Membrane Operations in Water Treatment and Reuse

Enrico Drioli
University of Calabria, Arcavacata di Rende (CS), Italy
WCU Energy Engineering Department, Seoul, South Korea

Francesca Macedonio
University of Calabria, Arcavacata di Rende (CS), Italy

ABSTRACT

In the last decades membrane operations have gained great success in water treatment and reclamation because their efficiency has been proven from a technical, economical and environmental point of view. Due to their unique advantages like high recovery factor, decreased footprint, low energy requirement and relatively high selectivity, membrane processes are being increasingly used in water treatment and their costs have decreased rapidly.

This manuscript gives an overview of the membrane operations used in water treatment, some details regarding their theoretical background and various examples of applications. Then, the advantages in the use of integrated membrane systems and the future development of membrane technology are presented.

INTRODUCTION

Nowadays membrane processes are essential operations for a wide range of applications, including energy generation, tissue repair, pharmaceutical production, food packaging, and the separations needed for the manufacture of chemicals, electronics and a range of other products (Rios et al. 2007). However, water treatment is the field that epitomizes the success of membrane technology, both for overcoming water scarcity and for preventing water pollution.

The modular design of membrane operations, the operational simplicity and flexibility, the compactness and small carbon footprint of these plants (Drioli and Curcio 2007; Peters 2010), the short construction time, the relatively high selectivity and permeability for the transport of specific components, the good stability under a wide spectrum of operating conditions justify the success of membrane science and membrane engineering. The low energy requirement as well as the economic and long term operational reliability are further advantageous aspects. These features result from the intrinsic properties of the membranes, from their combination with an appropriate module configuration and plant design, and from the work of researchers able to face the basic problems related to the understanding the final morphology of dense and porous membranes, their transport mechanisms, and to develop new membrane operations for molecular separation, mass and energy transfer between different phases.

Membrane operations have been able to show their potentialities in the rationalization of water treatment systems and the use of membrane systems has increased significantly: in 1997 the membrane sales were only US$ 900 million (Peter-Varbantes et al. 2009). Between 2006 and 2010, the global market in membrane systems for water and wastewater applications grew from US$ 6.7 billion to US$ 10 billion (Peter-Varbantes et al. 2009). 60% of the total worldwide desalination installed capacity is based on reverse osmosis (RO) technology. Conventional wisdom in the desalination industry says that thermal technology is in terminal decline because of the higher energy consumption and lower recovery factor with respect to

© 2012 by the Society for Mining, Metallurgy, and Exploration. All rights reserved. Electronic edition published 2012.

membrane based operations. Moreover, water price with RO is 23% cheaper than thermal processes (IDA Desalination Yearbook 2010–2011).

In the next sections, first an overview of the existing membrane-based water treatment processes will be given. Then, the future development of membrane technologies will be illustrated.

MEMBRANE PROCESSES FOR WATER TREATMENT

In many regions of the world, due to large population, tourist infrastructure and industrial development increase, it is no longer possible to satisfy the growing water demand by conventional methods of water supply and processing. Therefore, keeping in mind that water has a value and not only a price, in addition to a more conscientious use of natural resources, an increased utilization of advanced separation techniques such as membrane operations was witnessing.

Membranes are used to produce potable water from the sea, to clean industrial effluents, and to recover and reuse municipal wastewaters. The production of potable water from saline and polluted waters is essential for increasing the amount of available good quality water. The purification and reuse of wastewaters is crucial for rising the exploitation of potable water and reducing its consumption. The treatment and recycling of process waters (e.g., the purification of the effluent from sewage treatment plants) is indispensable for preventing further contamination of water resources.

In general, membrane processes are characterized by the use of a semi-permeable thin barrier (i.e., the membrane) that controls the exchange between two phases on the basis of the applied driving forces, the fluid properties and through the intrinsic characteristics of the membrane material itself. The driving force can be a difference in pressure, concentration, temperature or electric potential. Most membrane processes are pressure-driven (microfiltration, ultrafiltration, nanofiltration, reverse osmosis and membrane bioreactor), where the driving force is an hydrostatic pressure difference across the membrane. In water treatment, however, electrically driven (e.g., electrodialysis) and thermally driven processes (e.g., membrane distillation) are also used.

In a membrane process the water to be treated is separated into a stream of filtrate (or permeate) and one of retentate (or concentrate or brine, containing the components of the feed water rejected by the membrane). The quality of the produced filtrate depends on the characteristics of the membrane technologies in relation to the water-borne contaminants:

- Microfiltration (MF) is used, e.g., for suspended solids and large bacteria removal from waters. MF membranes are usually symmetric microporous structures, with pore size in the range of 10–0.05 µm (Mulder 1996). The membrane thickness can extend from 10 to more than 150 µm. Separation is accomplished by MF membranes via mechanical sieving and particles are separated solely according to their dimensions with respect to those of membrane pores. The hydrostatic pressure difference used as driving force is low (usually less than 2 bar).
- The membranes used in ultrafiltration (UF) have an asymmetric structure with pore size (1–50 nm) small enough to ensure high removal of all kinds of microbiological hazards such as Cryptosporidia, Giardia and total bacterial counts (Hagen 1998); suspended solids, large bacteria, dissolved macromolecules, colloids and smaller bacteria are retained; turbidity and suspended solids are completely removed. Substantial virus removal can be also attained with UF membranes since the size of viruses is in the range of 30–300 nm (Peters 2010). The operating pressure is up to 10 bar.

© 2012 by the Society for Mining, Metallurgy, and Exploration. All rights reserved. Electronic edition published 2012.

- Nanofiltration (NF) and reverse osmosis (RO) can be used to remove low molecular weight solutes (such as inorganic contaminants, inorganic salts or small organic molecules) from waters. Both processes are considered as one process since the basic principles are the same. RO is operated with tighter type of membrane than NF. Most NF membranes are effective for color, sugar and dye removal or for removing hardness, sulfate, bivalent ions (typical retention > 90%). RO membranes are required for monovalent ions removal (e.g., desalination of seawater or brackish water is currently performed with RO membranes), and for the separation of dissolved salts and ions with a molecular weight of less than 200 g/mol (Peters 2010). Compared to MF and UF, in NF and RO the organic and inorganic molecules are separated from a feed solution by a solution diffusion process. The operating pressure is up to 25 bar for NF and up to 80 bar for RO.
- Membrane bioreactor (MBR) is a separation process combining membrane filtration with biological treatment which is finding increasing applications for industrial and municipal water treatment.

  Conventional MBR uses low-pressure membrane filtration, either MF or UF, to retain the mixed liquor of the bioreactor, and delivers particle-free treated effluent (Lay et al. 2010). Because the membrane is an absolute barrier for bacteria and in the case of UF also for viruses, the MBR process provides a considerable level of physical disinfection. The resulting high quality and disinfected effluent implies that MBR processes can be especially suitable for reuse and recycling of wastewater.

  Advantages in the use of MBR are as follows: (i) the technology permits bioreactor operation with considerably higher mixed liquor suspended solids (MLSS) concentration than conventional activated sludge (CAS) systems, which are limited by sludge settling; (ii) compactness (up to 5 times more compact than a CAS plant).

  With respect to costs, MBR is considered a high tech process, with higher initial investment costs than conventional wastewater treatment. Moreover, the energy demand to cope with membrane fouling is the main contribution to the overall operating costs (Kraume and Drews 2010).

  Membrane bioreactors are by now almost exclusively used in wastewater treatment. However, the great potential of MBRs to produce high quality effluent could also be of great interest in the removal of a variety of anthropogenic organic pollutants and fouling agents that are increasingly present in sea/brackish-water.
- In electrodialysis (ED) charged membranes are used to remove ions from aqueous solution. A number of cation- and anion-exchange membranes are placed in an alternating pattern between a cathode and an anode. When a direct current is applied, the positively charged ions migrate to the cathode and the negatively charged ions to the anode. Therefore the cation-/anion-exchange membranes are ion-selective membranes which control the movement of ions. Thus, the concentration of ionic species is reduced in the so-called *diluted* compartments and increased in the *concentrated* compartments.

  In commercial applications several hundreds of cell pairs are assembled in a stack and in this way the applied driving force is very effective.

  ED has been in commercial use for desalination of brackish water for the past three decades, particularly for small- and medium-scale processes (AlMadani 2003; Charcosset 2009).

© 2012 by the Society for Mining, Metallurgy, and Exploration. All rights reserved. Electronic edition published 2012.

Table 1. Membrane distillation applications

Desalination and pure water production from seawater and/or brackish water
Nuclear industry (concentration of radioactive solutions and wastewater treatments; pure water production)
Textile industry (removal of dyes and wastewater treatment)
Industrial and municipal used waters (removal of small size and persistent contaminants)
Chemical industry (concentration of acids, removal of VOCs from water, separation of azeotropic aqueous mixtures such as alcohol/water mixtures and crystallization)
Pharmaceutical and biomedical industries (removal of water from blood and protein solutions, wastewater treatment)
Food industry (concentration of juices and milk processing) and in areas where high temperature applications lead to degradation of process fluids

ED process is non-economical for waters with high salts concentrations (Van der Bruggen and Vandecasteele 2002; Fritzmann 2007), but is competitive for brackish waters with up to 3000 ppm salt.

- Membrane distillation (MD) is a thermally driven membrane process which operates on the principle of vapour-liquid equilibrium. In this process, two solutions at different partial pressure are separated by a hydrophobic porous membrane and the solutions must not wet the membrane. When a vapour pressure difference exists across the membrane, the vapour molecules are transported through the membrane pores, from the high vapour pressure side to the low vapour pressure side. Only volatile components are transferred through the membrane, therefore 100% (theoretical) of non-volatile components are rejected and a high quality permeate can be obtained.

  MD is a membrane process in which the membrane does not distinguish between solution components on a chemical basis, does not act as a sieve and does not react electrochemically with the solution. Membrane in MD acts merely as a support for the vapour-liquid interface and the selectivity is determined by the vapour-liquid equilibrium involved.

  MD applications are essentially determined by the wettability of the membrane. To avoid wetting, the surface energy of the polymer must be low (polypropylene, polytetrafluoroethylene and poly(vinylidene fluoride) are usually used), the maximum pore size small (pore size in the range of 0.2–1.0 μm is desiderable), the surface tension of the liquid high (e.g., water). The latter implies that mainly aqueous solutions containing inorganic solutes can be treated. MD can be used for (Table 1): (i) water desalination, (ii) the treatment of water for the semiconductor industry or power plants, (iii) the treatment of wastewaters, (iv) the removal of volatile bioproducts.

POTENTIAL FOR INTEGRATION

Water treatment processes were revolutionized by the introduction of membrane operations. In particular seawater desalination was transformed by RO technology. In comparison to conventional water treatment, the main advantages of membrane processes are that, in principle, water can be treated in one stage without chemicals or utilities, the footprint is relatively small, the membrane system can be built in a modular form which enables easy adaptation of process scale. However, the main limitation of membrane systems is fouling. Components

© 2012 by the Society for Mining, Metallurgy, and Exploration. All rights reserved. Electronic edition published 2012.

present in the feed water can be deposited and/or absorbed on the membrane surface. This inevitable phenomenon, called membrane fouling, makes necessary to perform proper pre-treatment of the feed and periodic membrane cleanings in order to maintain the economic feasibility of membrane operations.

Also the handling of the produced retentate is not an easy task. The solution chosen for the brine rejection depends on several parameters, such as chemical composition, flow and dilution- rates of the concentrate, etc.

In the case of seawater desalination, the brine can be discharged directly in the natural environment (e.g., for desalination plants located near coastal areas the concentrate stream is discharged to the sea). In this case particular attention should be given to the possibility of dangerous ecosystem modifications. When the concentrate cannot be directly discharged (such as in some brackish water desalination plants), it is frequently discharged into solar evaporation ponds.

While well known technical solutions are usually available for the design and the manufacture of a membrane based unit, the pretreatment of the water to be processed as well as the handling of the retentate (here referred as post-treatment) represent crucial aspects of each water treatment process, those determining the success or the failure of a plant. Pre-treatment and post-treatment have to be adapted to the specific conditions at the construction site of a plant. These can differ over a wide range, depending also on the raw water characteristics. They include the systems for dosage and the handling of chemical agents for pretreatment and for the cleaning of membranes.

In addition, the wastewater generated in the pretreatment and the wastewater generated during membrane cleaning are polluted effluents whose final destination must be controlled. It is advisable to treat them separately and not to mix them for discharge (as it has been usual practice in the past). On one hand, the separate handling allows for recycling possibilities for certain partial streams and, on the other hand, an environmentally sustainable operation that avoids the contamination of the receiving water body is achieved (Peters 2010).

A significant possibility for improving further current water treatment systems is offered by the mutual compatibility of different membrane operations for integration. Integrating diverse membrane operations means coupling various membrane processes for (i) overcoming the limits of the single units and (ii) using their synergic effects in terms of better performance of the overall system. Integrated membrane systems offer new opportunities in the design, rationalization and optimization of industrial processes.

Seawater desalination is probably the clearest example of what can be achieved through integrated membrane systems: cheaper, better quality and more abundant water, with less brine production. Figure 1 shows a schematic integrated membrane based desalination system.

As earlier illustrated, RO pre-treatment and post-treatment steps are required to condition water before and after the membrane process.

The implementation of MF and/or UF technologies for the RO pre-treatment in place of the conventional pre-treatment is now expanding worldwide. Membrane pre-treatment can provide (i) high levels of contaminants removal (including particulates, colloids and pathogens) with lower chemicals addition and, therefore, with a lower environmental impact, (ii) reduced cost and foot-print, (iii) better capability to handle wide fluctuations in raw water quality, (iv) operation with a high and stable permeate flux during long term operation, (v) low energy consumption.

Moreover, it can be necessary to add a coagulation and settling/flotation for the treatment of very bad water quality. This coagulation and settling is considered "the pre-treatment

© 2012 by the Society for Mining, Metallurgy, and Exploration. All rights reserved. Electronic edition published 2012.

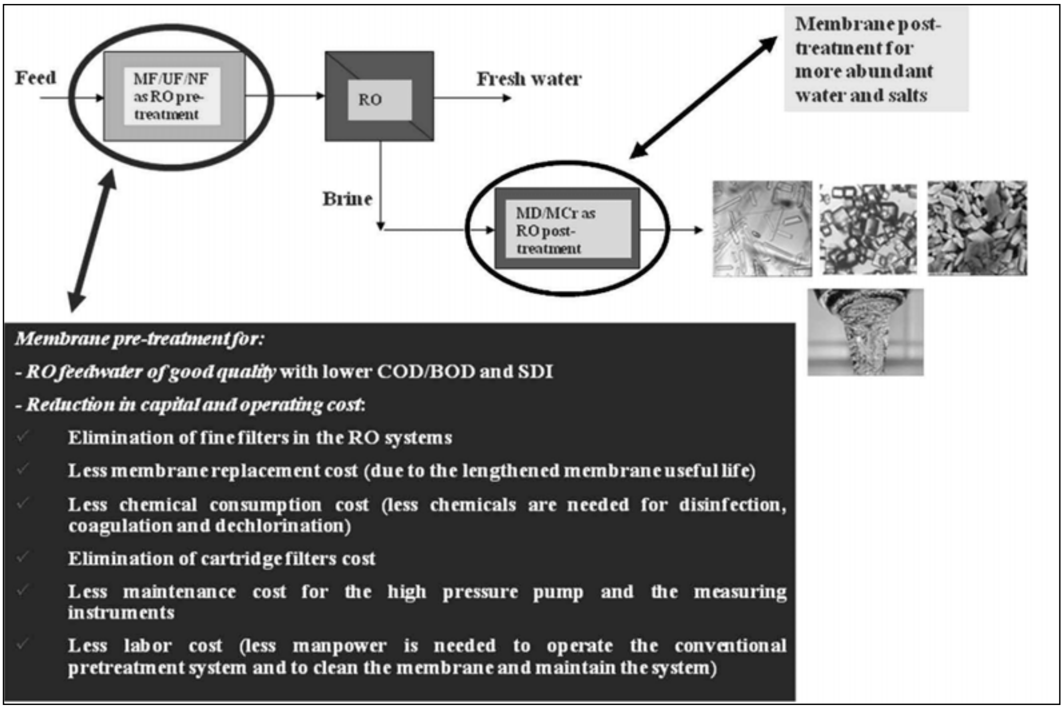

Figure 1. Scheme of an integrated membrane desalination system

of the pre-treatment" to face bad seawater quality, high turbidity, algae counts (red tide and blooms), hydrocarbon pollutions. It must be noted that the association pre-clarification plus UF/MF is more expensive than conventional pre-treatment. UF/MF and pre-coagulation is justified when associated with better control of membrane fouling and biofouling issue, reduction of RO cost, higher RO flux and/or higher recovery. The latter typically ranges between 40–50% because of the limitations imposed by scaling problems. Appropriate antiscalant dosages coupled to NF remove the large part of multivalent ions present in the feed water, thus decreasing the potential for salts precipitation even if the RO unit operates at higher recovery factors (Drioli et al. 1999).

To accomplish the ambitious objective of reaching recovery factor higher than 85–90%, conventional membrane operations (such as MF, UF, NF and RO) need to be combined with other innovative membrane processes (such as MD). With respect to pressure-driven membrane processes, MD does not suffer limitations arising from concentration polarization and can therefore be employed whenever high permeate recovery factors are requested. Actual experimental data and design studies in literature suggest that, if MD is operated on the RO retentate, the total amount of desalinated water represents almost 88% of the feed water (Drioli et al. 2006; Macedonio et al. 2007). Additionally, the use of a Membrane Crystallization (MCr, an interesting extension of MD concentration up to supersaturation) allows to exploit brine added value, not only increasing plant recovery factor, but also extracting the salts naturally present in the brine streams of the desalination plants thus decreasing brine disposal problem and its negative environmental impact (Macedonio et al. 2009; Macedonio and Drioli 2010).

The overall water recovery factor of an integrated desalination system constituted by MF-NF-RO and MCr working on both NF and RO brine can increase up to about 93%.

© 2012 by the Society for Mining, Metallurgy, and Exploration. All rights reserved. Electronic edition published 2012.

The drawback of the processes with MD/MCr units is their higher operating temperature with respect to RO. On the other hand, the MD/MCr required operating temperatures (typically below 70°C) are much lower than those of conventional thermal desalination processes, therefore low-grade waste and/or alternative energy sources can be coupled with MD/MCr for a cost and energy efficient water treatment system.

The benefits of MD, however, are not limited to the treatment of brine solutions of desalination plants. More recently membrane distillation has been also used in membrane bioreactor configuration (MDBR) for the treatment of industrial and municipal used waters (Fane et al. 2005; Phattaranawik et al. 2008). The development of MDBR system was due to the fact that, in a conventional MBR, the molecular weight cut-off of the utilized MF/UF membranes delivers a portion of the organic species of the feed. Lay at al. (Lay et al. 2010) reports that the effect of this is that recalcitrant organics may not be well degraded, and the direct reuse potential of the permeate may be limited. For overcoming this, the development of a number of innovative high retention membrane bioreactors (HRMBRs) have been developed such as membrane distillation MBR, where the MD membrane is used in place of MF/UF. Other examples are nanofiltration MBR (NFMBR) (Choi et al. 2002; Choi et al. 2007] and the osmotic MBR (OMBR) (Cornelissen et al. 2008; Oo et al. 2008]. The HRMBR systems are able, in principle, to retain effectively small size and persistent contaminants, which facilitates their biodegradation in the bioreactor, thereby producing higher quality product water (Lay et al. 2010). Moreover HRMBR systems potentially possess comparative economical advantage in removing pollutants from the used water more effectively. However, as these high rejection systems retain dissolved solids, they need to be operated under elevated salt condition (Lay et al. 2010).

FUTURE DEVELOPMENT OF MEMBRANE TECHNOLOGY

At present, important developments are taking place in industrial membrane applications focused on the integration of different membrane processes. Integrated systems offer new opportunities for reaching better quality products, more compact production plants, more sustainable and efficient processes with reduced energy consumption.

The future development of membrane technology are influenced by factors such as:

1. The development of membranes particularly adapt to specific applications, able to achieve the most increasingly stringent degree of purification of the raw feed waters as expected from the customer or imposed by law;
2. The handling and control of concentrate discharge;
3. The development of water treatment systems coupled with renewable energy sources for a significant reduction in energy consumption;
4. The realization of advanced integrated water management systems, at closed-circuit, that follow all the lines, from the water intake to water distribution and reuse (Macedonio et al. *accepted*), and based on *graduated quality requirements* (Peters 2010; Macedonio et al. *accepted*), i.e., on supplying water of diverse quality to the final users depending from their requirements (drinking, washing, agriculture, irrigation and industrial use);
5. The necessity to further reduce water treatment costs.

Among the technological developments, carbon nanotubes, fullerene, aquaporin channels, new protein-based membranes and graphene membranes are emerging in the recent years as innovative water technologies, as developed membranes with superior permeability, durability and selectivity for water purification (Macedonio et al. *accepted*).

© 2012 by the Society for Mining, Metallurgy, and Exploration. All rights reserved. Electronic edition published 2012.

CONCLUSIONS

Membrane Engineering is playing a dominant role in water treatment and reuse. This is mainly due to the operational simplicity and flexibility of membrane systems, their modular design, compactness, long term operation, high separation capacity and energy efficiency. Moreover, the experience gained in the last decades (in particular during the operation of reverse osmosis desalination systems), the improvements in material selection for membranes manufacturing as well as the mutual compatibility of different membrane operations for integration justify the success of membrane technology for a wide range of applications within the area of water treatment and purification, from desalination for potable water production, to industrial wastewater treatment, and to the recovery and reuse of municipal wastewaters.

REFERENCES

AlMadani, H.M.N. 2003. Water desalination by solar powered electrodialysis process. *Renewable Energy* 28:1915–1924.

Charcosset, C. 2009. A review of membrane processes and renewable energies for desalination. *Desalination* 245:214–231.

Choi, J.H., Dockko, S., Fukushi, K., and Yamamoto, K. 2002. A novel application of a submerged nanofiltration membrane bioreactor (NF MBR) for wastewater treatment. *Desalination* 146(1-3):413–420.

Choi, J.H., Lee, S.H., Fukushi, K., and Yamamoto, K. 2007. Comparison of sludge characteristics and PCR–DGGE based microbial diversity of nanofiltration and microfiltration membrane bioreactors. *Chemosphere* 67(8):1543–1550.

Cornelissen, E.R., Harmsen, D., de Korte, K.F., Ruiken, C.J., Qin, J.J., Oo, H., and Wessels, L.P. 2008. Membrane fouling and process performance of forward osmosis membranes on activated sludge. *Journal of Membrane Science* 319(1-2):158–168.

Drioli, E., and Curcio, E. 2007. Membrane engineering for process intensification: A perspective. *J. Chem. Technol. Biotechnol.* 82:223–227.

Drioli, E., Curcio, E., Di Profio, G., Macedonio F., and Criscuoli. A. 2006. Integrating membrane contactors technology and pressure-driven membrane operations for seawater desalination: Energy, exergy and cost analysis. *Chemical Engineering Research and Design* 84 (A3):209–220.

Drioli, E., Lagana, F., Criscuoli, A., and Barbieri, G. 1999. Integrated membrane operations in desalination processes. *Desalination* 122:141–145.

Fane, A.G. 2005. Module design and operation. In: *Nanofiltration: Principles and Applications*. Schaefer, A.I., Fane, A.G., and Waite, T.D. (eds.). Elsevier, pp. 67–88.

Phattaranawik, J., Fane, A.G., Pasquier, A.C.S., and Bing, W. 2008. A novel membrane bioreactor based on membrane distillation. *Desalination* 223(1-3):386–395.

Fritzmann, C., Löwenberg, J., Wintgens, T., and Melin, T. 2007. State-of-the-art of reverse osmosis desalination. *Desalination* 216:1–76.

Hagen, K. 1998. Removal of particles, bacteria and parasites with ultrafiltration for drinking water treatment. *Desalination* 119:85–91.

IDA Desalination Yearbook 2010–2011.

Kraume, M., and Drews, A. 2010. Membrane bioreactors in waste water treatment—Status and trends. *Chemical Engineering Technology* 33(8):1251–1259.

Lay, W.C.L., Liu, Y., and Fane, A.G. 2010. Impacts of salinity on the performance of high retention membrane bioreactors for water reclamation: A review. *Water Research* 44:21–40.

Macedonio, F., Curcio, E., and Drioli, E. 2007. Integrated membrane systems for seawater desalination: Energetic and exergetic analysis, economic evaluation, experimental study. *Desalination* 203:260–276.

© 2012 by the Society for Mining, Metallurgy, and Exploration. All rights reserved. Electronic edition published 2012.

Macedonio, F., and Drioli, E. 2010. Hydrophobic membranes for salts recovery from desalination plants. *Desalination and Water Treatment* 18:224–234.

Macedonio, F., Drioli, E., Curcio, E., and Di Profio, G. 2009. Experimental and economical evaluation of a membrane crystallizer plant. *Desalination and Water Treatment* 9:49–53.

Macedonio, F., Drioli, E., Gusev, A.A., Bardow, A., and Semiat, R. Efficient technologies for worldwide clean water supply. *Special issue of Chemical Engineering and Processing: Process Intensification*. (Forthcoming).

Mulder, M. 1996. *Basic Principles of Membrane Technology. London:* Kluwer Academic.

Oo, H., Kekre, K.A., Qin, J.J., Tao, G., Lay, C.L., Lew, C.H., Cornelissen, E.R., Ruiken, C.J., de Korte, K.F., and Wessels, L.P. 2008. Osmotic membrane bioreactor: Preliminary pilot study on effects of osmotic pressure on membrane flux and air scouring on fouling. In: *IWA Regional Conference "Membrane Technologies in Water and Waste Water Treatment*," Moscow.

Peters, T. 2010. Membrane technology for water treatment. *Chemical Engineering Technology* 33(8):1233–1240.

Peter-Varbanets, M., Zurbrugg, C., Swartz, C., and Pronk, W. 2009. Decentralized systems for potable water and the potential of membrane technology. *Water Research* 43:245–265.

Rios, G.M., Belleville, M.-P., and Paolucci-Jeanjean, D. 2007. Membrane engineering in biotechnology: Quo vamus? *TRENDS in Biotechnology* 25(6):242–246.

Van der Bruggen, B., and Vandecasteele, C. 2002. Distillation vs. membrane filtration: Overview of process evolutions in seawater desalination. *Desalination* 143:207–218.

© 2012 by the Society for Mining, Metallurgy, and Exploration. All rights reserved. Electronic edition published 2012.