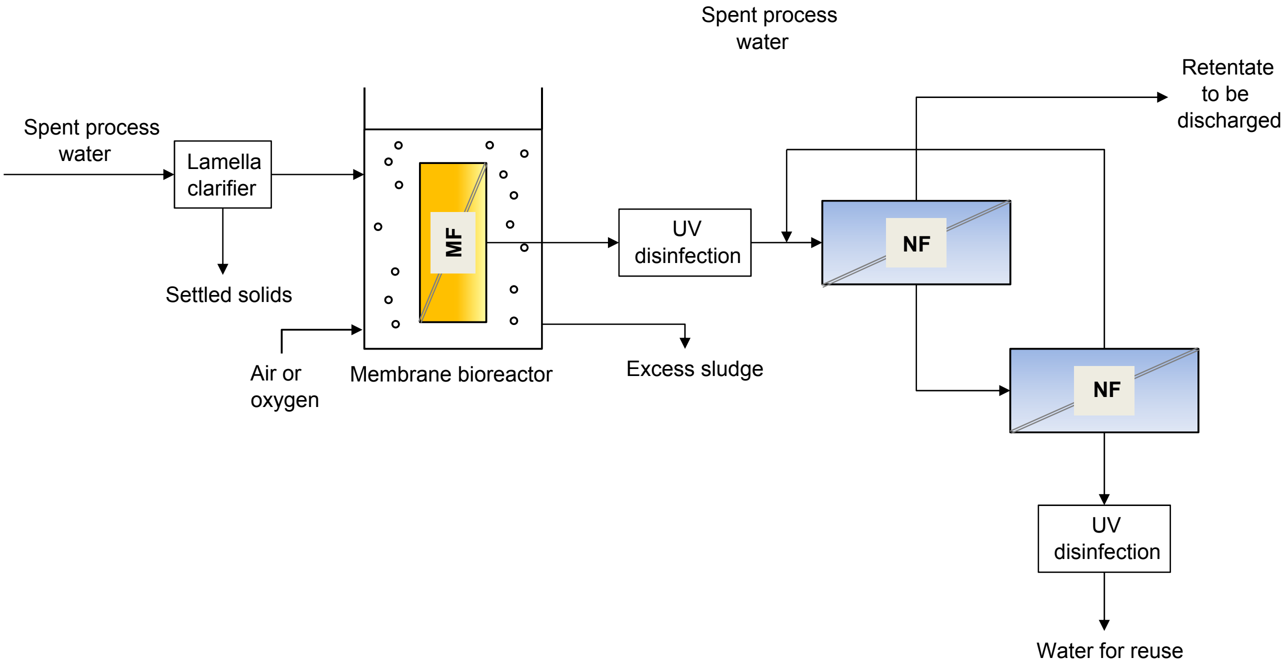


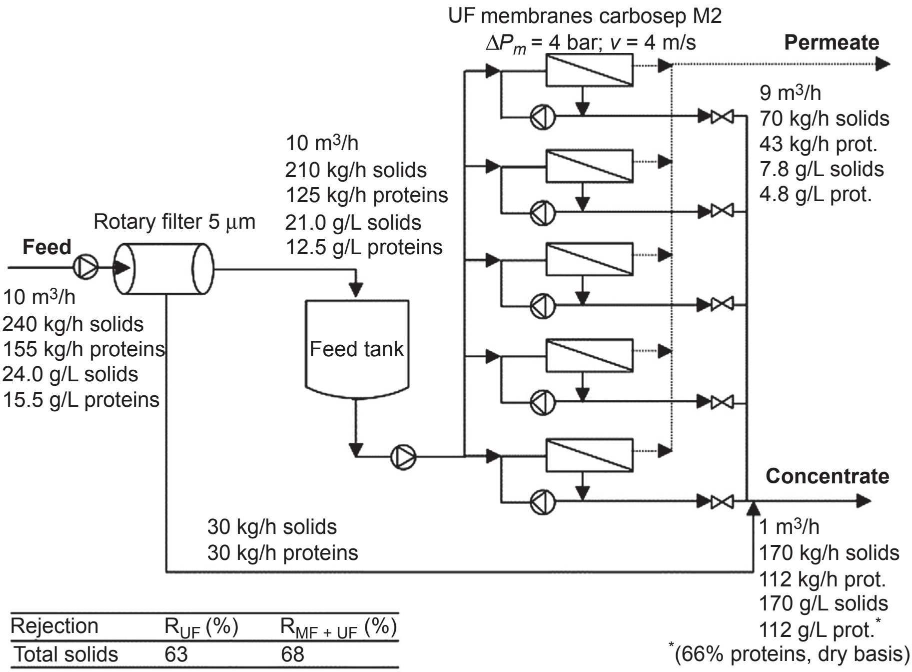
Figure 18.1 Flow diagram of integrated membrane process for the recycling of spent process water from the food and beverage industries. Adapted from Noronha et al. (2002).

18.3 Wastewaters from fish and seafood industry

The fish-processing industry produces several effluents (i.e., wastewater generated during fishmeal production and wastewater generated by washing, thawing, rinsing, and cooking treatments) exhibiting different characteristics. The polluting load and the flow rates of these effluents vary greatly according to the activity. The COD and salt content are in the range of 7–49 and 0.25–10 g/L, respectively. Although these wastewaters contain no toxic materials, they cannot be released into the environment; therefore, depolluting treatments are needed in municipal or private treatment plants. In addition, fish industry wastewater contains potentially valuable molecules for the food sector, such as proteins, flavor and aroma compounds, and *n*-3 polyunsaturated fatty acids, whose recovery can lead to appreciable productivity gains (Massé et al., 2008).

Membrane technology has great potential for the treatment of fish-processing effluents. In particular, key advantages of membrane processes over conventional technologies, such as coagulation/flocculation and dissolved air flotation, concern the production of good-quality permeate streams that can be disposed directly into the sea or recycled into the plant and the recovery of valuable compounds under mild conditions without using heat or chemicals. An extensive review of the application of pressure-driven membrane operations in the treatment of seafood-processing effluents was reported by Afonso and Bórquez (2002a). The authors also evaluated the performance of an integrated membrane process based on the use of MF and UF or NF to recover proteins from the effluents of a fishmeal plant. Microfiltration pretreatment reduced drastically the oil and grease content and the suspended matter, improving the performance of the subsequent membrane treatment. The selected UF ceramic membrane (Carbosep M2, tubular, 15 kDa molecular weight cutoff (MWCO)) reduced the organic load of the MF permeate and allowed the recovery of valuable raw materials including proteins. The protein rejection ranged from 49% to 62% depending on the operating conditions. A ceramic NF membrane (Kerasep NanoN01A, tubular, 1 kDa MWCO) produced a protein rejection of 66% when the MF permeate was processed. In both cases, the highest protein rejection was achieved at a TMP of 4 bar and a cross-flow velocity of 4 m/s (Afonso & Bórquez, 2002b; Afonso, Ferrer, & Bórquez, 2004). A conceptual process for the treatment of 10 m^3/h of fishmeal effluent based on the use of MF and UF membranes was designed (Figure 18.2). The plant would generate 1 m^3/h of concentrate containing 170 g/L of solids and 112 g/L of proteins. The economic assessment for the integrated MF–UF process yielded a net worth of US\$160 × 10^3, an interest rate of return of 17%, and 8 years' payback time, indicating the feasibility of the process for protein recovery and pollution reduction.

The UF treatment of fishery washing waters with polysulphone membranes of 20 kDa and a multichannel ceramic membrane of 0.1 μm produced similar apparent rejections (70% and 80%, respectively) toward proteins. The process increased the protein concentration in the feed solution from 5 to 35 g/dm^3 and reduced the BOD by about 80% (Mameri et al., 1996). Other applications related to the use of pressure-driven membrane operations in the treatment of wastewater from *surimi*



Rejection	R_{UF} (%)	R_{MF+UF} (%)
Total solids	63	68
Total proteins	62	69

Figure 18.2 Integrated membrane process for the treatment of fishmeal effluent. Reprinted from Afonso et al. (2004), with permission from Elsevier.

production (Huang & Morrissey, 1998), menhaden bail water (Abu, Rao, Khan, & Liuzzo, 1984), fish brine (Paulson, Wilson, & Spatz, 1984), and effluents discharged from fish plants (Chao, Asce, & Tojo, 1987) have been investigated.

An integrated process for the concentration of aroma compounds and the production of clean water from shrimp cooking juices was developed by Cros, Lignot, Jaouen, and Bourseau (2006). The process is based on a clarification step to remove suspended solids followed by a desalination step by ED and a final concentration step by RO (Figure 18.3). The pre-filtered juice (pore size, 500 μm) was treated by ED and consisted of 20 compartments alternating cation-exchange and anion-exchange membranes for a total surface area of 0.138 m^2. The RO unit was equipped with tubular polyethersulphone-polyamide membranes supplied by PCI (Beaupuy, France) with an effective membrane area of 0.033 m^2. The performance of both systems was evaluated for different juices containing from 20 to 200 g/L of organic matter and from 4 to 40 g/L of minerals. Experimental results showed that the integration of ED and RO seems technically and economically feasible. The payback time was evaluated as less than 3 years.

The size of the integrated process does not require a systematic evaluation of operating and capital costs; it can be evaluated by minimizing the total installed membrane surface area and energy consumption (Bourseau, Massé, Cros, Vandanjon, & Jaouen,

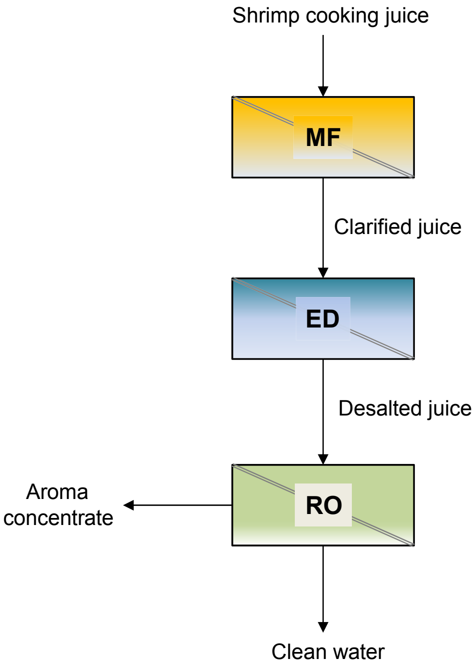


Figure 18.3 Integrated membrane process for the production of clear water and aroma concentrate from shrimp cooking juice.
Adapted from Cros et al. (2006).

2014). In the ED process the salt concentration can decrease from 20 to 2.8 g/L without changing the aromatic profile (Cros, Lignot, Bourseau, Jaouen, & Prost, 2005). However, a loss of volatile compounds under a critical salt concentration (2.3 g/L) was observed. This phenomenon was attributed to the salting-out of amino acids inducing a co-precipitation of hydrophobic aroma compounds and to the ionization of volatile compounds and water splitting in the presence of a low concentration of ionic species.

A desalination step before RO concentration is needed to avoid an increase in osmotic pressure in RO (RO membranes retain salt compounds), which limits the achievable extent of concentration. This will increase the production cost of aroma concentrates. The use of NF membranes overcomes these problems. The direct concentration of aroma compounds from tuna cooking juices with NF tubular membranes (AFC30, PCI Ltd, France) produced reasonable permeate fluxes (about 30 $L/m^2 \cdot h$) with retention factors of inorganic compounds between 70% and 76%. The aroma properties of the juice were slightly modified but the global characteristics of the juice remained unchanged. The MF pretreatment with ceramic multichannel membranes (Kerasep K01, Orelis) with a 0.1-μm pore size significantly improved NF permeation fluxes up to 90−100 L/m^2 h (Walha et al., 2011).

Integrated processes based on the use of UF as a pretreatment step followed by NF or RO for the concentration of aroma compounds from seafood cooking water were also investigated by Vandanjon, Cros, Jaouen, Quéméneur, and Bourseau (2002).

RO membranes were more efficient in retaining aroma compounds from shrimp and buckies cooking juices compared with 300-Da NF membranes, and also had higher removals of COD (95% for shrimp and buckies and 85% for tuna juices).

18.4 Wastewater from dairy industry

Among the food industries, the dairy industry is characterized by the production of huge quantities of polluted effluents (average of 0.2—10 L per liter of processed milk).

The pollution load of dairy industry wastewater can be defined by evaluating different parameters such as conductivity, pH, COD, TOC, TSS, and residual hardness (Gotmare, Dhoble, & Pittule, 2011; Passeggi, Lopez, & Borzacconi, 2009). Vapor condensates from evaporation and drying are considered to be low pollutant waters (Mavrov, Chmiel, & Bélières, 2001) whereas end-pipe wastewaters are highly polluted and require intense treatment to obtain clean water.

Membrane treatment of these wastewaters, including flushing water, white water, and whey, can give contribute greatly to reducing both total water consumption and the volume of produced wastewater. In addition, the recovery of valuable compounds such as whey proteins using membrane technology is of great economical interest considering their nutritional, biological, and functional properties.

NF and RO membranes have been shown to be useful for the concentration of milk constituents from raw wastewater and to simultaneously produce treated water that can be reused in the dairy industry (Koyuncu, Turan, Topacik, & Ates, 2000). The performance of NF and RO membranes in the treatment of diluted skimmed milk used as an effluent model solution (COD 36 g/L) was investigated by Balannec, Vourch, Rabiller-Baudry, and Chaufer (2005). Permeate flux and milk component rejections were evaluated in dead-end filtration experiments performed in selected operating conditions (25 °C and 14 bar for NF membranes, and 25 °C and 25 bar for RO membranes) up to a volume concentration ratio (VCR) of 3. Results of dead-end filtration experiments are summarized in Table 18.3. COD rejections were higher than 98.9% for all investigated membranes. Cross-flow experiments performed with NF and RO spiral-wound membranes produced similar results (Balannec, Gésan-Guiziou, Chaufer, Rabiller-Baudry, & Daufin, 2002). The quality of produced permeates did not meet the requirements of drinking water because of the high organic load of the effluent, which suggests the use of a two-step RO process or a single step with a low charged feed for the production of reusable water. Further studies performed by using model process waters through one-stage and two-stage (NF plus RO and RO plus RO) spiral-wound membrane (Desal 5 DL, Osmonics and TFC HR, Koch Membrane System) treatments indicated that after a single RO step or a combined NF plus RO process, the final permeate could be reused as a replacement for cleaning, heating, or cooling and for boiler feed water. More purified water with the typical requirements of drinking water can be produced by a two-stage RO process (Vourch, Balannec, Chaufer, & Dorange, 2005). Similar results were obtained when dairy wastewater was treated through a single RO stage. The process was carried out up to a recovery factor of 90—95% producing an average permeate flux of about 11 L/m^2 h (Vourch,

Table 18.3 **Performance of nanofiltration and reverse osmosis membranes in the treatment of model dairy effluent (initial COD, 36 g/L)**

Membrane process	Membrane type	Supplier	MWCO (kDa)	Membrane material	Initial permeate flux (L/m^2 h)	Permeate COD (mg/L)	R_{COD} (%)
NF	TFC S	Koch membrane systems		PA/PS/PE	6.3	1095	98.90
NF	Desal 5 DL	Osmonics	150–300	PA/PS	7.9	300	99.70
NF	Desal 5 DK	Osmonics	150–300	PA/PS	7.2	960	99.10
NF	NF45	FilmTec	200	PA/PS/PE	6.8	1055	99.00
NF	NF200	FilmTec	200	PA/PS/PE	7.0	173	99.80
RO	Desal 3 SF	Osmonics	–	PA/PS	7.1	45	99.96
RO	TFC HR	Koch membrane systems	–	Composite PA	6.7	54	99.95
RO	BW 30	FilmTec	–	Composite PA	6.9	120	99.88

MWCO, molecular weight cutoff; PA, polyamide; PS, polysulphone; PE, polyester.
Source: Adapted from Balannec et al. (2002).

Balannec, Chaufer, & Dorange, 2008). According to the proposed scale-up, a plant arranged with 18 spiral-wound, 8-inch elements (for a total membrane surface area of 540 m^2) permits the recovery of 95% of water from 100 m^3/d of treated wastewater.

Riera, Suárez, and Muro (2013) evaluated the effect of the main process parameters, such as pressure, temperature, and VCR, on the quality of permeate produced in a single-step NF treatment of flash cooler condensates from direct ultra−high temperature processing. The pilot plant was equipped with a spiral-wound membrane (SelRO MPS-34 2540 B2X, Koch Membrane Systems) with an MWCO of 200 Da. As a general trend, COD and TOC rejection increased by increasing the VCR (i.e., TOC rejection increased from 67.6% at VCR 3 to 82.1 at VCR 15). Low-molecular-weight compounds such as acetone, acetoine, and dimethylsulfide were partially retained by the NF membrane. Their increased rejection with VCR was attributed to the polarization concentration layer on the membrane surface.

In the investigated VCR values (between 1 and 15), average permeate fluxes between 100 and 110 L/m^2 h were measured (at a TMP of 23.7 bar and a temperature of 50 ± 1 °C). According to the experimental data, an NF plant with 20 m^3 h feed capacity and 87.5% water recovery was designed. The proposed plant was arranged with nine spiral-wound, 8-inch elements (total membrane area, 171 m^2) distributed in three series of feed and bleed loops (Figure 18.4). Savings and operating costs of the designed NF plant were estimated at 2.807 and 0.777 €/m^3, respectively. The thermal potential of permeate condensates suggested their reuse for heating purposes and in other miscellaneous services.

A process combination based on the use of NF membranes for the reuse of vapor condensate from milk processing was proposed by Chmiel, Mavrov, and Bélières (2000). The process involves pretreatment with cartridge filtration and UV disinfection followed by a two-stage NF process. The demonstration plant was designed to treat 1.5 m^3/h of feed and consisted of two membrane stages with spiral-wound membrane modules, each with a membrane area of 40 m^2. All of the parameters of the treated water met the requirements of drinking water (COD < 10 mg/L, TOC < 4 mg/L, and $Ca^{2+} < 0.4$ mg/L) as well as boiler makeup water.

Whey is a co-product of cheese making with a low content of solids (up to 5−6%) and a high BOD (30−50 g/L for 1,000 L of whey), which makes its disposal difficult and costly.

Conventional processes in whey treatment include thermal evaporation and drying. These processes are used to remove water from whey to diminish its volume but do not contribute to the recovery of valuable compounds. Anaerobic treatments are also used to remove organic compounds from whey. These processes are preferred over conventional aerobic treatments owing to the high COD of whey (about 60−80 g/L), which can produce biomass granulation during biological treatment. Other purification processes are based on the use of affinity chromatography, cation-exchange resins, and thermal precipitation (Pearce, 1983; Uchida, Sato, Kawasaki, & Dosako, 1996). However, these processes are not widely implemented on a large scale because of their complexity, poor selectivity, high cost, and low product degradation.

Whey processing is one of the most important applications in membrane technology in the dairy industry. Whey concentration, fractionation, demineralization, and

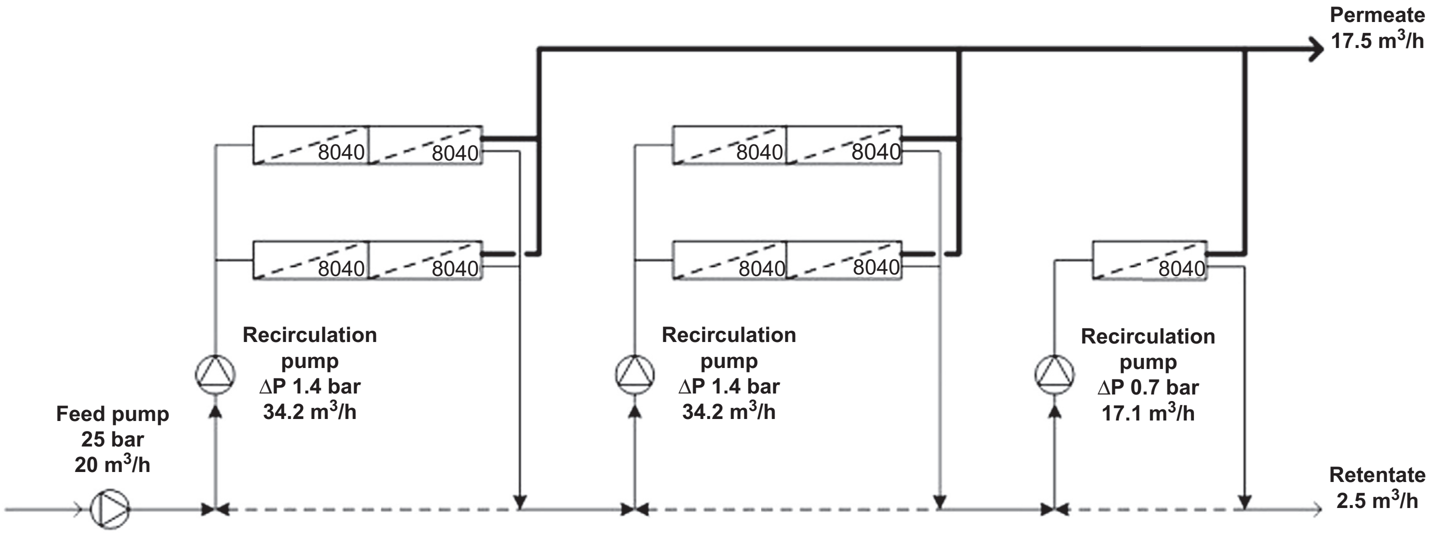


Figure 18.4 Multistage nanofiltration scheme for the treatment of flash cooler condensates from a dairy factory. Reprinted from Riera et al. (2013), with permission from Elsevier.

purification can be achieved by using a combination of different membrane processes. At the same time, the development of high value-added products from whey compounds is of great interest.

The production of whey protein concentrates (WPCs) by UF is a well-established application in the dairy industry. Ultrafiltration membranes separate lactose and minerals from whey proteins, producing a retentate stream that can be further processed by evaporation and spray-drying. The lactose and mineral content in WPC can be further reduced by using a diafiltration (DF) step in which deionized water is continually added to the retentate while lactose and minerals are continuously recovered in the permeate stream. By selecting a proper combination of UF and DF the protein content in the WPC can be modified in the range of 35–85%. The retentate can be used in a variety of beverages, processed meats, and baby foods or added to dairy products such as yogurt and cottage cheese (Zydney, 1998).

The concentration of whey and/or its partial demineralization can be also achieved by NF. NF membranes allow univalent ions (Na^+, K^+, and Cl^-) to pass whereas larger ions such as Ca^{++} or PO_4^{3-} are retained. Desalination degrees up to 40% can be achieved through a combination of NF and DF.

The performance of UF, NF, and RO spiral-wound membrane modules for the recovery of proteins and the production of clean water from white and curd cheese whey was investigated by Yorgun, Akmehmet Balcioglu, and Saygin (2008). In particular, the performance of the selected membranes was evaluated according to a single-stage or multi-step operation involving different membrane modules in series. Table 18.4 summarizes the experimental results in terms of COD removal and permeate flux for the single-step process related to white cheese whey treatment. The polysulphone NF membrane module (200 Da as an MWCO) was considered the best choice when the effluent had to be further concentrated or treated by conventional treatments. This module exhibited an initial permeate flux of 24 L/m^2 h when cheese whey was treated at a TMP and a recirculation flow rate of 8 bar and 2500 L/h, respectively. At the same time, it produced permeate with a COD load of 2787 mg/L with a COD removal of 97.4%. A further COD removal from the NF permeate required an additional RO stage as a polishing step. This combination allowed proteins to recover separately in the NF retentate while lactose was recovered in the second RO step with the simultaneous production of a clean effluent.

A combination of membrane-based cheese production was proposed by Atra, Vatai, Bekassy-Molnar, and Balint (2005) to decrease the amount of waste in cheese production with a simultaneous increase in cheese yields through the incorporation of whey proteins. A flow diagram of the proposed process is depicted in Figure 18.5. The UF of fresh milk and whey produces WPC (with a protein content of 12–14% and 8–10%, respectively) that can be used in cheese manufacturing, improving the nutritional value of the cheese. UF permeates containing about 0.1–0.5% of proteins and 5% of lactose are submitted to an NF process. By selecting the proper operating conditions (i.e., at VCR 5, 20 bar, and 30 °C), a concentrated solution containing 20–25% of lactose can be obtained. This solution can be reused in the dessert industry whereas the permeate stream depleted in lactose can be reused for cleaning or irrigation, or be discharged into sewers.

Table 18.4 **Performance of ultrafiltration, nanofiltration, and reverse osmosis spiral-wound membrane modules in treatment of white cheese whey (initial COD ~110 g/L)**

Membrane process	Supplier	Membrane material	Solute rejection (%)	Operating TMP (bar)	Initial permeate flux (L/m^2 h)	Permeate COD (g/L)	COD removal (%)
UF	Microdyn Nadir	PES	–	3	22.5	54.331	42.80
NF	Microdyn Nadir	PES	25–40 Na_2SO_4	5	27	43.658	58.50
NF	Microdyn Nadir	PES	80–95 Na_2SO_4	8	17	37.648	64.02
NF	Trisep Corp.	PA	95 $MgSO_4$	8	25	23.502	77.61
NF	Filmtec	PS	–	8	24	2.787	97.46
RO	Trisep Corp.	PA	99.5 NaCl	12	14.6	3.847	92.57

PA, polyamide; PS, polysulphone; PES, polyethersulphone.
Source: Adapted from Yorgun et al. (2008).

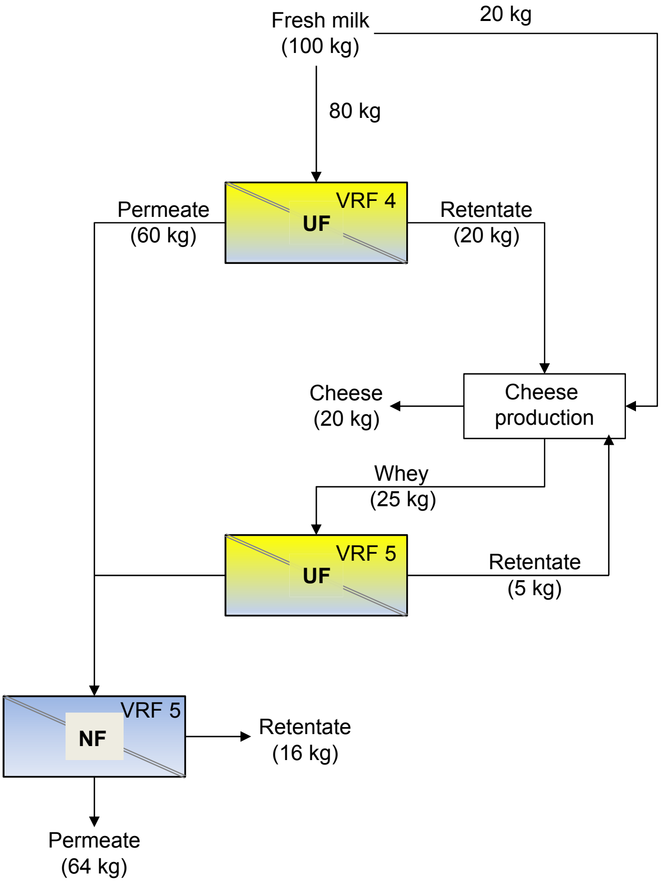


Figure 18.5 Membrane-based process for the treatment of milk and whey in cheese production. Adapted from Atra et al. (2005).

Most MBRs operate under aerobic conditions in which aeration is used to create cross-flow along the membrane to reduce fouling. The use of anaerobic systems has received great attention because of the energy balance achieved by biogas production and the lower amount of produced sludge compared with aerobic MBRs (Liao, Kraemer, & Bagley, 2006). The performance of a bench-scale submerged anaerobic MBR in the treatment of a synthetic wastewater consisting of cheese whey and sucrose was evaluated by Casu et al. (2012). The results indicated that the maximum applicable organic loading rates (OLRs) were in the range 6−10 g COD/g L. In this range the reactor showed a COD removal of 94%. Higher OLRs produced high concentrations of volatile fatty acids whereas the COD removal dropped to 33%. The maximum biomass concentration obtained in the system was of 40−50 g TSS/L owing the low filterability of the anaerobic sludge.

18.5 Wastewaters from meat industry

The meat-processing industry uses large volumes of water (approximately 62 Mm^3/y), generating polluting effluents for a total volume of about 80% of the freshwater input. The produced effluents contain huge quantities of organic compounds and salts and require several treatments before their release into receiving waters or industrial reuse. Sedimentation, coagulation/flocculation, and dissolved air flotation are typically used as primary treatments to remove suspended solids and fat substances, followed by aerobic or anaerobic systems to achieve the removal of COD and BOD. In general, anaerobic systems lead to higher BOD removal with lower cost and a smaller quantity of produced sludge compared with aerobic treatment. In addition, the generated methane can be captured for use as a fuel (Johns, 1995). Methods for microbial decontamination include chemical (chlorine, chlorine dioxide, chloramines, hydrogen peroxide, ozone, and paracetic acid) and physical (membrane operations and UV) processes (Casani, Rouhany, & Knochel, 2005).

The selection of a proper treatment system is a main challenge in supplying water of necessary microbiological and chemical quality. The treatment system should remove undesirable physical, chemical, and microbiological components, and in some cases prevent the subsequent growth of pathogenic organisms.

Membrane processes present some key advantages over conventional technologies because they can be used to purify water and recover valuable compounds. In addition, they are able to remove particles from wastewater, preventing microbial regrowth phenomenon.

Some integrated processes based on the use of membrane technology have been implemented in the meat-processing industry for the reuse of non-potable water within the plant.

Kane and Osantowski (1981) described a pilot-plant study in which wastewater was passed through chemical flocculation/clarification and dual-media filtration before further upgrading by ion exchange, RO, or ED. The latter three processes produced more than 90% reduction of total dissolved solids. However, RO exhibited lower capital and operating costs compared with the other two processes.

The treatment of meat wastewater in integrated systems including membrane operations such as coagulation—RO, UF—RO, and coagulation—UF—RO was investigated by Bohdziewicz and Sroka (2005). UF and RO were performed with different plate-and-frame membrane modules produced by Osmonics. Results indicated that the coagulation treatment, similar to UF, was not able to remove all pollutants from wastewater and the produced effluent could not be discharged into the receiving water. The combination of coagulation, UF, and RO resulted in the satisfactory removal of pollutants; in particular, the highest removal degree of contaminants was obtained in a sequence coagulation with PIX 113 ($Fe_2(SO_4)_3$ Fe_{og}, 12.8%, Fe^{2+}, 0.7%, H_2SO_4, 1%), UF with a 15- to 30-kDa cellulose acetate membrane (DSCQ, Osmonics), and RO with a cellulose acetate membrane (SS10, Osmonics). Analyses of polluting substances in each step of the hybrid system are reported in Table 18.5.

Table 18.5 **Performance of ultrafiltration (UF) and reverse osmosis (RO) membranes in treatment of meat wastewater**

Pollution indices (mg/L)	Raw wastewater	UF permeate	UF rejection (%)	RO permeate	RO rejection (%)
COD	2284.0	355.0	84.5	4.0	99.8
BOD	1900.0	350.0	81.6	3.9	99.8
Total nitrogen	285.0	40.0	86.0	2.5	99.1
Total phosphate	25.0	10.6	57.6	0.0	100.0

Source: Adapted from Bohdziewicz and Sroka (2005).

In a previous study, the authors demonstrated that in the biological treatment of meat wastewater, applying the activated sludge method to a sequencing batch reactor produced an effluent that could be discharged into the receiving water. The combination of biological treatment and the RO process obtained a higher degree of purification and the produced effluent could be reused in the production cycle of the plant (Sroka, Kamiński, & Bohdziewicz, 2004).

In the shower process, after boiling, sausage products are cooled by spraying with drinking water. The water generated in this process is commonly discharged into the sewage network. Its reuse requires treatment able to produce drinking-quality water. A demonstration plant for the treatment of water from shower processes was installed in a meat-processing company at the end of 1997 (Fähnrich, Mavrov, & Chmiel, 1998). A flowchart of the plant, based on the use of a two-step NF process, is depicted in Figure 18.6. The flow rate of the demonstration plant was of 1.5–2 m^3/h, corresponding to an average residence time of shower process water in the feed tank of about 45 min. TOC rejections were higher for the first NF membrane (95.6%) compared with the second one (55.1%). This was attributed to the presence of both dissolved and undissolved organic substances in the solution fed to the first NF stage. The original bacteria concentration in the feed tank of 1,100,000/100 ml was reduced to 1,600/100 ml by UV irradiation in the pretreatment stage. This step also allowed the reduction of membrane biofouling. After the second NF step, the produced water met required drinking water regulations (<100 bacteria/mL at 37 °C). The final UV disinfection produced bacteria-free water.

A similar approach was adopted by Mavrov et al. (2001) to treat chiller shower water in sausage production to reduce its salinity and hardness and achieve warm cleaning water for reuse. Polypiperazinamide NF membranes (NaCl rejection, 85–90%; $MgSO_4$ rejection, 99%) were used in both the treatment and posttreatment stages operating at constant TMP values of 4.2 and 2.5 bar, respectively. Permeate fluxes were on the order of 2.5–3 L/m^2 h in the first stage and 5–6 L/m^2 h in the second one. For both NF permeates the electrical conductivity was lower than 200 µS/cm. In the second NF permeate, TOC and Ca^{2+} were lower than 4 and 1 mg/L, respectively.

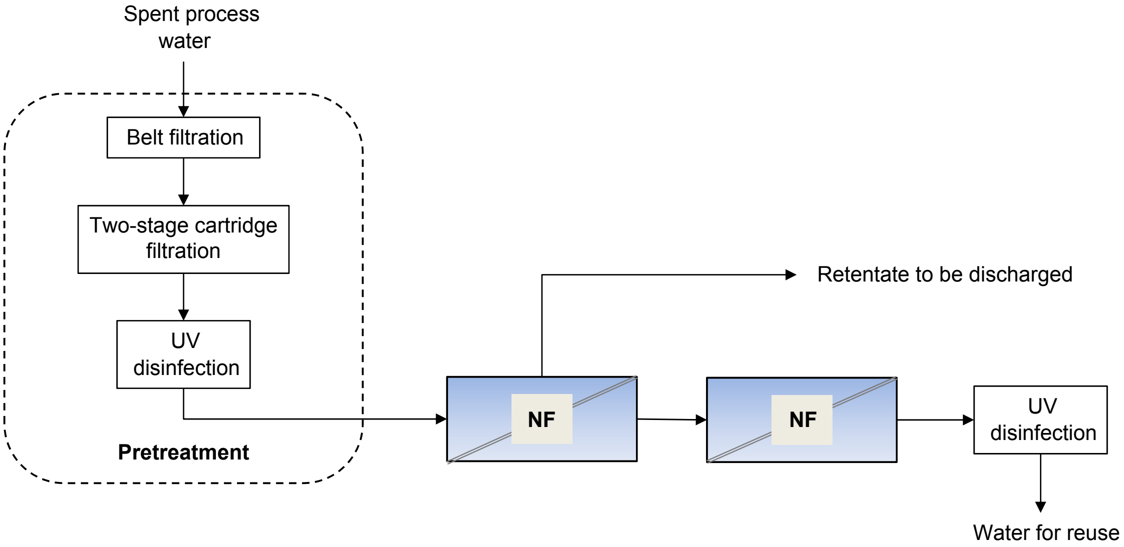


Figure 18.6 Flow diagram of a demonstration plant for the treatment of meat-processing wastewater. Adapted from Fähnrich et al. (1998).

The manufacture of cured hams requires several steps including the addition of salts and subsequent desalting and washing with water. This process generates polluted effluents containing solved salts (mainly NaCl) and a variable amount of organic matter. These effluents are generally dumped with no treatment, with consequent environmental problems. A treatment process to recover solved salts from liquid effluents of cured hams was proposed by Arnal, García-Fayos, Sancho, and Leon-Hidalgo (2013). The process is based on a pretreatment step to remove organic compounds, producing a clarified liquid mainly composed of water and dissolved salts, which is then submitted to a membrane process (i.e., an RO unit) where dissolved salts can be concentrated. The concentrated stream is finally treated in a natural assisted evaporation plant, where it is concentrated into a solid state while the permeate stream can be reused in the plant.

Poultry processing wastewaters (PPWs) contain organic compounds such as proteins, fats, and carbohydrates, resulting in high BOD and COD.

Conventional depolluting methods of PPWs include electrical (electrical stimulation), optical (UV irradiation), physical (dissolved air flotation, diatomaceous earth filtration and MF), chemical (ozonation and chemical separation of organic matter by coagulation and flocculation), and biological (anaerobic filter or sequencing batch reactors) treatment. However, most existing commercial processes present some disadvantages in terms of low clarification levels and low reduction of organic compounds (i.e., in UV treatment), precipitation of proteins when iron salts are used, and degradation of valuable compounds during biological treatment.

The recovery of proteins from PPWs by UF was investigated by several authors (Lo, Cao, Argin-Soysal, Wang, & Hahm, 2005; Saravia, Houston, Toledo, & Nelson, 2005; Shih & Kozink, 1980; Zhang, Kutowy, Jumar, & Malcolm, 1997). In the work of Lo et al. (2005) PPWs were pretreated by dissolved air flotation to remove most fat substances. The pretreated effluent was ultrafiltered using a polysulphone UF membrane (Minitan-S, Millipore) in flat-sheet configuration with an MWCO of 30 kDa. Almost all crude proteins were retained by the UF membrane and the COD in the effluent was reduced to less than 200 mg/L. The optimization of operating conditions (pH 6.74, flow rate of 683 mL/min, and TMP of 0.96 bar) by response surface methodology improved the permeate flux from 100 L/m^2 h to higher than 200 L/m^2 h. After a cleaning step with a commercial detergent containing 200 ppm sodium hypochlorite, the UF membrane surface appeared to be free of a gel-layer deposit. This step was able to restore more than 90% of original water permeability, indicating that the major flux reduction in the process was reversible.

In the UF process, most total solids can be recovered as by-products, avoiding the generation of solid sludge. In addition, a combination of UF and dehydration could produce a by-product containing up to 35% protein and up to 45% fat from PPWs (Avula, Nelson, & Singh, 2009).

Mannapperuna and Santos (2004) designed a membrane plant based on the use of spiral-wound UF membranes for the treatment of 480 L/min of poultry chiller overflow with a production of 380 L/min of reconditioned water at 80% recovery. The total cost of the system was estimated to be US$300,000 and the total electrical power requirement was 30 kW. The system is able to replace 346 L/min of freshwater makeup to the chiller with additional advantages in terms of disposal costs and energy savings.

18.6 Winery wastewater

Winery wastewater is typically generated from washing operations during grape harvesting, pressing, and fermentation, as well as from washing equipment and bottles.

The wastewater contains huge amounts of biodegradable organic compounds together with small concentrations of phenolic compounds, sugars, organic acids, and nutrients. COD values range typically between 800 and 12,800 mg/L. The quantity of produced waters and their pollution load vary in relation to the working period and the winemaking technologies used (Mulidzi, 2010). Therefore depolluting treatments should be highly flexible to counterbalance variations in both quality and quantity of pollutants.

In Europe, activated sludge processes are commonly used to pretreat winery wastewater before release into sewage systems. However, some operational problems arise from the need to treat waters with high organic loads for relatively short periods during harvesting and vintage. The use of MBRs offers different advantages over conventional biological processes, including reduced sludge production, better flexibility according to influent loading, low footprint, high efficiency in COD reduction, rapid startup, and complete suspended solids removal (Guglielmi, Andreottola, Foladori, & Ziglio, 2009; Judd, 2011).

The performance of a full-scale MBR in the treatment of a winemaking facility operating in Italy was evaluated by Bolzonella, Fatone, Pavan, and Cecchi (2010). The filtration unit consisted of plate-and-frame MF membranes (0.4 μm) with a total surface area of 276 m^2. The plant was able to treat 110 m^3/d of wastewater, producing permeate of good quality and a relatively small amount of wasted sludge. Average COD removal efficiency was about 95% for an organic loading rate up to 2 kg COD/m^3 of bioreactor per day. Energy consumption in the range of 2.0–3.6 kWh/m^3 of treated wastewater or 1 kWh/kg of COD removed was estimated.

COD removal higher than 97% was also observed in a pilot-scale hollow-fiber MBR system in the treatment of simulated wastewater with a COD between 1000 and 4000 mg/L (Artiga, Carballa, Garrido, & Méndez, 2007).

A comparison between an MBR pilot plant and a full-scale activated sludge system in the treatment of winery wastewater was studied by Valderrama et al. (2012). The MBR plant, which was equipped with flat-sheet membrane modules manufactured by Kubota, produced an average COD removal of 97%, whereas for the conventional system the removal was 95%. The MBR permeate achieved most quality specifications defined by international guidelines for water reuse and reclamation. A stable operation in terms of TMP and permeability was achieved despite the high variability in influent.

An anaerobic MBR with an external MF module was tested on a laboratory scale to treat winery wastewater, and compared with the performance of aerobic granulation technology (Basset, López-Palau, Dosta, & MataÁlvarez, 2014). The bioreactor was started up for 230 days and produced up to 0.35 L CH_4/L d when 1.5 kg COD/m^3 d was applied. The treated effluent was of better quality compared with that produced in the aerobic granular sequencing batch reactor: It was free of suspended solids with a COD concentration lower than 100 mg/L. Average permeate fluxes were on the order of 10.5 L/m^2 h.

The fractionation of phenolic compounds from winery sludge using UF membranes was investigated by Galanakis, Markouli, and Gekas (2013). Hydro-ethanolic extracts were prepared from winery sludge and treated with UF membranes of different materials and MWCOs. Results indicated that polysulphone membranes of 20 and 100 kDa were not able to fractionate phenolic compounds except for the separation between polymeric and monomeric anthocyanins. Both membranes exhibited high rejection (more than 60%) of polar compounds such as sugars and phenolic compounds. In addition, the 100-kDa membrane showed a low rejection toward pectin and allowed it to separate from phenolic compounds.

For these membranes, the solute rejection was mainly attributed to solute adsorption onto the membrane surface instead of size exclusion. The use of a nonpolar fluoropolymer membrane with an MWCO of 1 kDa produced good separation of hydroxycinnamic acids from anthocyanins and flavonols because the observed rejection toward acids was twofold higher than that observed for the other phenolic compounds.

18.7 Soybean wastewater

Soybeans are used to produce various oriental foods such as tofu (soybean curd), *shoyu* (soy sauce), miso (soybean paste), *natto* (fermented soybean), and soybean milk. A huge amount of water (about 12—15 times the volume of soybeans) is used in the soaking process to clean the beans before further processing. The produced wastewater contains soluble peptides and carbohydrates such as glucose, fructose, and raffinose, with COD values up to 10 g/L. It is commonly forwarded to wastewater treatment with a consequent disposal of valuable compounds and water resources.

An integrated membrane system for the recovery of water and soluble materials from soybean soaking water was developed by Guu, Chiu, and Young (1997). The process, depicted in Figure 18.7, is based on the use of NF and RO membranes. NF and RO retentates collected at weight concentration ratios of 7 and 6, respectively, were further treated by fermentation to assess the possibility of producing lactic acid from fermenting soluble materials. To this purpose, NF and RO retentates were inoculated with probiotic cultures of *Lactobacillus acidophilus* CCRC 10,695 and *Bifidobacterium longum* CCRC 11,847. Results revealed that a combination of both selected cultures produced up to 7.5 g/L organic acids mainly represented by lactic acid after 48 h fermentation at pH 5.5 and a temperature of 37 °C. After centrifugation and pasteurization, the fermentation broth is suitable for the formulation of lactic acid beverages whereas the RO permeate can be reused in the plant site for cleaning and soaking.

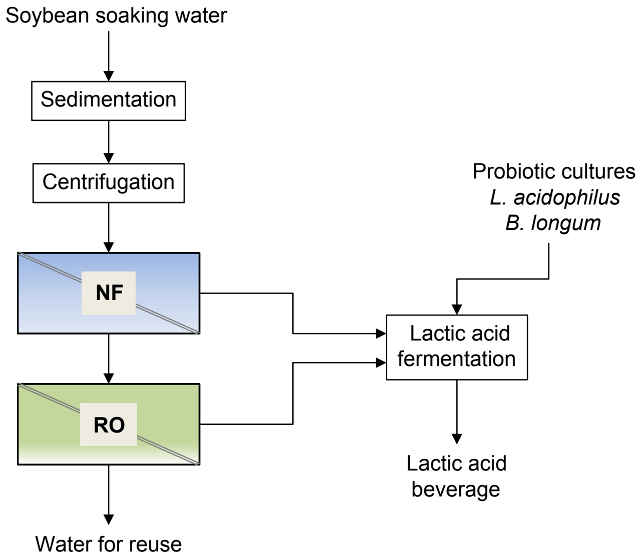


Figure 18.7 Recovery of soluble compounds and water from soybean soaking water. Adapted from Guu et al. (1997).

A membrane-based process to extract proteins, oligosaccharides, and isoflavones from yellow bean product wastewater was patented by Jiang and Wang (2013). The process involves a UF step to concentrate a soybean protein solution that can be then spray-dried to obtain a pure soybean protein powder. Soy isoflavones contained in the UF permeate are adsorbed onto weak polar macroporous resins and then eluted with ethanol, which is used in the production of soybean isoflavones. NF membranes separate soybean oligosaccharides from the resin effluent liquid and the concentrated liquid is used to prepare oligosaccharide powder. Finally, RO membranes remove inorganic salts from the NF permeate, producing pure water.

NF and RO membranes were also used to concentrate oligosaccharides from steamed soybean wastewater in tofu processing (Matsubara, Iwasaki, Nakajima, Nabetani, & Nakao, 1996). The wastewater was pretreated by UF membranes that rejected high-molecular-weight proteins; oligosaccharide components such as sucrose, raffinose, and stachyose scarcely rejected by UF membranes were concentrated by spiral-wound NF (NTR-7250) and RO (NTR-7199) membranes manufactured by Nitto-Denko. Concentrations of oligosaccharides of 10% (w/v) and 22% (w/v) were obtained by RO and NF, respectively, operating according to a batch concentration configuration.

18.8 Conclusions and future trends

The implementation of water reuse practices in the food industry presents a great challenge for both companies and public health authorities regarding knowledge, technical expertise, and documentation.

This chapter has given an overview of membrane-based processes for water reuse and environmental control in the treatment of wastewater from food-processing industries. High-strength wastewater can be successfully treated by MBRs. The performance of these systems can be improved by optimizing operating parameters and implementing methods to reduce membrane fouling. Future trends in this area will be devoted to enhancing performance, reducing operational costs, and prolonging the lifetime of the membranes.

Pressure-driven membrane operations and integrated membrane operations represent useful approaches to the treatment of food-processing wastewaters for reducing sludge production and improving the final purified water quality. Case studies referring to the treatment of individual wastewaters from agro-food production (dairy, meat, soybean, fruit juices, etc.) underline the key advantages of membrane systems over conventional methodologies in water regeneration and various reuses. Therefore, continuous growth of the membrane market can be predicted in upcoming next years, taking into account the increasing cost of main water sources and effluent sewer disposal.

List of acronyms

BEMR	bio-entrapped membrane reactor
BOD	biochemical oxygen demand
COD	chemical oxygen demand
DF	diafiltration
ED	electrodialysis
MBR	membrane bioreactor
MF	microfiltration
MLSS	mixed liquor suspended solids
MWCO	molecular weight cutoff
NF	nanofiltration
OLR	organic loading rate
PPW	poultry-processing wastewater
RO	reverse osmosis
SRT	solid retention time
TOC	total organic carbon
TSS	total suspended solids
TMP	transmembrane pressure
UF	ultrafiltration
VCR	volume concentration ratio
WPC	whey protein concentrate

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Membrane technologies for water treatment and reuse in the pulp and paper industries

19

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19.1 Introduction

Processes in the pulp and paper industry are based on the use of water and its properties. Although pulping processes can also be carried out using organic solvents, water is the dominating medium where the liberation of cellulose fibers from wooden material takes place. Water is also needed to transport raw materials, seal process equipment, cool and heat, wash and clean process equipment, remove impurities, and generate the necessary environment for the formation of the hydrogen-bonding network between fibers and fillers, which is the basic mechanism of paper formation. Therefore, a huge amount of water is necessary for pulp and paper production processes.

Water quality demands vary greatly. A relatively low purity of water can be used in less demanding applications. Therefore, the pulp and paper industry has succeeded in reducing freshwater consumption or wastewater discharge significantly by increasing water recirculation with no special purification processes. For instance, fiber recovery from water discharged from a paper machine is made by flotation or filtration and the residual water is typically reused in the process. This kind of water has a low content of suspended solids but contains almost all dissolved compounds. This water has a use, e.g., in shower water in low-pressure showers on the paper machine. However, without additional treatment further reuse of water causes severe problems because of the exponential accumulation of contaminants. For instance, dissolved impurities might plug the nozzles of high-pressure showers that are used to clean paper machine fabrics. This would lead to production breaks on the paper machine. Other detrimental influences caused by insufficient process water quality are problems running the paper machine or even the printing machine for end users. It is obvious that water quality significantly affects product quality. For instance, some residual organic compounds in liquid packaging cardboard might cause an unpleasant smell or taste in food supplies.

A modern paper machine consumes less than 10 m^3 water per 1 ton of produced paper. This is 10 times less than some decades ago. For instance, in Finland the pulp and paper industry has succeeded in decreasing their environmental impact significantly during the past 20 years by applying biological water treatment and by closing

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Table 19.1 **Total emission to waterways and reduction in environmental load related to amount of Finnish pulp, cardboard, and paper production between 1992 and 2012**

	Emission of pollutants in 2012, t/a	Reduction of emissions between 1992 and 2012
Amount of wastewater		45%
Suspended solids	10,000	69%
COD	133,000	69%
BOD	10,000	87%
Nitrogen	2175	47%
Phosphorus	133	76%
AOX	850	87%

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the water circulation. As Table 19.1 shows, the decrease in chemical oxygen demand (COD), for instance, and absorbed organic halogen (AOX) load per ton of paper or pulp was 69% and 87%, respectively, between 1992 and 2012. The high reduction in AOX load resulted from changes in pulp bleaching processes to elemental chlorine-free bleaching in the beginning of the 1990s. However, as the emission values from 2012 show (Table 19.1), significant amounts of pollutants are left in the discharge waters. Many can be removed more efficiently if membranes are applied in the purification processes, as will be shown later in this chapter.

19.1.1 Driving forces for the use of membrane filtration

In Nordic countries water scarcity is not usually a reason to reduce water use in mills. However, the situation is totally different in central Europe or New Mexico, for instance, where water scarcity has forced the McKinley cardboard mill to move to a liquid effluent-free operation (Pohjalainen, 1999). Probably the most common cause for reducing water discharge comes from legislation and environmental demands that lead the mill to use advanced water treatment such as membranes for wastewaters. Sometimes a mill is situated close to a sensitive waterway such as the Artic Paper Munkedal paper mill in Sweden, where in 1999 a tubular ultrafiltration unit was installed to purify 50% of the mill effluent (Hepp, Joore, Schonewille, & Futselaar, 2005). The mill is located next to one of the finest salmon rivers in the country; therefore, there is high demand for environmentally friendly paper production: for example, by closing the water circulation. In the future there might be limitations on how much water can be used in the production of a specific product, and the so-called “water footprint” might be a more important parameter when sustainability of different products are evaluated. Therefore, legislation and sometimes customer demand might lead companies to reduce water consumption and environmental emissions.

Less often, the reason for reducing water consumption comes from the economy, especially if water purification is the main reason for using membrane filtration. However, this was the case in Albert Köhler Pappen in Gengenbach, Germany, where the local government increased the fee for wastewater sevenfold, which led the company to invest in purification and water recirculation technologies (Junk, Dorfer, Stratz, & Lausch, 2008).

Economically, the most attractive applications for membrane processes are where membranes can be used to recover valuable raw materials from waste streams. A good example is all of the ultrafiltration processes that are used to recover coating pigments, e.g., titanium dioxide from waste coating streams. In these applications, the payback time might be less than 1 year for ultrafiltration (Anon, 2013b).

19.1.2 Barriers to membrane processes

There are also many barriers that restrict the use of membrane processes in the pulp and paper industry. Typically, volumes that need to be treated are huge and contain many possible foulants for membranes. This makes it challenging to retain the filtration capacity and causes many challenges for membrane usability. Obviously, this also leads to large membrane areas and causes the cost of the membrane filtration to be high. Sometimes, the attitude toward the incompatibility of membrane filtration with pulp and paper industry streams is a difficult barrier to surpass. In the case of old mills, the lack of space might also restrict the installation of membrane filters, although they usually use a small floor space efficiently (Nuortila-Jokinen, 2005).

19.1.3 Characteristic properties of waters

As mentioned, the water quality requirements vary at different stages of pulp and paper manufacturing processes. Naturally, the characteristics of process and wastewaters also differ significantly depending on the process stage from which they originate. Generally, the waters contain different amounts of suspended solids such as fibers, fillers and fines and dissolved wood-based compounds such as polysaccharides, oligo- and monosaccharides, lignin, and other phenolic compounds such as lignins and lipophilic wood extractives. Some, such as dissolved bark compounds, e.g., phenolic compounds, sterols, or resin acids, are known to be toxic to aquatic animals. In addition, the waters contain chemicals or additives used in to process of raw materials or manufacture end products. It has been estimated that thousands of different compounds exist in pulp and paper mill process and wastewaters (Nuortila-Jokinen, Mänttäri, & Nyström, 2003).

Moreover, every mill and papermaking process has its own fingerprint related to the process and wastewater quality. The content of the waters varies, but the amount of impurities can also change remarkably even at the same production stage. For instance, it has been reported that a more than 10 times variation in dissolved organic compound concentrations in the same paper machine circulation waters has occurred because of the breaks and different paper qualities (Mänttäri & Nyström, 2004). Therefore, membranes are exposed to great variation regarding the amount and quality of impurities. In addition, if all of the pulp and paper manufacturing processes are taken into account, there is great variation in temperature and pH. Temperatures, for instance, vary from very low (external wastewater treatment (WWT)) to above 100 °C (process waters and liquors in pulp plants) and pH varies from less than 2 to 14 (Anon, 2010).

19.1.4 Special demands for membranes and modules in pulp and paper capacity and stability

Process streams in the pulp and paper industry are huge, as much as cubic meters per second. Therefore, membrane permeability needs to be high and the flux stable, with minimal operational breaks. Unfortunately, characteristic properties of waters and their quantitative and qualitative variations seldom lead to stable filtration capacity, i.e., fouling leads to decline of capacity and to operational breaks and cleaning. A high operation temperature, the existence of hard particles, and a wide variety of foulants as well as periodical cleaning processes might shorten the operational lifetime of a membrane.

Generally, the higher the capacity is, the lower retention is. Sometimes plugged membrane pores affect the flux of MF membranes more dramatically than UF membranes and the flux can be even higher with tighter UF membranes. Therefore, the selection of an optimal membrane cannot be based only on the membrane properties stated by the manufacturer. Process and wastewaters have different compositions and filtration experiments are the only means by which to judge the applicability of membrane processes for the cases in question. Despite the challenging environment in the pulp and paper industry, it is possible to achieve stable capacity over years by selecting a correct hydrophilic membrane and an appropriate filter, as the example of a paper mill in Lohja, Finland proves (Section 19.3).

19.1.5 Selectivity

Another requirement for a membrane is selectivity. In WWT, selectivity is not the most crucial requirement, but if membranes aim to separate product compounds in future biorefinery applications, selectivity will be an extremely important characteristic. In process and WWT, selectivity is obviously needed, but high and stable capacity overtime is an even more important property for the membrane.

One important advantage offered by membrane is that separation efficiency (selectivity) can be tailored by selecting an appropriate membrane filtration process. As shown in Figure 19.1, the purified water is free from suspended solids when MF is used or it can be almost completely free from dissolved materials when reverse osmosis (RO) is used. Depending on demands, the most suitable membrane processes are chosen. Using nanofiltration (NF), it is possible to retain metal ions such as barium, iron, and manganese, which are sparingly soluble or cause the higher consumption of bleaching chemicals. Nanofiltration is also efficient when sulfate ions need to be removed. However, as will be discussed later, chloride concentrations can be even

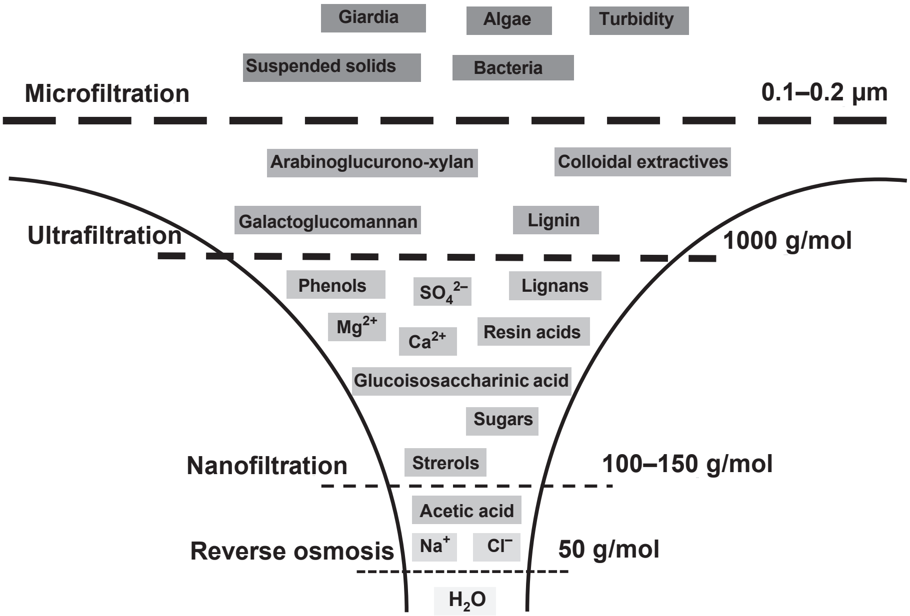

Figure 19.1 Separation scheme for pressure-driven membrane processes.

higher in permeate of NF than in the feed solution. Therefore, to remove monovalent ion, RO, electrodialysis (ED), or ion exchange is needed.

19.1.6 Module configurations

Because of a very demanding environment in which membranes are in the pulp and paper industry, special module configurations are commonly used. In particular, modules in which high shear forces are generated on the membrane surface are commonly applied to prevent flux decline. They can frequently be operated with minor pretreatment compared with conventional spiral-wound modules. A drawback is that the shear might cause a shorter lifetime for the membranes. Although high shear rate modules dominate industrial-scale applications, all kinds of membrane modules are in use.

A high shear rate on the membrane surface can be achieved in tubular modules by increasing the pumping velocity, but this strongly influences energy consumption because under turbulent conditions power will vary with velocity up to a power of 2.75 (Merry, 1999). In addition, it is estimated that in conventional cross-flow filtration systems only about 10% of energy is converted into shear on the membranes. Therefore, high shear rate modules have been developed to better use energy in generating turbulent conditions. Culkin, Plotkin, and Monroe (1998) claimed that the so-called vibratory shear—enhanced processing (VSEP) filter allows nearly 99% of total energy used to be converted into shear at the membrane surface. This is because the energy is directed to create shear forces only into a thin zone near the membrane surface. The VSEP is a vertical plate-and-frame type construction in which membrane sheets are stacked on top of each other and the whole membrane stack is vibrated. The VSEP process imposes an oscillatory motion on the whole module, which generates a shear rate as high as 150,000/s on the membrane surface, about 10 times that achievable in conventional cross-flow filtration.

Similarly with the cross-rotational (CR) filter, the rotor blade mixes only small volumes on the membrane surface. Fouling control in the CR membrane unit (CR filter from Valmet Corp.) is achieved by rotating rectangular plates between all membrane sheets, thus generating shear directly at the membrane's surface. In this construction the membrane itself does not move. In industrial-scale applications, the CR filter is the most commonly used high shear rate filter. The maximum pressure in the VSEP is 38 bar, which is significantly higher than what can be achieved with CR filters (around 8 bar). Therefore, the VSEP is an attractive choice especially for NF processes. Recently, several other membrane filters based on rotating membrane plates have been developed. Both polymeric and ceramic membranes can be applied in these filters, but they have not yet found a place in the pulp and paper industry (Jaffrin, 2008).

Spiral-wound modules have also been used for several years to treat waters in paper mills. A prerequisite for their successful use is appropriate pretreatment, which needs to remove suspended solids to prevent plugging of the feed channels and reduce the amount of foulants. Therefore, pretreatment consists of several processes including traditional physical and chemical separation processes (Lien & Simonis, 1995). A second membrane process such as UF has also been shown to be a sufficient pretreatment for NF with spiral-wound modules (Sutela, 2008).

19.1.7 Use of membranes in pulp and paper mills

Membranes are an excellent choice for purifying raw water, recirculating process water, purifying effluents, and recovering and purifying valuable compounds from different streams in the pulp and paper industry. Figure 19.2 illustrates the use of membranes in water and WWT in pulp or paper mills as presented in this chapter.

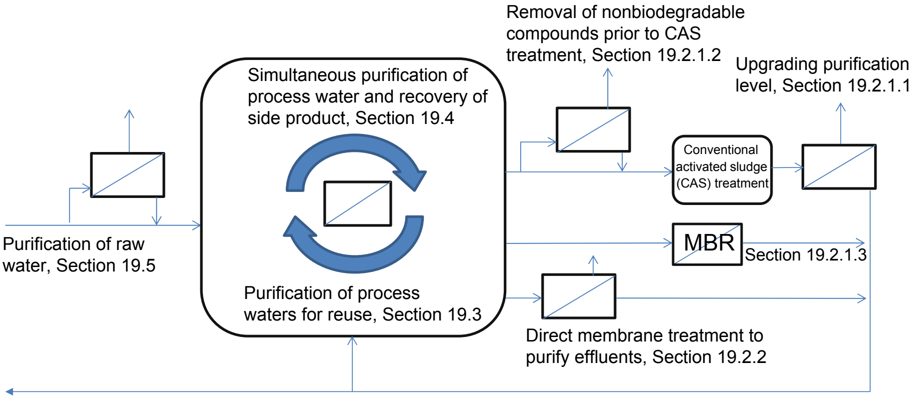

Figure 19.2 Simplified drawing of different options for using membranes related to pulp and paper manufacturing.

Membrane processes can be used as internal kidneys close to the place where wastewater is generated. It might be beneficial to retain the purified water temperature and pH level equal to the process levels. These advantages are achieved when, e.g., paper machine process waters are recirculated (Section 19.3). In addition, by keeping specific water streams unmixed, membrane processes can be focused on the most relevant streams, and thus only smaller volumes would need to be treated (as in the treatment of evaporator condensate and coating wastewaters; see Sections 19.2.2 and 19.4.1, respectively). Today, coating color recovery from waste coating streams is the most common membrane filtration application in the pulp and paper industry. Furthermore, membranes are applied to treat a wide variety of process streams and effluents, such as paper mill process water and bleaching effluents (Section 19.3). Membranes can operate either alone or combined with biological or other chemical and physical processes (Sections 19.2.1.1−19.2.1.3).

19.2 Purification of wastewaters

19.2.1 Membrane processes combined with biological WWT

Membrane processes are used to upgrade the purification results of biological WWT and, before biological treatment, to reduce the amount of scarcely biodegradable compounds in effluents. In addition, about 15 years ago some paper mills implemented membrane bioreactors (MBRs) as an essential part of their wastewater purification systems.

19.2.1.1 Membrane processes to upgrade purification results of biological WWT

Membrane filtration makes it possible to upgrade existing WWT plant efficiency. For instance, the Eltmann newsprint mill of Papierfabrik Palm has used NF to improve the quality of activated sludge process effluent since 1999. Sand filtration was applied to polish effluents before spiral-wound NF. Nanofiltration succeeded in reducing about 90% of COD and color and about 60% of AOX. As thought, NF retained divalent ions excellently but the apparent retention of chloride ions was −40% (Schirm, Welt, & Ruf, 2001).

Depending on the membrane, filtration conditions, amount of multivalent anions, and ratio of multivalent to monovalent ions, NF can concentrate monovalent anions (chloride) into permeate because of the Donnan effect. Therefore, the apparent retention of chloride ions can be negative, even some as much as 100%. This might limit the reusability of NF permeate. When removal of monovalent ions such as chloride ion is needed, RO, ED, and ion exchange are the choices of technology.

Electrodialysis is commonly defined as an electrochemical separation process in which electrically charged membranes and an electrical potential difference instead of pressure are used to separate ionic species from an aqueous solution and other uncharged components. In the pulp and paper industry, ED is being studied for the removal of chloride ions and other nonprocess elements before reuse of purified waters

(Ferreira, Amaral, & Machado, 2004; Geraldes & De Pinho, 1995; Pfromm, Tsa, & Henry, 1999; Rapp & Pfromm, 1998).

In the Eltmann newsprint mill, the membrane concentrate is recirculated back into the activated sludge plant after lime precipitation. The lime precipitation removes about 99% of iron, 60% of silicate, and about 30% of sulfate ion. In addition, 40% of organic compounds (measured as COD and AOX) and over 70% of colored compounds are removed by this lime precipitation. Therefore, precipitation removes a significant amount of organic compounds in which biodegradability is not obvious. In principle, compounds that have already been treated biologically (activated sludge process) are probably not the most biodegradable, and therefore, their recirculation back into the activated sludge process might not lead to their degradation (Schirm et al., 2001).

Another alternative for treating membrane concentrate before recirculation back into the activated sludge process is a mild oxidation, which has been reported to enhance the biodegradability of NF concentrate (Mänttäri, Kuosa, Kallas, & Nyström, 2008; Mauchauffee, Denieul, & Coste, 2012). For instance, ozonation was demonstrated to improve the biodegradability of NF concentrate, although the amount of dissolved organic carbon did not change. Recently, Panorel et al. (2014) reported that pulsed corona discharge treatment can oxidize lignin, for example, using about one-third of the energy needed in ozonation. Therefore, the reduced cost of oxidation processes enables the wider use of oxidative treatments in WWT and will help treat membrane concentrates in the future.

Mauchauffee et al. (2012) tested different process alternatives for the treatment of printing paper mill effluents. They concluded that the best process concept would be to upgrade existing anaerobic and aerobic treatment with suspended solids removal, softening to reduce the scaling potential of the effluent, NF to remove organic compounds, and evaporation or oxidation to treat NF concentrate. In addition, softening by adding lime, calcium, and carbonate with a specific mixing reactor and settler significantly improved NF performance; i.e., a higher recovery and better permeate quality was achieved after the softening process. Lime softening was also applied by Mänttäri, Daltrophe, Oren, Gilron, and Nyström (2001) to remove hardness from paper mill process waters.

Several studies have also been published in which high shear rate CR NF or low-pressure RO is studied directly as a polishing stage after biological treatment. For instance, a permeate flux of 150 L/(m^2h) at a volume reduction of 12, a pressure of 10 bar, and a temperature of 40 °C was achieved when discharge water from a pulp and paper mill WWT plant (activated sludge treatment) was nanofiltered (Mänttäri et al., 2008). The reported flux from spiral-wound NF in the Eltmann newsprint mill was significantly lower, at 10–30 L/(m^2h) (Schirm et al., 2001). It is clear that a high shear rate facilitates flux by reducing concentration polarization and fouling on the membrane surface.

Generally, the permeate fluxes obtained from the filtration of biologically treated effluents are significantly higher than those obtained in the filtration of paper machine process waters (Mänttäri & Nyström, 2007). This is because of the lower amount of impurities left in the biologically treated water. On the other hand, heat recovery is more difficult to perform when biologically treated water is circulated back into the mill.

In the United States, a closed cycle paper mill combines biological treatment, membrane technology, and evaporation to prevent the discharge of liquid effluent (McKinley Linerboard Paper Company, New Mexico). There is no water recipient near the mill for discharging even a minimal amount of effluent, and raw water availability is restricted because the mill is located in the desert of northwestern New Mexico. Thus, raw water consumption has been minimized to only 1.5 m^3/ton cardboard product. A waste stream of 3.3 m^3/ton cardboard produced is cleaned and finally concentrated using MF and RO membranes. First, flotation is used to separate fibers, fines, and stickers from the water; then, activated sludge treatment in sequenced batch reactors is carried out before membrane filtration. Concentrated salts after RO treatment are crystallized by a tube-type falling film evaporator and its condensate is recirculated back into the process (Durham, 2000; Pohjalainen, 1999). This example shows that it is technically possible to recirculate all water, but some fresh water is always needed because of evaporated process water during the manufacturing process.

19.2.1.2 Membrane processes to improve functioning of biological WWT

One of the most studied applications for membranes in the pulp and paper industry is the purification of the strongly colored effluents from bleached kraft pulp mills. The first alkaline extraction stage effluent is a good example of a stream whose environmental impact is remarkably high compared with its volume. For instance, it has been estimated that the first alkaline extraction stage effluent constitutes only 5−10% of the total effluent volume of the mill, but it contains about half of the color discharge. The strong color results from the high molar mass lignin molecules that are difficult to biodegrade in conventional activated sludge treatment. Also, the COD and the BOD loads of the first alkaline extraction stage effluent are high. Fortunately, the large sizes of the molecules and their high charge densities owing to high pH make the alkaline bleach plant effluents easier to filter using UF than the preceding chlorination stage effluents containing smaller molar mass compounds (Jönsson, 1989; Zaidi, Buisson, Sourirajan, & Wood, 1992). Therefore, many researchers have studied membrane filtration with the aim of purifying the alkaline extraction stage effluents for reuse. Ultrafiltration membranes with cutoff values of some thousands of grams per mole have been shown to significantly decrease the color, BOD, COD, and AOX loads of bleaching effluents and enable the use of the treated effluent: for example, for washing purposes. Permeate of UF-treated bleaching effluent can also be more efficiently purified in biological treatment plants because UF removes slowly degrading high molar mass lignin compounds and decreases the amount of chlorinated compounds, which are resistant to attack by most microorganisms used in the biological treatment plant. Accordingly, the load on the treatment plant decreases and the average biodegradability of the remaining compounds increases. The concentrate of the UF process is generally burned in the recovery furnace where the cooking chemicals are recovered.

In Sweden, in the StoraEnso Nymölla pulp mill, UF has been used since 1995 to reduce the COD load of the mill effluent before treatment in the activated sludge plant. The mill produces pulp from both hardwood and softwood using the magnesium bisulfite process and oxygen bleaching. The UF plant is based on tubular membranes with a total membrane area of 4638 m^2 (Greaves, 1999). On average, about 400 m^3 effluent water is treated by the membrane plants in Nymölla every hour. The effluent of the oxygen bleaching stage on the pulping process has an average COD of around 10 g/L. The aim for UF was to reduce 50% of the COD load; in addition, the aim was to concentrate the organic compounds to the point where the concentrate could be incinerated. Therefore, a high-volume reduction (50–60 times) was needed in UF to increase the COD of the concentrate to 180 g/L.

Permeate is discharged to an activated sludge plant. In this mill, different tight UF membranes were needed in the filtration of hardwood and softwood effluents because of variations in effluent composition. The fluxes are about 60 and 70 L/(m^2h) at 7 and 8 bar pressure for softwood and hardwood effluents, respectively. The high UF operation temperature (up to 82 °C) eliminates the need for rapid cooling before the membrane plant and decreases the fouling of the membrane caused by extractives. Furthermore, the pH of the softwood effluents is controlled to keep it above 11. This was also observed to reduce fouling of the membranes. Reported energy consumption from the Nymölla mill is approximately 3.9 and 1.5 kW/m^3 for hardwood and softwood, respectively (Anon, 2013b; Greaves, 1999; Nordin & Jönsson, 2008).

19.2.1.3 Membrane bioreactors

Conventional aerobic WWT systems (conventional activated sludge [CAS]) are established as end-of-pipe technology in the paper industry. It is estimated that the activated sludge process is used in 60–75% of all biological effluent treatment plants in the pulp and paper industry. The activated sludge plant consists of two main units: the aeration basin and the secondary clarifier (sedimentation basin). In the aeration basin, the effluent is treated with a mixture of microorganisms (activated sludge), which are present in high concentration. The biomass (sludge) and water are separated by settling biomass in large clarifiers or by flotation after microbial degradation. Generally, the activated sludge process achieves high treatment efficiencies. However, the biomass is vulnerable to disturbances such as spillages of concentrated liquor and operational instability, and the purification efficiency varies somewhat.

An MBR usually consists of an aerated bioreactor, similar to the activated sludge process, combined with a membrane process to separate the biomass from the effluent. In an MBR, a membrane replaces the settling or flotation stage in the conventional activated sludge plant and separates completely suspended solids, i.e., biomass. In both systems, dissolved organic components are converted by aerobic microorganisms to inorganic products such as carbon dioxide and water. The filtered effluent from the membrane stage can be reused in the process while the separated biomass is recirculated into the bioreactor. Sometimes surplus biomass is discharged. Two basic MBR configurations exist: one in which the membranes are immersed in the reactor and are an integral part of the biological reactor (internal/submerged; Section Paperie du Rhin) and one in which the membranes are a separate unit process after the biological reactor (external/sidestream; Section Ugchelen BV).

In principle, there are several advantages of MBR processes over CAS treatment, such as a longer sludge age, a higher biomass concentration (mixed liquor suspended solids (MLSS)) up to 30 g/L, a lower hydraulic retention time, and a higher volumetric load. In MBR, complete retention of sludge by a membrane process makes it possible to maintain high MLSS in the bioreactor, which causes long sludge retention time and a low food-to-microorganism ratio. The long sludge retention time also causes less sludge production whereas a low food-to-microorganism ratio enables the hydraulic retention time to be reduced. It has been pointed out that sludge production is inversely proportional to the hydraulic retention time when MLSS is fixed. Therefore, the shortest hydraulic retention time and minimal sludge production cannot be achieved simultaneously. In addition, the cost of aeration increases when sludge production is minimized, and vice versa. The high MLSS restricts oxygen transfer in the aeration tank and membrane scouring by air and increases membrane fouling. Therefore, there is an optimum point at which the total operational cost is minimized and operating an MBR at very high MLSS is not common. As a result, the apparent excess sludge production is not much different from CAS, although in principle even zero sludge production is possible with MBR (Stephenson, Judd, Jefferson, & Brindle, 2000; Yoon, Kim, & Yeom, 2004).

The use of chlorine in the pulp bleaching process and the existence of slowly biodegradable compounds in the waste and process waters may cause problems for microorganisms in biological treatment. The microbes in the MBR process operate at a high MLSS concentration and a long solids retention time is shown to be faster when adapted for this kind of wastewater. Therefore, the purification results might improve with time, as was shown after a 3-month operation period at VHP Security paper mill owned by Ugchelen BV. The full-scale plant outperformed results achieved in pilot experiments. The COD was reduced from 3500 to 600 mg/L in pilot experiments and to 450–500 mg/L in the full-scale plant (Amaral, Lange, & Borges, 2012; Hepp et al., 2005; Ramaekers, van Dijk, Lumpe, Verstraeten, & Joore, 2001; Simstich & Oeller, 2010).

Additional advantages are almost total retention of suspended solids, high organic matter removal, and a low footprint, which might sometimes be a critical demand when purification capacities of an existing plant are enlarged. Membrane separation excludes the sludge bulking problems often caused by unstable organic loading rate in CAS; an MBR is therefore more tolerable to organic loading chock. However, in MBR a stable incoming load is needed to minimize membrane fouling. When wastewater is purified for reuse, an important advantage and goal is bacteria- and suspended solids–free water. Typically, MBR processes use membranes with pore sizes of 0.01–0.45 μm. Therefore, it can be assumed that all suspended solids and bacteria are removed by the membrane filtration stage. The high quality of the purified effluent makes MBR technology ideally suited for use as an internal water circuit treatment. However, dissolved organic or inorganic compounds are not retained by the membrane and their removal efficiency depends on the functioning of the biological process. In addition to water reuse, an MBR process, especially when applied at thermophilic conditions, enables the reuse of energy. At thermophilic conditions, an MBR is operated in the same temperature range as the paper machine (40–65 °C); thus, there is no need to cool or heat the process water.

As in all membrane processes, including MBR processes, membrane fouling management needs to be taken into account. Depending on the MBR configuration, this is done by backflushing, bubbling air close to the membrane surface, and controlling permeate flux. Air is also consumed by microorganisms, and typically air bubbling causes more than 50% of operation costs. In many cases, membrane and operational costs are somewhat higher than in CAS processes, but to evaluate total costs, benefits such as water recirculation, energy recovery, operation at thermophilic conditions, reliability of the process, effluent quality achieved, and possible reduced costs for sludge treatment have to be taken into account (Anon, 2013b). Helble and Möbius (2009) reported that total specific operation costs for MBR with submerged and with aerated vertical tubular cross-flow membranes amount to 0.22 €/m^3. Membrane bioreactors with classical tubular cross-flow membranes consume slightly more energy and the operation cost is around 0.33 €/m^3. When capital costs are included, the total annual costs are in the range 0.56–0.59 €/m^3.

Paperie du Rhin

A paper roll mill in Paperie du Rhin in France installed an MBR process based on hollow-fiber membranes (Table 19.2). The mill uses recycled (not de-inked) paper as the raw material for the production of 40,000 tons of paper rolls annually. The bioreactor (1500 m^3) is operated at an MLSS content of 12–16 g/L. The wastewater from the mill is first prescreened with drum screens; then it is sent to an equalization basin, from which it is pumped directly into the bioreactor. The MBR process decreased the COD from 4000 mg/L to less than 200 mg/L and the BOD from 1700 mg/L to less than 5 mg/L. Permeate is partly recycled as process water. The main reasons for choosing MBR treatment were on-site space limitations and the need to recirculate the purified water (Ramaekers et al., 2001).

Ugchelen BV

VHP security paper mill owned by Ugchelen BV, located in Apeldoorn, The Netherlands, produces bank notes and other security papers (Table 19.2). The paper mill uses cotton as a raw material, which it bleaches with hydrogen peroxide at a temperature of approximately 100 °C and a pH between 11 and 12. The high pH of the wastewater makes purification a challenge. The mill developed a wastewater purification process in which dissolved carbon dioxide was used in a flotation process to remove fibers and debris, and reduce the effluent pH from 11 to 8.2 before the MBR unit. The MBR operates at thermophilic conditions to reduce the need to heat the purified water (temperature around 55 °C). The 8-mm tubular polyvinyl fluoride membrane is installed outside the bioreactor (volume, 250 m^3). The MBR effluent COD is stabilized to about 500 mg/L (influent, 3500 mg/L). The MBR-treated effluent is recirculated with no detrimental effect on product quality. This enables the mill to reduce the freshwater intake for bleaching by 80% and the mill wastewater discharge by 50% (Hepp et al., 2005; Joore, Wortel, & Bronold, 2001; Ramaekers et al., 2001).

Table 19.2 Examples of existing membrane bioreactors in pulp and paper industry

	Köhler Pappen, DE	Ugchelen BV	Paperie du Rhin
MBR type	Hollow fibers, submerged	Tubular, external	Hollow fibers, submerged
Amount of wastewater, m^3/day	670	240	900
Pore size, nm	40	40	40
Membrane area, m^2	5000	83	
Average flux, L/(m^2h)	8	120	15
Operating pressure, bar		3.5	0.15
Cross-flow velocity, m/s	–	3.5	–
Biomass concentration, g/L	10–12		12–16
Food to biomass ratio, kg BOD/kg SS × d	<0.2		
COD reduction, %	94	86	95

Adopted from Ramaekers et al. (2001), Hepp et al. (2005), Anon (2013b).

Albert Köhler Pappen

One benefit of MBR compared with conventional activated sludge treatment is the usability of the MBR filtrate for further purification with spiral-wound membranes. An MBR was combined with downstream RO in a cardboard mill (Albert Köhler Pappen in Gengenbach, Germany) (Table 19.2). The mill annually manufactures 35,000−40,000 tons of high-quality cardboard on three paper machines. Many different grades are produced, some of which are heavily colored. Process water was taken from wells, and before implementing the MBR, the wastewater was discharged into the municipal sewer after sedimentation. The main reason for investing in their own WWT was because of a decision by the local government to dramatically increase wastewater fees from EUR 0.35 €/m^3 up to EUR 2.05 €/m^3. In addition, the mill has to pay for the use of well water. Therefore, the mill decided to close the water loops by recirculating 600 m^3/day of treated water back into production. This reduced well water use to one-fourth (250 m^3/day) and significantly decreased the need for energy to heat well water for the cardboard-making process. The two-stage RO further cleaned the filtrate by removing the remaining dissolved salts of the filtrate from the MBR plant. To prevent possible scaling problems in RO, calcium was reduced in the decarbonization reactor. Soda, lime milk, and iron (II) chloride and some acids are added to the calcium-rich wastewater and mixed; then, microparticles of calcium carbonate are formed. After flocculation and sedimentation, the suspension of removed calcium carbonate (50−300 g/L) is used as filler for cardboard grades. By recirculating the filtrate from the MBR and by further treatment of the MBR filtrate (50%) by RO, the original flow of the wastewater could be reduced by more than 90%. The remaining flow (approximately 0.6 m^3/ton) of wastewater (the concentrate of the RO) is fed into the municipal sewage treatment plant. Chemical oxygen demand concentrations were reduced from 2600 to about 150 mg/L in the MBR process and to 10 mg/L by RO and BOD from 1300 mg/L to less than 5 and 1 after MBR and RO, respectively (Anon, 2013b; Junk et al., 2008; Wagner, 2010).

19.2.2 Direct membrane filtration for wastewaters

In Canada, a pulp mill in New Brunswick produced bleached kraft pulp without conventional biological WWT because of the limited land area. In the effluents an evaporator condensate stream was identified that caused significant amounts of BOD and toxicity. Therefore, an RO plant was installed to purify the condensate stream. Permeate of RO was recirculated into the bleaching process, which led to a 40% reduction in water consumption. Compound identification of the RO process streams showed that the RO feed contained significant concentrations of low molar mass phenolics, including phenols and guaiacols, which were effectively removed and concentrated by RO. In addition, RO is reported to remove compounds responsible for endocrine disruption in fish. Although RO eventually exceeded the expected purification level, permeate was still somewhat toxic and the BOD content was higher than allowed. Therefore, a moving bed bioreactor was installed to reduce the BOD (Anon, 2007; Webb, 2002).

Table 19.3 Reverse osmosis treatment for evaporator condensate of kraft pulp mill

	Clean condensate	RO concentrate[a]	RO permeate
Volume, m^3/day	6000	100	5900
BOD, mg/L	560	41,000	67
COD, mg/L	1067	78,000	115

[a] Calculated from mass balances.
Adopted from Dubé et al. (2000).

The mill achieved an extremely high water recovery of 99% in RO, and thus only a small amount of concentrate was incinerated in the bark boiler or was first sent to the high solids crystallizer to be subsequently burned in the recovery boiler (Table 19.3). Over 90% and 80% reduction was measured for COD and BOD, respectively (Dubé, McLean, MacLatchy, & Savage, 2000). In RO, one could assume even higher retention for organic molecules. A somewhat low retention probably resulted from a high-volume reduction in filtration. Especially in solutiondiffusion type membrane processes, such as RO and NF, an increase in the feed concentration owing to the concentration of impurities leads to lower permeate purity. The permeate purity can be improved by filtering permeate again.

19.3 Membrane processes to recirculate process water

High shear rate modules such as CR filtration technology and VSEP, tubular modules, and conventional spiral-wound modules have been used in several mills as internal kidneys to purify paper mill circulation waters such as white water and clear filtrates (Kreutzman & Sutela, 2004).

The only known industrial-scale example of the use of the VSEP in the pulp and paper industry is from NF. The Linpac recycle paper mill in Cowpens, South Carolina, has a two stage tubular UF system and VSEP filters to remove impurities from water circulation. The UF systems (Koch membrane systems) treat the overflow from dissolved air flotation (DAF) clarifiers. Total suspended solids in the DAF units are improved significantly by pressurized ozone injection before DAF. To reduce the concentrate (reject) volume from the UF system and improve the reused water quality, a VSEP NF system was installed to further concentrate the two-stage UF concentrate. This unconventional way of combining membrane processes produces an NF concentrate with a solids content over 20% (Linpac, 2006).

One of the best reported membrane filtration processes exists in a paper mill in Lohja, Finland. When the fine paper machine was built in the 1990s, the authorities would not accept an increase in effluent load. Thus, the mill was forced to find advanced methods to reduce the environmental load. By circulating the paper machine process waters efficiently after UF, the mill succeeded in obtaining environmental permission. During the 1990s, 19-CR filters were installed to treat white water from paper machines and recover coating color from the mill. The membrane area installed for white water treatment is 1428 m^2, and for coating color treatment, 336 m^2. The fine paper machine membrane filtration plant operated in three stages, recovering 94% of the feed into permeate (235 m^3/h). The permeate stream was used in paper machine showers and for chemical dilution. A part of UF permeate (50 m^3/h) was further purified by spiral-wound NF. Whereas UF removed only about 10% of dissolved COD, NF removed about 85% at a water recovery of 70%. The main benefit of UF is that it makes suspended solids—free water in which the amount of anionic trash (extractives) has also been significantly reduced. Ultrafiltration permeate has proven suitable for reuse in showers, sealing waters, and dilution of wet-end chemicals. Because of the high purity of NF permeate, it can be used to replace warm freshwater on the paper machine.

Sutela (2008) reported a high average flux of 315 L/(m^2h) in UF at 0.8 bar and 60 °C for a 7-year filtration period. Total operating costs for CR UF were about 0.19 €/m^3 in 2008 (used energy price, 0.05 €/kWh). Advanced water purification enables the fine paper machine to operate with about 6 m^3 freshwater intake per produced ton of paper. The high shear CR-filtration technology was also applied in the newsprint mill of Holmen Paper in Madrid, Spain, and the UPM Kymmene mill in Valkeakoski, Finland. Approximately 20—50% reduction in the use of freshwater was achieved in these mills (Sutela, 2008).

Typically, UF almost completely removes suspended solids (fibers) and bacteria and partly organic dissolved compounds (lignin, hemicellulose, etc.), but ions only when they are bound, for instance, to fibers. The removal of dissolved organic compounds depends on the process water and membrane used; it is typically from 10% to 40% in UF. Membranes are typically needed when freshwater consumption needs to be reduced below 10 m^3/ton of paper. Nanofiltration removes 70—90% of dissolved organic compounds (COD and TOC), color, and lignin degradation products. Very high retention for multivalent ions has also been reported. The retention efficiency in NF depends on the filtration conditions and pH, and naturally on the membrane properties. For instance, increasing pH of slightly acidic paper machine process water to neutral increased the retention of COD about 20%.

19.4 Simultaneous recovery of valuable by-products and purification of process waters

19.4.1 Recovery of coating color

Probably the most economical application for membrane processes in the paper industry is the recovery of coating effluents by UF, especially when valuable coating pigments are used. Effluents that contain coating color are generated during the flushing of coating equipment, paper breaks, and production changes in paper and cardboard mill manufacturing coating grades (papers that are used in magazines, catalogs, or books, for example) (Lipnizki, 2008).

Coating wastewaters create a lot of color in discharge water systems because they are not easily treated by conventional treatments although their volumes are usually negligible compared with overall mill effluents (about 2−5% of total flow). The heavy solids load and compounds that are sticky by nature in these wastewaters may cause operating problems in treating effluent if discharged into sewers without appropriate pretreatment. On the other hand, pigments are expensive, so the (partial) recovery of coating color for reuse is cost-effective in most cases. Therefore, the separate treatment of coating wastewater is an attractive, environmentally friendly alternative to reducing color in the effluents; at the same time, the mill can benefit from reusing the coating material. Diluted coating materials are recovered mostly by UF to obtain a solid-free permeate stream and a retentate stream that contains the coating materials, preferably at a concentration suitable for recycling or discharge. In UF, the pore size of the membrane is sufficiently small to prevent pore plugging and the permeability is still high. The solid-free permeate stream can be either easily discharged or recycled. The permeate stream can be reused, for example, in coating preparation, as washing water or as shower water for the paper machine. Cross-rotational technology dominates new installations (more than 20 mills have begun to recover coating color by CR technology over the past 15 years) (Alho, Roitto, Nygård, & Hietanen, 1998; Anon, 2013b; Jönsson, Jönsson, Teppler, Tomani, & Wännström, 1996; Singhet al., 1999).

Payback time is typically around a year when treating valuable coating color (e.g., when TiO_2 pigments exist in coating wastewaters). High shear modules can recover coating color from wastewater to higher dry solids content than traditional modules. On an industrial scale, effluent fed into the process typically contains 2−4% solids, and by UF its concentration is increased to 30−44%, depending on the system. A high concentration is needed so that the concentrate can be added to fresh coating color without overly diluting the coating color.

19.4.2 Recovery of by-product

Only about half of the wood material is converted to pulp in the pulping process; the rest of it is dissolved during the process. Dissolved wood compounds, e.g., galactoglukomannan (GGM), can be recovered from thermomechanical pulp mill process waters (Figure 19.2). Other possible products are lignosulphonates and monosaccharides, in which spent sulfite cooking liquors are rich. Furthermore, kraft lignin and hydroxy acids are possible valuable products in black liquor from the sulfate pulping process. All of these compounds are recoverable by using different membrane processes. Membranes are used to recover compounds into concentrate (e.g., hemicelluloses or lignosulphonates) or into permeate (e.g., monosaccharides or vanillin). In Sarpsbog, Norway, Borregaard Industries have concentrated lignosulphonates by UF since the 1980s (Jönsson & Wimmerstedt, 1985; Wagner, 2000). Nanofiltration can purify, e.g., xylose into NF permeate. As a result, xylose purity can increase from 16% up to 65% (Heikkilä, Mänttäri, Lindroos, & Nyström, 2005). When high molar mass compounds such GGM, lignosulphonates, and kraft lignin are recovered into the UF concentrate stream, diafiltration can be used to purify them. All of these streams are water streams, and water itself can be used to carry away impurities. It can be assumed that the importance of membrane technology in the recovery and purification of valuable compounds from different streams will increase in future.

19.5 Purification of raw water

Membranes are used to purify process waters and effluents in the mills, but also to purify incoming water. Two examples of mills - Bahia Sul Celulose in Mucuri, Brazil, and Stendal pulp mill at Arneburg near Stendal, Germany - purify raw waters from a river using spiral-wound RO. Both installations needed tailored and complicated pretreatment systems to manage the seasonal variations of river water. In the case of the Bahia Sul Celulose mill, complicated pretreatment including chlorination, flocculation, sedimentation, sand filtration, and filtration through activated carbon was not sufficient before RO because the standard BW30-365 membrane had high levels of biofouling that generated a high pressure drop on the system and demanded frequent cleaning. After replacing the standard membrane with the more fouling-resistant BW30-365FR membrane (FilmTec, currently Dow), and after optimizing the operation (maximum flux, 22 L/m^{2}h) and cleaning conditions, fouling was significantly reduced and the cleaning interval doubled to 12 days. Salt retention is 98%, corresponding to a permeate conductivity of less than 6 mS/cm (Soalheiro, 2000).

The Stendal pulp mill in Germany started to use RO to treat raw water from the Elbe River in 2004. After multilevel pretreatments, this water is led to RO. The RO plant produces about 2500 m^3/h (feed, 3100 m^3/h) of permeate, which is used as process water and is further treated (300 m^3/h) with demineralized water. Differences in the quality of water taken from the Elbe River, which result from seasonal and weather conditions, are compensated for by a complicated pretreatment system including different physical and chemical stages. The RO removes 98.6% of salts and the conductivity levels in permeate are about 15 mS/cm (Kremser, Dreshner, Otto, & Recknagel, 2006). As these examples show, spiral-wound modules need appropriate pretreatment so that their functionality can be ensured.

19.6 Conclusion and future trends

This chapter reviewed membrane filtration related to water treatment in the pulp and paper industry. The need for water has not decreased in paper manufacturing processes, but the need for freshwater and at the same time the amount of effluents can be significantly decreased when advanced water purification technologies such as membrane filtration are used. The strongest driving force will also be legislation that sets demands on effluent quality and how much effluent can be discharged. The

Best Available Techniques (BAT) reference document for the production of pulp, paper, and cardboard is an excellent source of information on effluent treatment in the pulp and paper industry; it provides guidance to the industry, member states, and the public regarding achievable emission and consumption levels when using specified BAT techniques.

Several successful examples have shown membrane processes to improve the material, energy, and cost-efficiency of pulp and paper manufacturing processes and decrease the environmental impact of mills. They have also encouraged companies to test membranes. In the future, the importance of membrane processes will increase for water treatment purposes, but also for the recovery and purification of valuable products from different liquors and water-based streams from pulp and paper mills. Biorefineries based on lignocellulosic biomasses are under intensive development, and the use of membranes is an essential issue in this. Membranes will enable the simultaneous recovery, purification, and concentration of monomeric, oligomeric, and polymeric wood compounds from various process streams and extraction liquors, and they can also be used to dewater ethanol for biofuel use.

The development of more resistant polymeric and cheaper ceramic membranes will enable the use of membranes under very alkaline or acidic conditions even at high temperatures, which makes membrane processes an attractive alternative in pulp and paper mill applications. The need for water is increasing worldwide; therefore, purification and reuse of process waters and effluents will increase in importance.

19.7 Further information and advice

A comprehensive review on industrial-scale membrane filtration plants is presented by Mänttäri and Nyström (2009). The review consists of about 30 different industrial examples on the use of membrane processes, excluding coating color applications. Nuortila-Jokinen et al. (2003) intensively discussed water use in pulp and paper making processes and their effluents. Kallioinen, Nyström, and Mänttäri (2013) presented requirements and factors affecting the selection of membranes in pulp and paper applications, in which they deal with key properties of membranes to be taken into account.

The BAT reference document for the production of pulp, paper, and cardboard is an excellent source of information on effluent treatment in the pulp and paper industry; it provides guidance to the industry, member states and the public on achievable emission and consumption levels when using specified BAT techniques. The document also reviews existing industrial-scale purification systems including membrane processes. The last adopted document was in 2001 but the final draft of the new version (July 2013) was published and adopted in spring 2014.

In the future, membrane processes will probably be applied mostly in the fractionation and purification processes in biorefineries. Nanofiltration is a promising fractionation and purification technology for biorefinery applications (Mänttäri, Van der Bruggen, & Nyström, 2013). Almost all of the potential applications are water-based; therefore, water treatment is and will be an essential part of biorefineries.

Membrane Filtration Handbook: Practical Hints and Tips (Wagner, 2001) is recommended as reading material when an industrial-scale membrane filtration process is planned.

List of acronyms

AOX	Absorbed organic halogens
BAT	Best available techniques
BOD	Biological oxygen demand
CAS	Conventional activated sludge
COD	Chemical oxygen demand
CR	Cross-rotational
DAF	Dissolved air flotation
ED	Electrodialysis
GGM	Galactoglucomannan
MBR	Membrane bioreactor
MF	Microfiltration
MLSS	Mixed liquor suspended solids
NF	Nanofiltration
PCD	Pulsed corona discharge
PVDF	Polyvinylidene difluoride
RO	Reverse osmosis
TOC	Total organic carbon
UF	Ultrafiltration
VSEP	Vibratory shear-enhanced processing
WWT	Wastewater treatment

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Membrane technologies for water treatment and reuse in the power industries

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20.1 Introduction

20.1.1 General

In industry, water is used for many purposes such as pure water for the water/steam cycle, as a raw material for chemical reactions, to extinguish fire, and for cleaning and cooling. In particular, power- and energy-intensive industries are major consumers of water.

20.1.2 Water streams

When considering industrial and power plants, one needs to recognize that most water is used for cooling purposes. According to the European Environment Agency (EEA), 44.8% of total available freshwater is abstracted for cooling in energy production. In comparison, the manufacturing industry consumes about 11% of water, half of which is used for processing and the remainder of which is for cooling (EEA, 2010). In other words, the total abstracted freshwater for cooling purpose accounts for approximately half of all water use across Europe. Likewise, in the United States, the thermoelectric industry consumes 46% of all water (Judd & Jefferson, 2005). Most industrial plants typically choose a once-through cooling water system. There, cooling water is not consumed but it is chemically and thermally treated and discharged into the environment. There are ways to minimize the impact on the environment: for example, by limiting chemical use.[1] Cooling water is also used for evaporative cooling towers; the consumption of this water can be in total two-thirds or more of the total water use of industrial plants (fossil fuel and nuclear plants, petroleum refinery plants, etc.). More information about this subject and cooling water systems in general can be found in the literature (Rajagopal, Jenner, & Venugopalan, 2012).

Aside from water consumption the industry needs demineralized (demin) water and produces large sums of wastewater. With regard to wastewater, an important stream

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[1] Thermoshock is an alternative to biocidal dosing; however, a high energy penalty/cost is associated with its use. Also, it is less effective than biocidal dosing against biofouling, corrosion, operational reliability, etc.

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arises from water used to clean flue gases, which must be treated before discharge and/or reuse. This is usually done through physical/chemical processes. In relation to future legislation, the use of organics is expected.

This chapter focuses on water treatment required for the production of demin water used for the water/steam cycle in industrial plants. First, to better understand treatment requirements, the water quality requirements for a water/steam cycle are explained.

20.1.3 Water quality

20.1.3.1 Water quality requirements

The best way to understand water quality requirements is first to understand the water/steam cycle in an industrial plant. The water/steam cycle can be considered as the blood circulation of the boiler/turbine installation (Figure 20.1) because this is the heart of a power plant. Here, as with other living organisms, the quality and health of the blood circulation are key factors for the correct functioning of a boiler/turbine installation. The pure water (boiler water) ensures that the energy freed through combustion is transferred to steam, which in turn drives a turbine. The turbine then drives a generator to produce electricity. Just as in living organisms, the water/steam cycle has different names or distinctions to identify where the blood, or water in this case, is within the system. Giving a clear distinction of water/steam in the cycle helps prevent misunderstanding. Figure 20.1 shows the water/steam cycle with the distinctions: makeup water, feed water, boiler feed water, boiler water, saturated steam, superheated steam, condensate, and condensate return.

Boiler feed water is normally a mixture of makeup water and condensate. This condensate is created after steam has passed the turbine. Because losses occur along the way, new water (makeup water) is needed. The use of poor-quality water here would result in serious problems for the boiler/turbine installation. Corroded boiler pipes in the water/steam cycle are shown in Figure 20.2. Hence, the choice of a raw water source and its treatment are essential to supply appropriate-quality makeup water. A main quality parameter of this makeup water is the sum conductivity, which has a maximum value of 0.10 μS/cm. In comparison, theoretically pure water in which no minerals are present has a conductivity of 0.055 μS/cm.

20.1.3.2 Raw water source

For the production of demin water, the following raw sources are used:

1. Drinking water
2. Well water
3. Industry water (grey water)
4. Surface water
5. Brackish water and seawater

Because of costs and the need to involve authorities, drinking water is used less frequently as a source of raw water. Drinking water originates from surface water treatment and well water. Well water (and drinking water where the source is well water) is

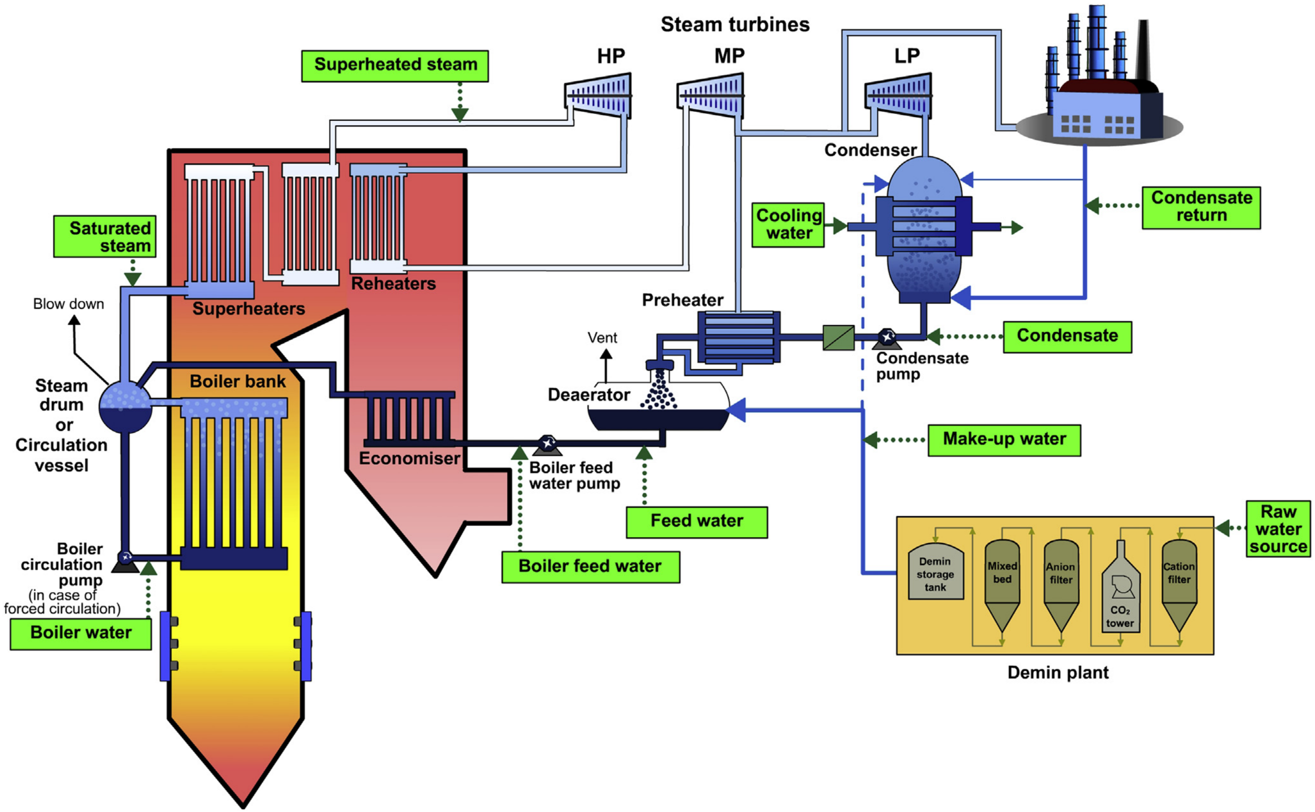

Figure 20.1 Scheme of the water steam cycle.

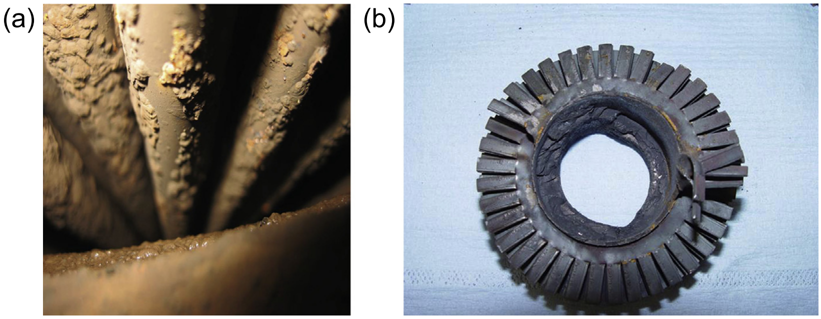

Figure 20.2 (a) Corroded pipes in a combined heat and power plant. (b) Cross-section of a boiler tube-fin with a thick corrosion layer.

the least problematic when it comes to removing minerals; these water sources only possess minerals but no organic material (humic acids). Minerals are relatively easy to remove compared with organic material.

Surface water needs much more treatment for use as demin water. Aside from salts or minerals, surface water has a lot of nondissolved substances that have to be removed. In other words, pretreatment is necessary. Also, surface water contains natural organic matter (NOM), the composition of which changes seasonally. These compounds are not all removed during the demineralization process and hence influence the quality of the end product. The demin water can be of different compositions during spring and autumn. An example of the change in NOM of an industrial water sample (treated surface water) is shown in Figure 20.3, which shows examples in the spring and autumn.

The height of the curve in the figure informs us about the concentration of organic compounds. Most the compounds are removed through ion exchange (IX) and membranes. The removal of polysaccharides, which are found in higher concentrations during autumn, can create a challenge for IX because a great deal of polysaccharides will pass through the resins and end up in the demin water. For membrane technology (reverse osmosis (RO)), these compounds can be prevented from passing through the membrane. However, these compounds cause unwanted fouling of the membranes. An illustration of the diversity and individual concentration of different organic compounds in raw water, such as surface water and drinking water, at different locations in The Netherlands is given in Figure 20.4. The composition of the total organic carbon (TOC) is given; in practise, the TOC is often measured, but not the individual compounds.

20.2 Water purification technologies

The most common technologies used to demineralize water are:

1. IX technology
2. Membrane technology
3. Thermal processes

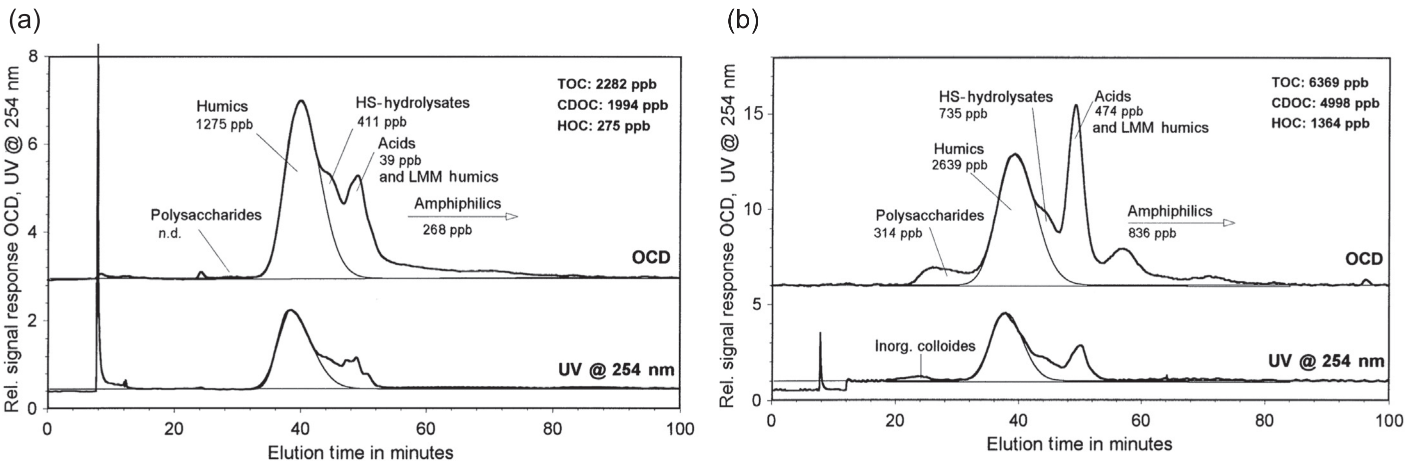

Figure 20.3 Natural organic matter composition in the spring (a) and during autumn (b).

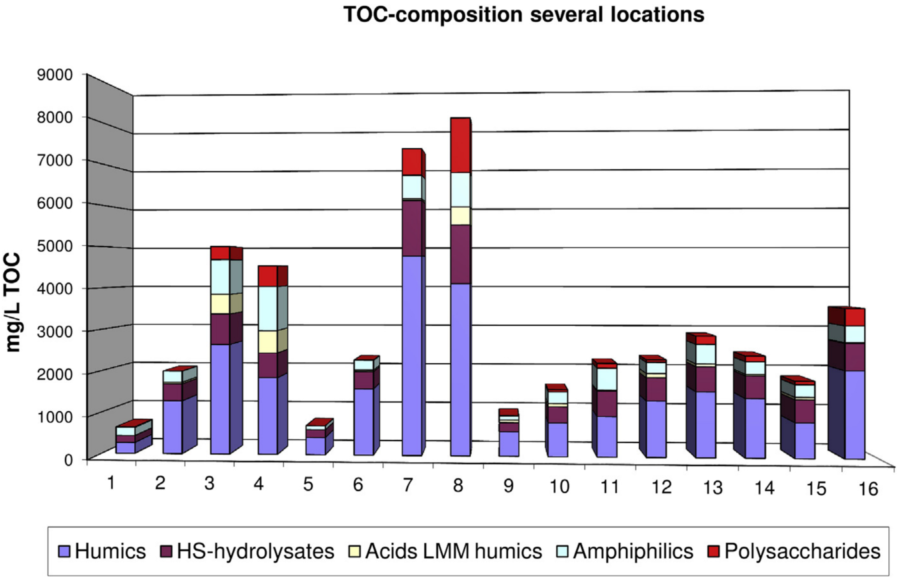

Figure 20.4 Total organic carbon (TOC) composition at different locations throughout The Netherlands.

A description of the two most common technologies is given below. Thermal processes are primarily used in the Middle East as thermal desalination technologies for drinking water (and industrial water) and are not described here. For further reading on this topic, one may refer to the European Desalination Society.

20.2.1 Ion exchange technology

20.2.1.1 General

An IX resin consists of plastic spheres with a diameter smaller than a millimetre. Primarily two different plastics are used: one is based on polystyrene and the other on polyacrylate. Through chemical modification of the polymer, an active group is made on the spheres, where the actual exchange takes place. Figure 20.5 shows an example of an IX resin. The figure shows that the spheres have a uniform size and shape, which is the current state of the art. In the past, different production processes were used and resulted in spheres of different sizes and forms. These nonuniform resins can still be found in older industrial plants.

Because of their active groups there is a distinction between cation and anion resins. A salt that is dissolved in water dissociates in positive ions (cations) and negative ions (anions). A cation resin removes only the cations and the anion resin removes the anions. For this reason, a demin line normally consists of a cation and an anion filter. If the water quality is not according to specifications after leaving these two filters, a mixed bed (anion and cation resins in one tank) is used. A simple representation is given in Figure 20.6.

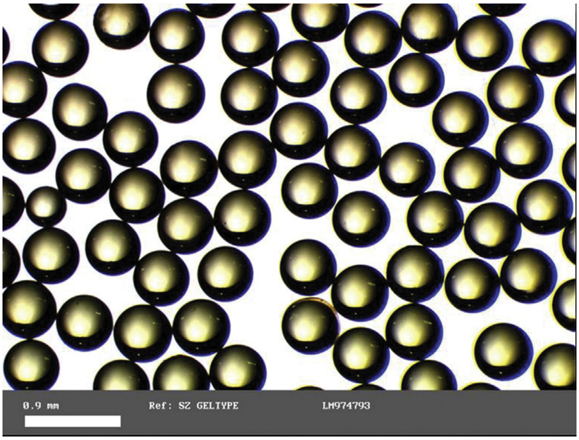

Figure 20.5 Ion exchange resin with spheres of uniform size and shape.

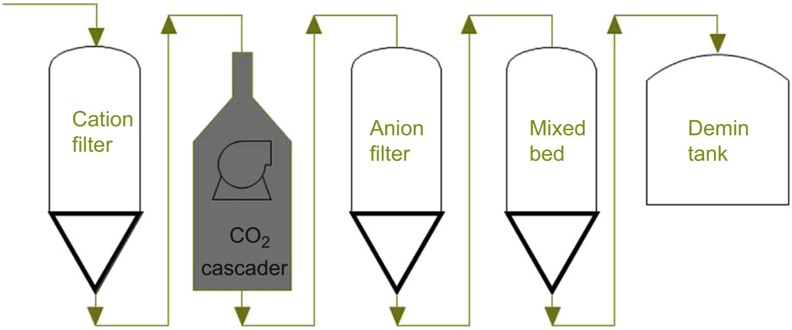

Figure 20.6 Demin line using ion exchange (IX) technology.

Figure 20.6 also shows a carbon dioxide (CO_2) cascader or tower, where CO_2 is removed. This is the result of acidic water coming from the cation filter and the hardness of the water. Therefore, it is not necessary to remove this hardness (present as carbonate and bicarbonate) in the anion filter. This results in savings in the amount of resin needed for the anion filter.

Currently, demin lines are run against current flow. At a certain point the resins will be fully loaded with ions and will have lost their capacity to demineralize. To revert to normal operation cation resins are treated with an acid such as hydrochloric acid, and anion resins with sodium hydroxide. The most effective way to have this treatment done is in a countercurrent flow.

20.2.1.2 Operational experience

In practise, anion resins are less stable than cation resins. This is primarily related to the maximum operating temperature of 40 °C for anion resins. Above these temperatures the anion resin loses active groups, and hence its functionality.

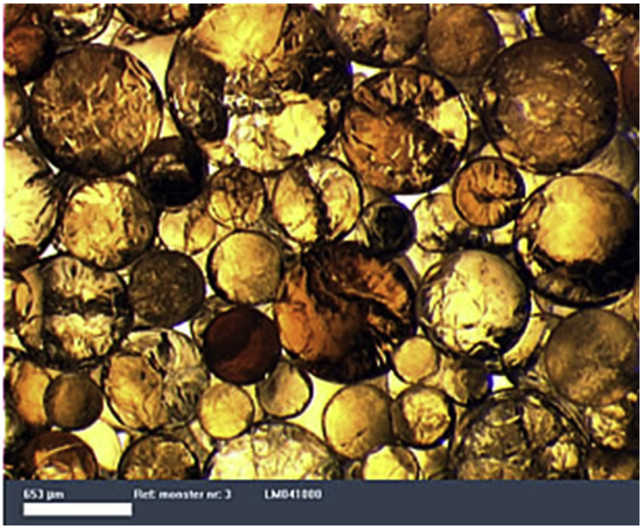

Figure 20.7 Dried-out resin.

The resins can be of a flexible gel or the 'tougher' macro-porous resin type. Both types consist of polymers. As such, the exchange groups in the resin network attract a lot of water from the outside. A dry resin grain swells like a sponge; in doing so, waterways are created inside the resin grain. The macro-porous type resin also takes up water; however, it already has high porosity. This porosity ensures a rapid exchange but results in a lower capacity of the resin.

As mentioned, the resin grains take up a lot of water and thus swell. If the grains dry out, they shrink and cracks can form. The grains still have the capacity to demineralize, but because of the cracks they could break into pieces. This can lead to blockages in the resin bed and pressure buildup in the column. An example of dried resin grains is shown in Figure 20.7. Aside from the many cracks visible on the grains, the shape and form of the spheres are not similar to new IX resins. The photo also shows an older resin.

20.2.2 Membrane technology

20.2.2.1 General

Aside from the preparation of ultra-pure water for the power industry, membrane process systems are used to treat different types of water such as wastewater and to produce drinking water.

In general, membranes act as filters. Depending on the pore size, one can distinguish among the following types (see also Figure 20.8):

1. Microfiltration (MF) with pore sizes of >0.1 µm
2. Ultrafiltration (UF) with pore sizes of 0.01–0.1 µm
3. Nanofiltration (NF) with pore sizes roughly between 0.01 and 0.001 µm
4. RO membranes, which are <0.001 µm

The actual pore sizes will differ from the theoretical ones. In the literature a wide variety of classifications for different membrane types can be found.

Microfiltration and UF membranes are normally used to separate particles, whereas NF and RO change the chemical or ionic composition of the water because they remove small molecules and ions from the water (source: prime water Web site). Figure 20.8 shows a membrane filtration spectrum, indicating the type of contaminants that can be removed by different membrane types.

Under normal operation conditions, membrane systems are easy to operate with low chemical consumption and constant water quality, which increases the reliability of the system. The main drawback of membrane technology is the relatively high energy consumption. This is particularly true in areas where, for example, seawater has a high salt content, such as in the Middle East. There, RO systems have become popular for desalination purposes and for demin water production for the power industry.

According to Kabsh-Korbutowicz (2006), the economic use of membrane filtration systems is often limited by fouling, because this results in increased pressure drops that affect energy consumption. Hence, there is an increase in the frequency of cleaning, which affects the production rate of the membranes. Therefore, it is important to prevent the membranes from fouling. This can be done by applying the right pretreatment, using membrane materials that are less susceptible to fouling, and ensuring good control and operation of the system.

Over the years, the energy consumption of membrane systems has been further reduced by the introduction of energy recovery systems that recover the pressure of the concentrate stream, using this energy to increase the pressure of the feed flow (Avlonitis, Kouroumbas, & Vlachakis, 2003).

20.2.2.2 RO membranes

Most RO membranes are constructed as a spiral-wound module, as shown in Figure 20.9. There are hollow-fibre membrane modules, but these are much less

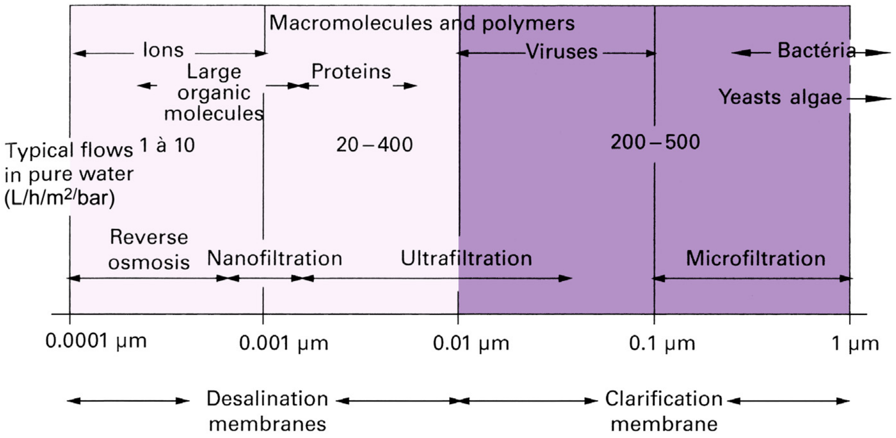

Figure 20.8 Membrane filtration spectrum (Water treatment handbook, 2007).

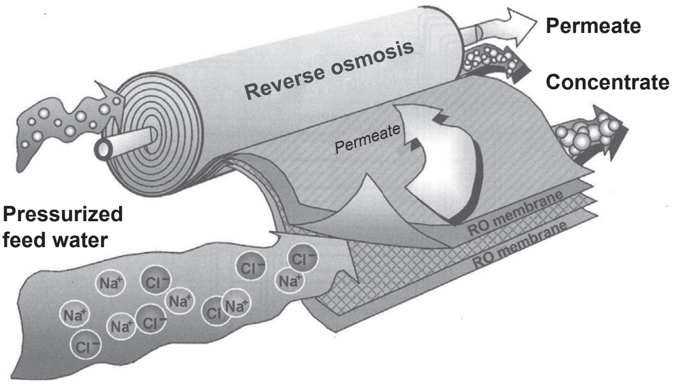

Figure 20.9 Spiral-wound membrane (Judd & Jefferson, 2005).

common. The spiral-wound module consists of a membrane, mesh paper (or spacer), and permeate tube. The spacers are used to create flow channels within the module and ensure equal distribution of the flow. The membrane is glued on three sides and the open side is connected to a central permeate tube, around which the membrane sheets are rolled (Figure 20.9).

RO membranes are made of polymers, mostly cellulose acetate or composite polyamide-type membranes.

In practise, individual membrane modules are called elements. Multiple membrane modules (or elements) behind each other will form a train, and several trains together form the system. If it is a large system, several trains can also form a stage and more stages are needed to complete the entire system. Depending on whether the system is used to concentrate the brine product or to produce high-quality permeate, the connection between the modules will be of the concentrate or the permeate.

20.3 Operational experience with membranes

20.3.1 General

Most membranes for water treatment can withstand temperatures of up to 50 °C. However, this should be verified by the manufacturer's specifications because some membranes have a lower temperature limit (Bates, 1998). Another important parameter is pH. Cellulose acetate membranes can be operated only within a small pH range; the pH should be kept between 4 and 6. On the other hand, these membranes are resistant to oxidation by chlorine. Thin-film composites membranes can be operated within a large pH range, 3—11, but they are sensitive to the presence of chlorine. When using these membranes, steps have to be taken to ensure no residual chlorine will reach the RO modules. To combat residual chlorine, sodium metabisulphite can be added to the intake. Intake pipes for desalination plants and cooling water intake pipes can have free chlorine present to prevent biofouling. In the power industry, demin plants typically extract their raw water source from the cooling water circuit and discharge the brine there as well.

Another method to reduce the risk of fouling and reduce energy consumption is to increase the flow rate. To increase the flow rate, hydrophilic membranes are often used. With these membranes, water will easily pass through the membranes, whereas hydrophobic contaminants will be repelled, reducing fouling. Cellulose acetate membranes are most hydrophilic, but have a lower salt rejection compared with polyamide membranes.

Another factor that determines fouling and the fluxes of the system is the surface charge of the membranes. Cellulose acetate membranes are neutrally charged, whereas polyamide membranes can attract charged organic and colloidal material from the feed water (Membrane Web site).

The most important fouling mechanisms will be discussed next, together with ways to prevent fouling, and how the effects of fouling can be minimized.

20.3.2 Fouling

One of the most important aspects of the operation of membrane systems is fouling. Fouling increases the pressure loss over the membrane surface, resulting in higher energy consumption and lower salt rejection. Also, higher fouling rates increase the cleaning frequency, lowering the production rate (or the availability of a plant) and increasing chemical consumption.

Therefore, it is essential to reduce fouling and minimize its effects. The first step to combat fouling is to determine what kind of fouling the system is dealing with, because different types of fouling require different measures. Furthermore, good control of the process and cleaning conditions is essential to prevent and overcome the effects of fouling.

20.3.3 Types of fouling

Different fouling sources can be described as follows:

1. Fouling through concentration polarization
2. Organic fouling
3. Biological fouling
4. Colloidal and suspended fouling
5. Scaling

20.3.3.1 Concentration polarization

This type of fouling occurs when salts and other rejected solutes concentrate near the membrane surface. A laminar boundary layer will be present as the fluid adjacent to the membrane moves slower than the main stream (Porter, 1990). As a consequence, the salt rejection of the membrane decreases and therefore negatively affects the quality of permeate. Also, the osmotic pressure will increase owing to the concentration of the salts. This results in an increase in energy consumption.

Concentration polarisation cannot be avoided. The only way to combat this phenomenon is to reduce the boundary layer by optimizing the hydraulic conditions. This is done by increasing the flow rate across the membrane surface or introducing turbulence promoters into the feed/reject stream. To increase turbulence, end spacers are designed in spiral-wound membrane modules to optimize hydraulic conditions within the module.

20.3.3.2 *Organic fouling*

Organic matter originating from feed water has different compositions throughout the world and its composition can change dramatically over time. This makes it challenging to combat organic fouling. Organic fouling will increase the pressure drop over the membrane (trans-membrane pressure (TMP)). Figure 20.10 shows a fouled RO membrane.

Because most natural organic matter is charged, it will bind to charged membrane surfaces from polyamide membranes. In these situations, organic matter will prefer the membrane over the water phase and will stick to the membrane causing fouling. One of the most important compounds leading to organic fouling is humic acid in the feed water, which acts as a weak acid and retains metals such as iron. Furthermore, organic matter can serve as a feeding source for bacteria and enhance biofouling.

Also, for organic fouling, when coagulation and flocculation are applied as pretreatment, the addition of too much flocculation chemical will lead to increased organic fouling. The same is true for the addition of antiscalants.

Organic fouling will take place over all membrane stages. To combat organic fouling, new membrane types with a neutrally charged surface have been developed. In this way, the charged organic material will have fewer tendencies to attach to the membranes.

Figure 20.10 Fouled membrane photo taken near the collector of the membrane module.

20.3.3.3 Biofouling

Biofouling is a major concern for membrane systems. Biofouling can be divided into microfouling and macrofouling. Because macrofouling (mussel growth) occurs in intake pipes and cooling water systems, it is not a direct threat to membrane operations. On the other hand, microfouling will occur on membranes and will have an effect on the performance of the water treatment. Microfouling refers to bacterial growth, which can occur on the organic matter of the membrane surface and result in increasing TMP. Also, bacteria can produce extracellular polymeric substances, mostly polysaccharides, which also result in fouling. The formation of polysaccharides combined with bacterial growth makes cleaning measures less effective because these microorganisms are embedded with polysaccharides and hence are not easily removed.

Within membrane modules, 'dead zones' should be avoided. They lead to the increased growth rate of microorganisms (Ho, Altman, Jones, Khalsa, & McGrath, 2008). By applying equal flow conditions, biofouling can be prevented. Spacers of spiral-wound membranes can also be a growth place for microorganisms, augmenting biofouling.

To prevent the growth of macro- and microorganisms in the intake (pipe of the plant) and on the membranes, installations are often disinfected. This is often done by applying free chlorine. As already discussed, the addition of chlorine can damage the membranes, but they also can potentially have negative effects on biofouling. Organic matter can be broken down into bite-size pieces that can be readily taken up by bacteria present on the membrane surface.

Biofouling typically occurs in the first membrane stages. Biofouling can be observed by following the flux and the salt rejection. In this case, the flux will decrease in the beginning, with increasing salt rejection (AEDyR, 2009). After this initial phase, salt rejection will also decrease.

20.3.3.4 Colloidal and suspended fouling

Excessive volumes of colloidal and suspended material will plug the RO element feed path regardless of the membrane type. Fortunately, as with all other types of fouling, this type can easily be combated with proper pretreatment. This can be done through filtration, coagulation, sedimentation, flotation, and decanters. Typical levels of colloidal and suspended particles would be less than 1.0 NTU for turbidity and a silt density index value below 4 (AEDyR, 2009).

20.3.3.5 Scaling

From the information about concentration polarization, it is clear that within the laminar boundary layer of the membrane, the concentration of rejected solutes strongly increases. Salts will also be concentrated in this layer. When the concentration exceeds the solubility product, salts will precipitate and can even form crystals on the membrane surface, thus increasing the TMP and lowering the salt rejection.

Known scaling compounds are calcium carbonate, barium sulphate, calcium phosphate, strontium sulphate, and calcium fluoride.

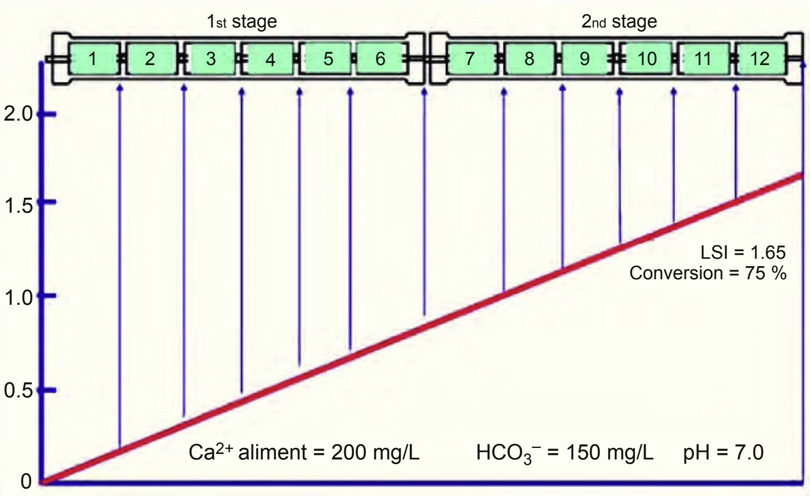

Figure 20.11 Langlier saturation index with membrane steps (AEDyR, 2009).

The scaling effect increases with the different stages, when concentrate from the previous stage is used as feed water for the next. This is illustrated by the Langlier saturation index, which increases with each membrane separation stage (Figure 20.11).

According to Al-Shammiri and Al-Dawas (1997), four methods can be used to reduce the risk of scaling:

1. Lowering the pH to remove carbonate from the system
2. Adding antiscalant, which will broaden the solubility limits of the salts
3. Reducing the recovery rate so that the concentration on the outside of the membrane is reduced
4. Dehardening the feed water

Furthermore, the addition of chemicals may be a source of fouling. For example, when coagulant is added during pretreatment, the membranes can be fouled with iron oxides if the coagulant addition is not controlled correctly.

20.3.4 Combating fouling

20.3.4.1 Pretreatment

Pretreatment is required to suppress fouling and/or clogging of membranes, or to remove chemically aggressive constituents such as chlorine (Judd & Jefferson, 2005). The objective is to clear the feed stream from everything potentially harmful to the membrane performance and/or lifetime. Measures taken are:

1. Mechanical prefiltration
2. Acidification to reduce carbonate hardness, followed if necessary by aeration to reduce CO_2
3. Addition of antiscalants to keep divalent salts (sulphates) from precipitating

4. Chlorination (or alternative oxidation) to deactivate microorganisms, usually followed by dechlorination to safeguard against membrane degradation (Böddeker, 2008)
5. Removal of colloids and metals from the feed water by coagulation and flocculation

Pretreatment can consist of sand filtration, dissolved air flotation, and activated carbon filters, as well as other membrane systems such as MF and UF. This last combination (MF−UF followed by RO) has become increasingly popular.

20.3.4.2 Cleaning-in-place

Notwithstanding the measures applied to combat fouling, it is inevitable that some will occur. In time, the fouling rate will increase and should be removed or controlled to make sure fouling does not become irreversible. Therefore, it is important to clean the membranes when they are only lightly, not heavily fouled. Heavy fouling can impair the effectiveness of the cleaning chemical by impeding the penetration of the chemical deep into the foulant and in the flushing of foulant out of the membrane elements (Technical Service Bulletin 107.20. Hydranautics). According to the same source, some fouling is allowed as long as:

1. Normalized permeate flow decrease is less than 10%
2. Normalized permeate quality decrease is less than 10%
3. Increase in normalized pressure drop, as measured between the feed and concentrate headers, is less than 15%

Fouling increases the TMP, which increases pressure on the membranes, increasing the risk of mechanical damage to the membrane surface.

By controlling the fouling rates, the cleaning frequencies can be reduced, resulting in a higher production rate and lower chemical consumption.

RO membranes cannot be back-washed because of the high pressure that would be needed, which could potentially damage the permeate side of the membranes. Therefore, RO membranes are flushed from the feed to the concentrate side or from the concentrate side to the feed. Besides flushing, so-called ‘cleaning-in-place’ is applied: Membranes are soaked for several hours with a chemical solution and are flushed afterward to remove the chemicals.

Organic fouling can be removed using high-pH cleaning: for example, with sodium hydroxide. Inorganic fouling can be removed with acid cleaning agents such as sulphuric acid or citric acid.

Normally, it is advised first to apply alkaline cleaning, followed by acid cleaning. In the case of multistage systems, it is recommended to clean every step separately to avoid fouling that would go through the whole system before it is removed.

Often, the effectiveness of the cleaning increases with temperature; in that case, the cleaning chemicals can be heated. This option should be taken into consideration during the design phase.

Another important factor for cleaning is the flux. Turbulent conditions will increase the shear forces on the fouling and increase the removal rate.

20.3.5 Route cause analysis

In practise, one can encounter poor membrane performance. If the likely cause is assumed to be membrane fouling, the following route cause steps can help identify the type and cause of fouling:

1. Check on process conditions
2. Check on monitoring equipment
3. Conduct visual inspection of pretreatment and water production installation
4. Gather previous inspection reports and process condition data
5. Conduct visual inspection of membrane modules from different stages
6. Gather the fouled material and conduct a composition analysis

With respect to process conditions, trends in flux, TMP, and permeate quality normally give a good indication of the type of fouling taking place. This is shown in Table 20.1, where the effects of different types of fouling on process conditions are given.

Table 20.1 **Troubleshooting matrix**

Possible cause	Possible location	Pressure drop	Feed pressure	Salt passage
Metal oxide fouling (e.g. Fe, Mn, Cu, Ni, Zn)	First stage lead elements	Rapid increase	Rapid increase	Rapid increase
Colloidal fouling (organic and/or inorganic complexes)	First stage lead elements	Gradual increase	Gradual increase	Slight increase
Mineral scaling (e.g. Ca, Mg, Ba, Sr)	Last stage tail elements	Moderate increase	Slight increase	Marked increase
Polymerized silica	Last stage tail elements	Normal to increased	Increase	Normal to increased
Biological fouling	Any stage, usually lead elements	Marked increase	Marked increase	Normal to increased
Organic fouling (dissolved NOM)	All stages	Gradual increase	Increase	Decreased
Antiscalant fouling	Second stage most severe	Normal to increased	Increase	Normal to increased

Source: Hydranautics.

One may need to calibrate and check the monitoring equipment to make sure that it is operating correctly. The manner of sampling is also important, as is the processing and recording of data in the plant's data collection system. Operating personnel, who have many obligations, have been known to fail to identify the need to pay attention to monitoring equipment.

This is also true when inspecting the operating water production installation. For example, the antiscalant or coagulant supply tank could be empty or the flow of these units could be incorrectly set. Thus, it is important to visually conduct a regular check on the monitoring equipment and operating water production installation and pretreatment units.

When adopting a route cause analysis, vital pieces of information are the gathered data and the process information from the supplier, i.e. inspection reports, operating conditions, performance trends, age of the unit and the membranes. With this historic data, one can compare the operating ranges with those of the supplier or during the commissioning phase.

Visual inspection of one or more membrane modules that have been taken out of use, preferably of each stage, gives valuable information on the type of fouling. For some fouling types the formation of salt crystals versus organic/biofouling can easily be distinguished. Documentation through photographs is important.

Samples can be gathered for further characterization by collecting them over the length of the membranes to check for differences in fouling with the flow, and also between different membrane stages (Figure 20.12). The samples can be analysed for inorganic and organic matter or through further analysis using, for example, scanning electron microscopy with electron diffraction spectroscopy and/or atomic absorption spectroscopy.

Alternatively a nondestructive technique is to conduct a leakage test over the membranes.

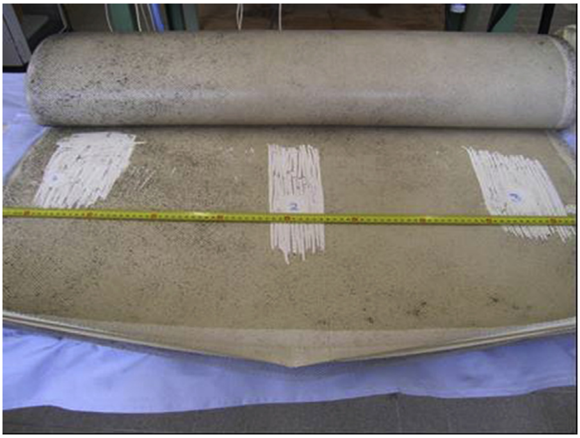

Figure 20.12 Fouling and sampling points of the membrane.

20.4 Future trends

20.4.1 Evaporated water capture

A hidden source of relatively clean water is the evaporated water present in many industrial processes. In these processes, water is produced and/or liberated and escapes as 'waste' water into the atmosphere. This evaporated water can be captured using gas separation membranes. With a sufficiently selective membrane, purified water can be produced in a single process step. Advantages of the proposed process compared with traditional separation are:

1. High energy efficiency: no phase change is required to achieve separation
2. Temperature neutral to the source, which makes heat recirculation in industrial processes interesting
3. High reliability: no moving parts
4. Small footprint: it generally easily fits in existing spaces, factories, etc.
5. Environmentally friendly: no use of chemicals, no waste streams
6. Energy savings: aside from recirculation, reheating of flue gases is no longer necessary and latent heat can be reused in the process
7. Corrosion benefits: removal of water vapour from flue gas streams helps mitigate corrosion

Considering these benefits, the demin water produced with this technology can compete with existing demin water technologies. To this end, the European Commission funded the CapWa project to bring this technology a step closer to realization. More information can be found in http://www.watercapture.eu.

20.4.2 Forward osmosis

In contrast to RO, in which water is pushed through a semipermeable membrane, forward osmosis needs almost no pressure to have the water flow to the other side of the membrane. The difference between both techniques is that in the case of forward osmosis, the water crosses the membrane from the lower osmotic pressure to the higher osmotic pressure side. This process requires very little energy because it is a natural process (see Figure 20.13); RO osmosis uses a lot of energy to pressurize water to overcome osmotic pressure, because the water needs to cross the membrane from the higher osmotic pressure to the lower osmotic pressure side.

In forward osmosis, the higher osmotic pressure is artificially created by adding salts. This addition takes place on the retentate side of the membrane, rather than on the permeate side. Thus, by creating a controlled saline water stream, water from a dirty stream (seawater or wastewater) will pass the membrane and leave pollution behind with almost no energy consumption. The challenge of forward osmosis is to recover clean water from this artificially created saline water stream. Therefore, a second process is required; this could be physical separation, a thermal process, membrane separation, or a combination of all three. Also, there are some applications in which a second step is not required, such as makeup for cooling towers and 'hydration

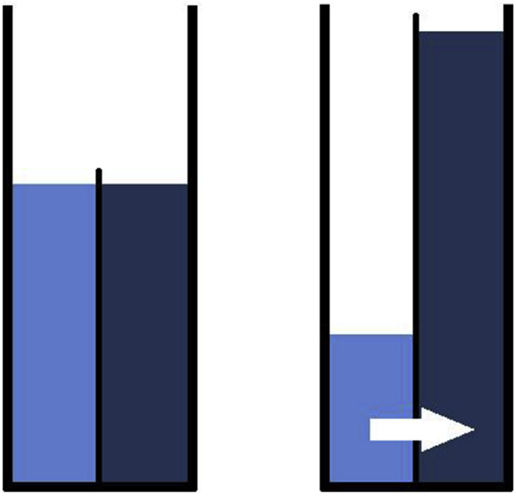

Figure 20.13 Principle of forward osmosis.

bags’. In hydration bags, high concentrations of sugars provide the difference in salinity; by putting this bag into ‘dirty’ water, it will attract only clean water, which ends up as a drinkable sugar solution (McCutcheon, McGinnis, & Elimelech, 2005; Salter, 2005).

20.5 Recommended reading

Journals and recommended reading are as follows:

Journals:

1. *Power Plant Chemistry*
2. *Ultra Pure Water*
3. *VGB Powertech*
4. Local journals: for example, in The Netherlands, H_2O. Similar journals can be found in your respective country

Conferences:

1. European Desalination Society
2. Chemie im KraftWerk
3. Aquatech

Web sites:

1. EDS
2. Global Water Intelligence

List of acronyms/symbols

CA	Cellulose acetate
IX	Ion exchange
NF	Nanofiltration
NOM	Natural organic matter
RO	Reverse osmosis
SDI	Silt density index
TOC	Total organic carbon
TMP	Trans-membrane pressure
UF	Ultrafiltration

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