Chapter 8
Role of Membranes in Wastewater Treatment

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Contents

Abstract Demand for water is on the rise as population and human activities increase including industries and agriculture. Freshwater resources have a skewed distribution besides being inadequate to meet the demands. Even though actual water consumed by humans and their activities is much less, large quantum of water is used for peripheral activities and discharged into the environment as wastewater. Hence, to meet the demand for water and to protect the environment, wastewater

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treatment is necessary. Conventional methods of treatment are cumbersome requiring large footprints, use of chemicals, and subsequent management of sludge generated.

Membrane is a barrier which helps in the preferential transport of some species under a potential gradient, be it mechanical, chemical, or electrical. Membranes can be made from different materials, in different forms, and with different morphologies. Membranes can be porous or nonporous, charged or neutral, and solid or liquid. Because of its flexibility, a variety of membrane processes has been developed and is being used to mitigate many industrial challenges. Membrane processes used in wastewater treatment are ambient temperature processes with no phase change and are rate-governed. The chemical requirements are significantly less compared to conventional processes leading to less sludge production.

An overview of different membrane processes motivated by pressure, concentration, and thermal and electrical gradients is discussed in the context of mitigating water stress situations. The technologies discussed include desalination, water recovery, and recycle and removal of toxic contaminants from wastewater streams including the latest developments in application areas. Utility of membrane contactors in improving the performance of the conventional separation processes is highlighted through membrane solvent extraction, supported liquid membranes, and membrane bioreactors. The potential applications of forward osmosis in water treatment are also indicated.

The roles of electrically driven membrane processes such as electrodialysis, bipolar membrane-based electrodialysis, electrodialysis reversal, and electro-deionization in water treatment are explained along with its limitations and challenges. The role of membranes in providing safe drinking water at the point of use has also been highlighted.

The prospects of combining two or more membrane processes like nanofiltration, reverse osmosis, and electrodialysis in water and wastewater treatment are highlighted. With increasing environmental consciousness and the need to recover value from waste, the concept of decentralization of wastewater treatment is proposed wherein the source of waste is isolated, as membrane processes can operate on any scale.

In the future, environmental protection is going to become a critical concern, and the best strategy is to recover everything in the wastewater stream as value toward realizing the concept of “Waste is unutilized Wealth.” The best way to achieve this is by isolating the individual wastewater streams as produced and treating them at the source without mixing with other waste streams. In this context, membrane processes have varieties and are economically viable for different capacities. Since the various streams are isolated, both the product and retentate streams can be recycled, thus leading not only to recovering value but also zero discharge to the environment. This chapter aims at providing necessary background knowledge to select a suitable scheme for the treatment of the specific wastewater including point-of-use devices and value recovery.

Keywords Membrane · Porous · Nonporous · Pressure-driven · Thermal gradient · Electrically driven · Reverse osmosis · Ultrafiltration · Nanofiltration · Forward osmosis · Size enhanced ultrafiltration · Electrodialysis · Liquid membrane · Hybrid membrane processes · Water recovery and recycle · Wastewater treatment · Membrane bioreactors · Membrane solvent extraction · Value recovery · Point-of-use device

8.1 Introduction

In the current scenario, water has become a scarce commodity compared to its free availability as a natural resource. The transformation is basically triggered by increase in population and the consequent growth in industries, agriculture, and lifestyle conveniences. Further, the supplies have dwindled due to a variety of reasons including climate change resulting in skewed rainfall pattern, inefficient use of water, pollution, overexploitation of groundwater, etc. This calls for an approach whereby demand is decreased and supply is increased. Demand can be reduced by improving water use efficiency, economizing specific consumption on various products and activities, quality use linkages, and recovery and reuse of water from spent streams. Supply augmentation can be achieved by improving the collection and storage efficiencies of natural resources including rain harvesting, linking the different sources of water to guard against avoidable overflows, and using desalination technologies in coastal areas.

Water being a universal solvent carries along with a variety of chemical species, essential minerals, and toxic components both in dissolved and suspended states. It is necessary that humans get safe water and the industries get water as per their requirement. Since most of the sources are contaminated physically, chemically, and biologically, water treatment is necessary. The contaminants of natural water can be either geo-genic or anthropogenic in origin. The former depends on the local geology, while the latter depends on human activities surrounding the water source. Conventional method of water treatment is primarily *point-of-source* treatment requiring chemicals and large footprint area. The treatment process is also quite sensitive to operating parameters such as pH, efficiency of mixing, and dosage of chemicals and generates significant amount of sludge for disposal.

The early 1980s witnessed the induction of large-scale commercial desalination plants based on reverse osmosis, and the subsequent phenomenal growth of membrane desalination over the conventional thermal processes has triggered the development of membrane applications in other areas of water treatment. The entire water treatment scenario has changed consequently with reference to time, efforts, and costs for both domestic and industrial uses. Since the late 1990s, a variety of membrane processes have been developed to suit different streams of water requiring much less footprint area and chemical requirement. These membrane processes operate on different energy gradients leading to separation of pure water (Schrotter et al. 2010); specific removal of contaminants such as heavy metals (Qudais and Moussa 2004), dyes (Karisma et al. 2017), and microorganisms; production of sterile and safe drinking water both as *point-of-use* and *point-of-source* devices; and splitting of salts to produce parent acid and base (Reig et al. 2016). Membrane processes, using *porous membranes*, operate on physical or physicochemical mechanisms and are mostly rate-governed ambient temperature operation without phase change. Being modular in nature capacity addition is simple, and the economics is not sensitive to capacity.

8.2 Membranes and Membrane Configuration

Membranes can be understood as physical barriers which can selectively allow permeation of particular species, under an appropriate gradient, when in contact with a solution. The separation mechanism can be physical, physicochemical, or chemical in nature independently or severally. The membrane materials can be natural or synthetic products, organic or inorganic. The commercial membrane processes use mostly organic membranes made up of synthetic polymer materials and operate under pressure, concentration, or electrical potential gradient.

8.2.1 Membrane Preparation

Membranes can be in any state, solid, liquid, or gas. As of now, the gaseous membranes are not known, while the liquid membranes are used in small scale, high value separations (K. K. Bhatluri et al. 2014). All the commercial membranes used otherwise are solid matrices. Depending on the mechanism of separation, the membranes used can be porous or nonporous.

Membranes can be prepared using different techniques involving *phase inversion*, *stretching*, *sintering*, *track etching*, and *electrospinning* (Zare and Kargari 2018). *Phase inversion* technique involves the dissolution of the polymer in a solvent and precipitating the same by the release of the solvent from the matrix. Any of the techniques such as evaporation-induced phase separation, non-solvent-induced phase separation, vapor-induced phase separation, and thermally induced phase separation (Ulbricht 2006) can be used depending on the nature of solvent. In evaporation-induced phase separation, the polymer is dissolved in a volatile solvent and cast as a film. The solvent is then allowed to evaporate under controlled conditions. The solvent is withdrawn from the cast sheet by immersing it in a non-solvent medium in the case of non-solvent-induced phase separation. In vapor-induced phase separation, non-solvent vapor is kept in contact with the cast film, allowing the solvent to saturate the non-solvent present in the vapor phase and enabling precipitation of the membrane. The thermal energy enables evaporation of the solvent, leading to the formation of membranes in thermally induced phase separation. Among these techniques, non-solvent-induced phase separation and thermally induced phase separation are mostly used for the production of commercial membranes (Liu et al. 2011; Lalia et al. 2013). In *stretching*, the polymer is heated above the melting point and then extruded into a thin film, which is subsequently stretched to form a porous matrix (Sadeghi et al. 2007). This technique does not need any solvent. In *sintering*, the polymer powder is pressed into a thin film and is sintered at a temperature just below the melting point. *Electrospinning* is a developing technology which produces nano-fibers (Ray et al. 2016) under the application of an electric field. *Track-etched* membranes are prepared by bombarding a thin nonporous film with accelerated heavy ions, followed by etching (Apel 2001).

Membranes used in water treatment are required to exhibit good solute rejection and water-flux characteristics. Accordingly, the membranes should have less resistance for water flow without compromise on the strength of the membrane to withstand the operating conditions. Reverse osmosis and nanofiltration membranes by design have pores less than 2 nm and have to withstand operating pressures ranging from 20 to 70 bars. In order to achieve these properties, membranes are prepared in a two-step process. First, a porous support layer is prepared by phase inversion, and then a very thin active layer is formed on its surface by in situ polymerization of two reactive monomers (Petersen 1993).

Phase inversion techniques allow the preparation of porous membranes with different ranges of pore-size distribution by varying the dope composition, the casting conditions, and the posttreatment of the membranes. The average pore size can be controlled by the variation of size and quantum of *pore-inducing additives* in the membrane dope solution. The pore formation in the phase inversion technique is a stochastic process, and hence, there would be a distribution of pore sizes, which is assumed to follow *normal distribution*. On the other hand, stretching leads to somewhat uniform pore size. Track etching gives nearly uniform pore size, but the pore density would be very low, and the cost is very high. Charged membranes are nonporous and prepared using resins mixed with some binding materials and cast into films (Drioli and Giorno 2010).

Depending on the chemicals used and conditions of casting, membranes can be prepared with hydrophilic or hydrophobic characteristics. The membrane processes relevant to water treatment are pressure-driven ultrafiltration, nanofiltration and reverse osmosis, concentration-driven forward osmosis and diffusion dialysis, thermally driven membrane distillation and electrically driven electrodialysis, electrodeionization, and bipolar membrane electrodialysis. Capacitive deionization is also an electrically driven desalination technique but without the use of membranes and is not to be discussed further.

Membranes used in pressure-driven membrane processes are on the hydrophilic side. Reverse osmosis and nanofiltration membranes operate at high pressures and are asymmetric in nature to reduce the resistance for water flow. Electrodialysis and bipolar membrane use nonporous charged membranes and remove ions from solution. Forward osmosis and diffusion dialysis are passive processes using neutral porous and nonporous charged membrane, respectively. Membrane distillation is the process where the hydrophobic membranes are used for the recovery of water.

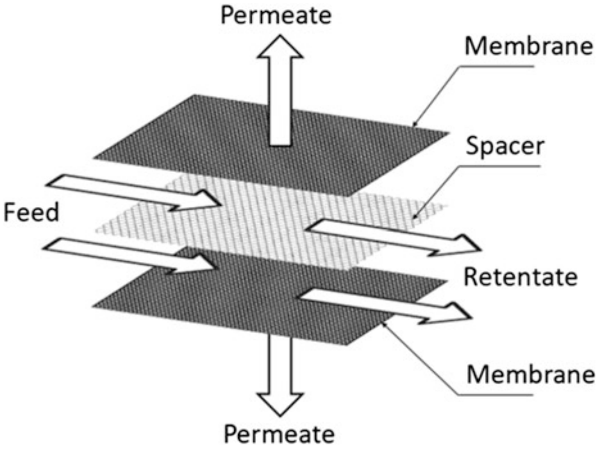
Membrane contactors are a class of membrane products, which are used to carry out conventional separation techniques by providing large interfacial contact area without the bother of mixing the contacting phases. These are porous inert membrane matrices with potential application in the removal of pollutants from water. Membrane bioreactor, which is extensively used in the treatment of wastewater, is a contactor between the microorganisms and waste stream. Further applications include membrane solvent extraction, gas absorption, etc.

8.2.2 Membrane Configuration

The commercial membranes are prepared as either flat sheets or cylindrical ones with different diameters. The membranes so prepared are configured in different geometries such as plate and frame, spiral, tubular, and hollow fiber. Each of these configurations has their unique characteristics and suited for certain environment. A *membrane element* describes the membrane housed in a particular configuration with inlet and outlets as a single unit. These membrane elements can be connected in series to assemble a *membrane module*. For large capacity plants, the modules can be connected in series or in parallel depending on the design objectives. Selection of a configuration depends on the compactness, hydrodynamic characteristics, ease of cleaning and maintenance, and economics. Plate and frame and spiral elements are prepared from flat sheets, while tubular and hollow fiber elements are based on cylindrical membranes.

Plate and Frame Flat sheets are used directly in a plate and frame configuration (Fig. 8.1). Membranes supported by nonwoven fabric are placed on either side of the pressure plate and sealed to the plate with gaskets, glue, o-rings, etc., with the active

Fig. 8.1 Plate and frame module concept. Water permeating the membrane is transported to the channels provided on the plates to the collection tube. (Modified from Mulder 1996)



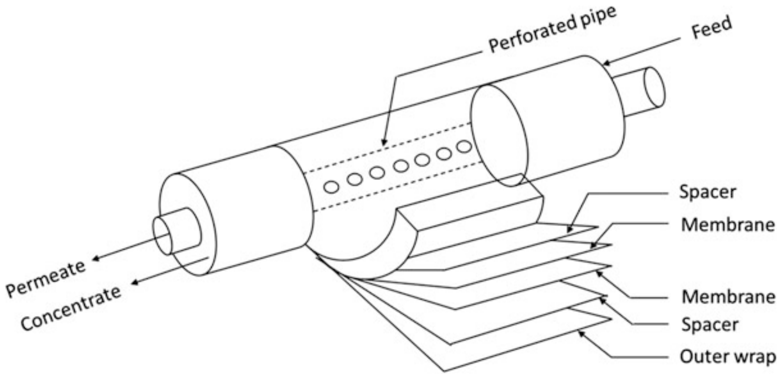


Fig. 8.2 Spiral element configuration. Assembly of membranes and feed spacer wound over a perforated central pipe is illustrated

surface of the membrane facing the plate surface. The pores provided by design in the plate allow the feed to be in contact with the membrane. The water permeating the membrane is transported via the nonwoven fabric to the channels provided on the plates and then to the collection tube. Many such plates assembled one over the other constitute a membrane module. The end plates would have only one membrane and a blinder plate. For example, a 50-plate configuration can hold 98 membrane sheets with the outer side of the end plates sealed. The sheets can be of any shape, circular, square, or hexagonal, depending on the pressure plate configuration (Pal 2017).

Spiral Element Alternately, a pair of long flat sheets can be made into an envelope with active surface membrane facing out and sealing three sides leaving one of the sides (breadth) open. Through the open side, a nonwoven fabric is inserted into the envelope covering the entire area. Many such envelopes are made. After inserting the feed spacer between the envelopes, the envelopes are wound over a porous central tube. The wound envelope is secured by using adhesive tape or fiber-reinforced plastic. The spiral element (Fig. 8.2) so prepared can be inserted in a pressure vessel.

Tubular Element The membranes are cast in a tubular form, inserted into porous support tubes, and assembled similar to a shell and tube heat exchanger (Fig. 8.3). The inner diameter of the tubes can vary from 6 mm to 18 mm normally.

Hollow Fibers Hollow fibers can be prepared by any of the three techniques, namely, wet, dry, or melt spinning (Vandekar 2015), even though wet spinning is the most used technique. The dope containing the polymer, solvent, and additive is extruded into the non-solvent where the precipitation of the polymer occurs. The inner diameter of the membranes may vary from 0.5 mm to 1.5 mm and the outer diameters from 0.7 mm to 2.00 mm. After extruding, the fibers are bundled and sealed together on both the ends with an adhesive (without affecting the flow channels) and inserted into a pressure vessel (Fig. 8.4).

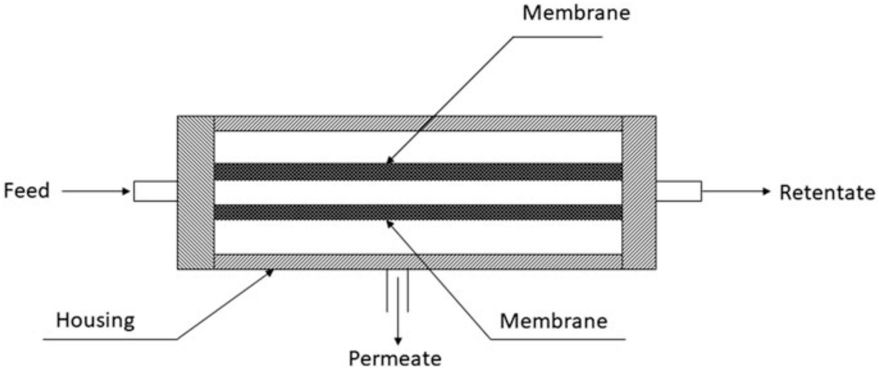


Fig. 8.3 Tubular element configuration. Tubular membranes are inserted into porous support tubes and assembled in shell and tube manner

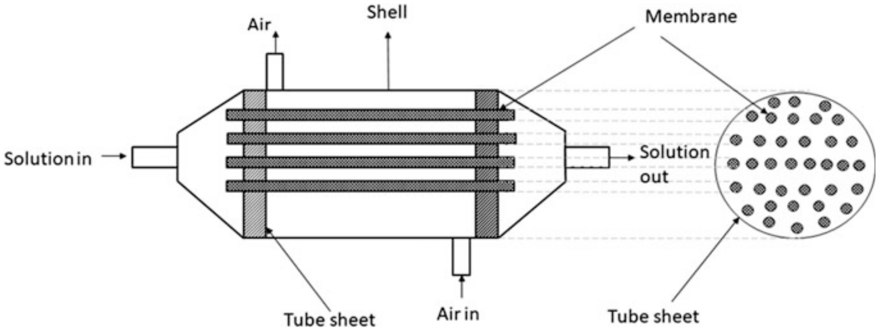


Fig. 8.4 Hollow fiber element. Hollow fiber elements are bundled and sealed together on each end of the module, making arrangements for inlets and outlets for shell and tube sides. (Modified from Mulder 1996)

The membranes can be made with different pore-size ranges normally designated in terms of molecular weight cutoff. Hollow fiber-based membrane elements with fiber dimensions around 100–150 microns were used for reverse osmosis applications. The use of hollow fine fiber for reverse osmosis is almost discontinued due to operational and maintenance problems. After the unsatisfactory performance of polyamide-based hollow fiber elements, cellulose triacetate membrane-based hollow fine fibers were assessed at some field reverse osmosis plants, but further progress is not reported. However, hollow fine fiber configuration is the most popular for many ultrafiltration applications. Comparative characteristics of the membrane module configurations can be found in Table 8.1.

Table 8.1 Comparison of membrane module configurations

	Tubular	Plate and frame	Spiral	Hollow fiber	Characteristics
Compactness (packing density)	Least compact	Better than tubular	Fairly compact but less than hollow fiber	Maximum compact	Relates to foot print area requirement
Flow regime	Turbulent	Promoted turbulence	Turbulent promoters	Laminar	The more the turbulence, the less will be the fouling tendency
Fouling tendency	Least	Less	High	Very high	
Cleaning and maintenance	Easy	Easy but slightly cumbersome	Difficult	Very difficult	Individual membranes can be removed in tubular and plate and frame. In spiral and hollow fiber, whole element requires to be replaced
Application areas	Food industry	Food industry/ships for drinking water	Desalination/ wastewater treatment	Pretreatment for desalination As membrane contactors	Desalination – mostly spiral Filtration – hollow fiber Food industry – tubular/plate and frame

Bhattacharjee et al. (2017) and Belfort (1988)

8.3 Membrane Processes

The membrane processes can be divided into two categories: passive and active. Passive processes do not require external energy for carrying out the separation, while the active processes require an external source of energy to bring out the separation. Passive processes include forward osmosis, diffusion dialysis, hemodialysis, membrane solvent extraction, supported liquid membranes, etc., while the active processes include reverse osmosis, electrodialysis, ultrafiltration, nanofiltration, and membrane distillation. Membrane is a barrier, and its surface controls the separation excepting in cases where the separation is diffusion controlled like membrane solvent extraction (in such cases, membrane provides a large interfacial contact area to enhance the separation).

8.3.1 Principle of Membrane Separation

One can visualize the membrane separation as described in the diagram (Fig. 8.5).

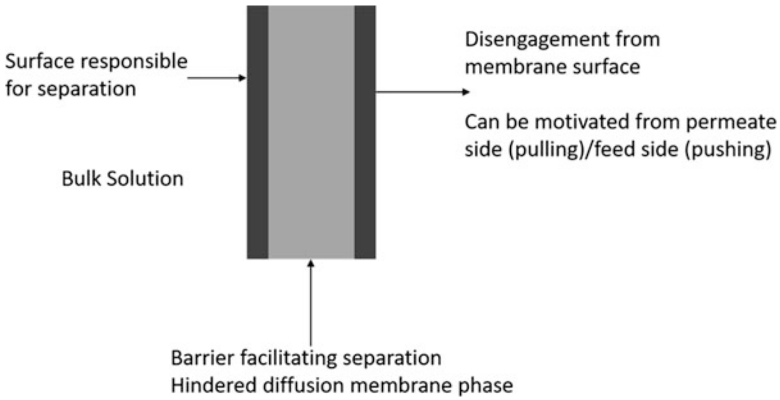


Fig. 8.5 Principle of membrane separation. Membrane serves as a barrier and facilitates separation of desired components

From the bulk, the species present in the solution reach the active surface of the membrane (either by diffusion or forced convection), where the separation occurs because of the specific property of the membrane. The species which is not allowed to pass through accumulates on the boundary surface or diffuses back to the bulk. The species permeating through the membrane flows through the capillary pores (in case of porous membrane) or diffuse through the membrane (in case of nonporous membrane) and gets disengaged from the other side of the membrane. The force for disengagement can be a pulling force like application of vacuum on the permeate side or lower concentration of the permeating species. Alternately, it can be a pushing force like hydrostatic pressure or higher vapor pressure (induced by thermal energy) on the feed side. The preferential separation at the membrane surface can be physical (size exclusion), physicochemical like sorption, chemical (ion exchange), or dissolution (chemical affinity) in the matrix.

The membrane processes are normally classified based on the driving force under which the separation occurs such as pressure-driven, concentration-driven, thermally driven, and electrically driven. Pressure-driven processes which include reverse osmosis, nanofiltration, ultrafiltration, and microfiltration are the ones mostly used in water treatment. Recent developments in forward osmosis and membrane distillation are slowly becoming tools for water treatment.

8.3.2 Pressure-Driven Membrane Processes

The membranes used in pressure-driven processes are almost neutral membranes. Reverse osmosis and nanofiltration have pore sizes less than 2 nm and 1 nm, respectively, and the interaction between the species and membranes plays a role in the separation process. Reverse osmosis membranes have a surface which has a balance of hydrophilic and hydrophobic character so that water alone can be preferentially sorbed onto its surface, and under the application of external pressure greater than the osmotic pressure. The sorbed water flows through the capillaries, thus effecting the separation of water from solution. Nanofiltration membranes are also similar to reverse osmosis membranes except that the pore sizes are slightly larger. These membranes may have slight positive or negative charge depending on the type of chemical treatment (Teixeira et al. 2005). In both the processes, hydrostatic pressure in excess of osmotic pressure of the boundary layer has to be applied for the removal of water from the solution. Since nanofiltration allows the permeation of monovalent solutes, the product water will have significant osmotic pressure compared to reverse osmosis permeate which is nearly pure. In view of this, for the same values of total dissolved solids (containing a mixture of ionic solutes), nanofiltration would require less applied pressure compared to reverse osmosis. When macromolecules like dyes are to be separated from a given solution, nanofiltration would be a better choice, as it would allow the solutes to permeate through the membrane retaining macromolecules. Both in reverse osmosis and nanofiltration, as the process proceeds, the feed solution becomes more and more concentrated resulting in rise of osmotic pressure and becomes susceptible for scaling, consequently limiting the percent separation (percent recovery). The inability to achieve total separation is one of the major limitations of nanofiltration and reverse osmosis.

Ultrafiltration whose pores are larger than nanofiltration operates based on size exclusion mechanism. The attractive features of the process are the flexibility to operate both in dead-end and cross flow mode and the backwash possibility. Unlike reverse osmosis and nanofiltration, osmotic pressure has no significant impact on the performance of ultrafiltration membranes affording the operation at very low pressures in the range of 1–5 bar. Table 8.2 presents the comparative aspects of pressure-driven membrane processes.

8.3.3 Electro-membrane Processes

Electro-membrane processes are performed under electrical potential gradient, where ions migrate from the solution toward the corresponding electrodes. Depending on the arrangement of the membranes, desired separation can be achieved. The processes include electrodialysis, electrodialysis reversal, electrodeionization, and electrodialysis with bipolar membrane.

Electrodialysis In electrodialysis (Campione et al. 2018), a number of pairs of cation and anion exchange membranes (cell pair) are arranged alternately in between two electrodes. Feed solution containing ionic solutes are fed parallelly between each pair of membranes (Fig. 8.6). When connected to power source, the ions (cations and anions) start moving in opposite direction toward their respective electrodes. During the migration, the cations pass through cationic membranes and

Table 8.2 Comparison of pressure-driven membrane processes

Description	Microfiltration	Ultrafiltration	Nanofiltration	Reverse osmosis
Membrane characteristics	Porous	Porous marginally asymmetric	Porous with marginal surface charge	Porous
Pore-size range	>0.1 μm	2 nm and 0.05 μm	1–2 nm	0.1–1.0 nm
Mechanism	Size (solid/liquid separation)	Size exclusion	Physicochemical + size exclusion	Physicochemical mechanism
Operating pressure	0.5–2 bar	1 and 10 bar	5–20 bar	7–80 bar (pressure > osmotic pressure)
Application areas	Industrial filtration systems	Sterilization of water, removal of colloids, microorganisms, etc. pretreatment for reverse osmosis	Water softening, separation of macromolecules from solutions	Desalination. Recovery and recycle of water
Process characteristics	Colloids and dissolved solids cannot be separated	Backwashing is possible, tolerant to chlorine. Also used as membrane contactors	Requires less pressure. Separation of multivalent contaminants possible. Constrained by recovery limitation	Constrained by recovery limitation. Disposal of membranes might be a problem in future

Van der Bruggen et al. (2003)

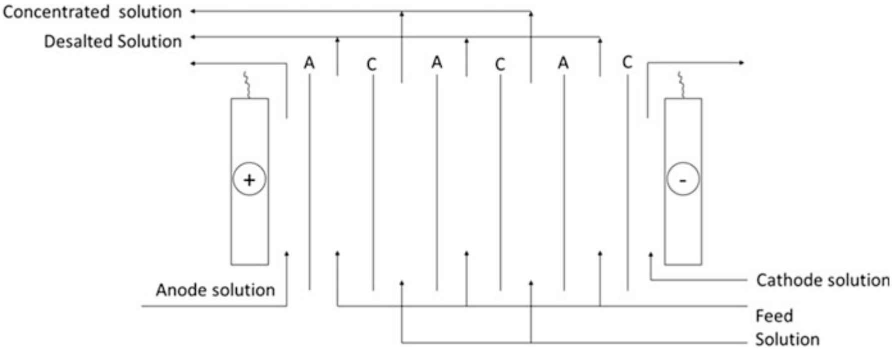


Fig. 8.6 Electrodialysis. Several pairs of cation and anion exchange membranes are arranged in alternate fashion between cathode and anode

are stopped by anionic membranes, and similarly, anions are stopped by cationic membranes since the direction of migration is fixed by the polarity of the electrodes. This results in the feed solution getting split into two streams (one dilute stream and another concentrate stream) in alternate compartments. The diluent is the desalinated solution.

Electro-deionization This process is the modified version of electrodialysis (Nagel 2005) wherein ion exchange resins are filled in each compartment. The process is applicable to very low-salinity water (much less than 50 ppm). Upon application of the electrical potential, ions migrate and saturate the resins of alternate compartments. As the ionic concentration reduces, water splitting occurs leading to the migration of hydrogen and hydroxyl ions which regenerate the resins, thus avoiding the need for acid and alkali. This process is useful only at very low concentrations. Hence, it is used as a polishing step for the preparation of ultrapure water from reverse osmosis product.

Electrodialysis with Bipolar Membrane This is another modified version of electrodialysis where a bipolar membrane (anion and cation membrane joined together) is inserted between two pairs (each pair having one anion exchange and one cation exchange) of membranes, and as a result, the dissolved salt is converted to parent acid and base from the solution (Oztekin and Yazicigil 2007). Further studies have indicated the possibility of fractionation of the ionic species (Reig et al. 2016). These processes are still in the development stage particularly with reference to the membranes whose stability under the process conditions is a challenge.

8.3.4 *Other Membrane Processes*

Concentration-Driven Processes

Forward Osmosis All the concentration-driven processes are passive in nature. In forward osmosis, water flows through the membrane from the feed solution toward the draw solute motivated by the osmotic pressure difference through the semipermeable membrane. The draw solution gets diluted, but the ultimate osmotic pressure of the draw solution is always greater than the feed solution. A second step separation is required to get pure water as shown in Fig. 8.7.

Selection of draw solute, which can be separated by a simple process, is critical to the performance.

The challenges are the development of membranes with a good flux and a suitable draw solute from which water could be recovered. Recent development of aquaporin (Ma et al. 2012) membrane with a water channel to transport water is expected to trigger practical applications in many areas including wastewater treatment.

Diffusion Dialysis Diffusion dialysis describes the movement of ionic species through a charged membrane. The membrane can be anionic or cationic. Unlike electrodialysis, where both cationic and anionic membranes are used, diffusion dialysis requires only one of the two membranes. When an anion membrane is

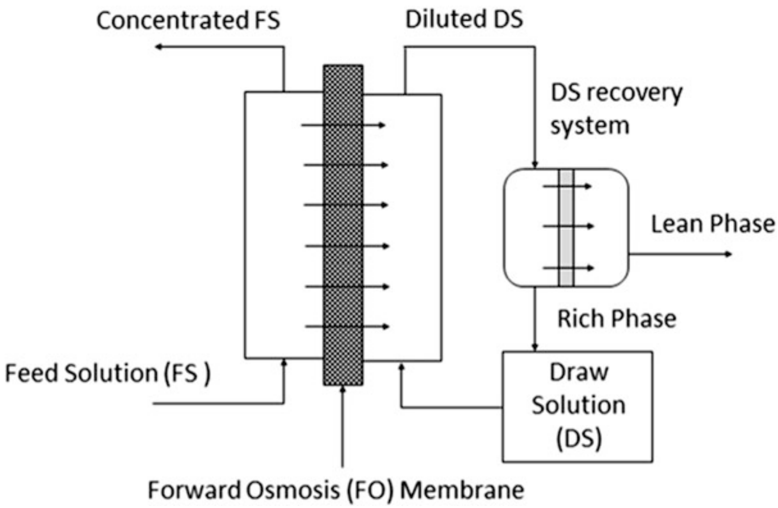


Fig. 8.7 Forward osmosis. Water flows from the feed solution toward the draw solute due to osmotic pressure difference through the semipermeable membrane. (Modified from Luo et al. 2014)

interfaced between the acid solution along with its metal salts (say hydrochloric acid) and water, chloride ions would diffuse through the anionic membrane. Hydrogen ions as well as metal ions would also tend to pass through the membrane to maintain *Donnan criteria* of electroneutrality (Luo et al. 2011). Since the mobility of hydrogen ions is higher compared to metal ions, hydrogen ions move faster, thus enabling the separation of acid from its solution. Based on the same philosophy, bases can also be separated from its salt solutions.

Thermally Driven Processes

Membrane distillation is a thermally driven membrane process which uses hydrophobic membranes (Fig. 8.8). When a hot stream of water is circulated through the membrane, the water vapor passes through the membrane pores and gets condensed on the permeate side by any of the techniques such as direct contact with a *cold water* stream, application of vacuum, air gap condensation, or sweep gas process (Wang and Chung 2015). This is a low-flux process with an ability to use waste heat. Liquid water which does not wet the membrane cannot permeate through the hydrophobic membrane up to a particular pressure commonly known as liquid entry pressure, whereas water vapor, which does not exhibit hydrophilicity, passes through the membrane. The critical points of concern are the maintenance of feed pressure less than the liquid entry pressure with reference to the membrane, the low flux, and the ease of recovering water. As the vapor produced is indirectly related to temperature, the possibility of increasing the flux is low unless some external source of thermal energy is provided.

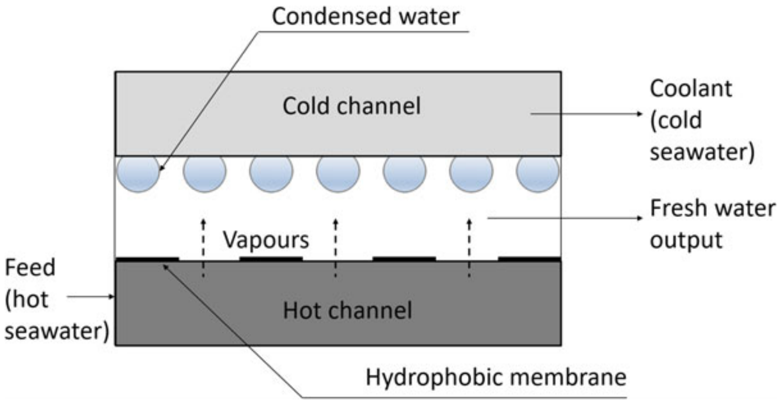


Fig. 8.8 Concept of membrane distillation. Thermally driven separation process allows vapors to pass through porous hydrophobic membrane that condense on the permeate side

Membrane Contactors

Membrane contactors are porous membrane devices mostly in the ultrafiltration range which provide interfacial contact between two phases to facilitate mass transfer. The driving force is concentration difference or chemical affinity. Membrane contactors provide very high contact area depending on the membrane configuration. Normally, hollow fiber/capillary membranes are used which offer about one to two orders of higher contact area per unit volume compared to conventional systems. As the two phases are separated by the membrane, problems related to intermixing of phases such as flooding and emulsification do not arise. Moreover, the choice of contacting fluids is not restricted by physical properties of the fluid such as density. The processes are less energy-intensive and mostly rate-governed and do not depend on the physical properties of the contacting phases. The limitations include additional mass transfer resistance and transmembrane pressure. Being compact and adaptable to different capacity operations, these contactors have potential use in replacing or supporting the conventional unit operations such as membrane bioreactors, liquid–liquid extraction, and gaseous separation (Drioli et al. 2011).

8.4 Application of Membrane Processes in Water Treatment

Membrane process made its foray into water treatment as reverse osmosis technology for desalination of brackish seawater. With the phenomenal success, the applications of reverse osmosis were extended to effluent streams for water recovery and recycle. Further innovations in membranes led to the development of membrane distillation, forward osmosis, and nanofiltration which are impacting desalination, wastewater treatment, and other separation processes. Development of ultrafiltration initially as a pretreatment for reverse osmosis systems has found more utility as membrane bioreactors for the secondary treatment of wastewater and many other applications in the production of safe drinking water and sterile water. These membranes can be used as membrane contactors for carrying out conventional unit operations such as membrane solvent extraction, gas separation, and crystallization. Charged membranes have been demonstrated for processes such as electro-deionization and electrodialysis with bipolar membrane besides electrodialysis which are more environment-friendly and are capable of not only treating wastewater but also recovering value. The membranes available today separate either water or a few solutes from its solution. Consequently, all these processes have a role to play in the water treatment.

8.4.1 Pressure-Driven Processes

Applications of Reverse Osmosis

Desalination Reverse osmosis application for seawater desalination has recorded a tremendous growth with the developments of membranes (Yang et al. 2018), energy recovery devices (Kadai and Bosleman 2018), and rugged pretreatment systems. A state-of-the-art review published (Qasim et al. 2019) recently recounts the various developments taken place over the last few decades. The present specific energy consumption for seawater desalination is reported to be around 2.5–4 kWh/m^3 (Voutchkov 2018; Karabelas et al. 2018). The advent of ultrafiltration membranes as a pretreatment system has contributed to the improved design with higher specific recoveries for the membrane element. Even though desalination systems can be designed using any of the four configurations, spiral configuration is extensively used in large-scale installations. Hollow fiber configuration was used in the initial period but later discontinued due to practical problems with reference to maintenance. Even though the first demonstrated reverse osmosis plant was in tubular configuration, it is not the preferred configuration in many applications being the least compact configuration. Plate and frame modules are used for small-capacity desalination systems particularly for seawater desalination in ships where constraints of space, head room, and inventory-carrying capacity exist.

A membrane element is the basic unit which can be assembled in series. A number of spiral membrane elements (not more than seven) assembled in a pressure vessel is called a module. When feedwater flows through the module, two streams emerge: one concentrated stream and the other permeate stream normally designated as “product.” The performance parameters are solute rejection, recovery, product water (permeate) flux, and module pressure drop. Solute rejection is defined as the fraction of the solutes, which is retained in the feed side (concentrate) and is mathematically represented as follows:

Solute rejection = (feed concentration – permeate concentration)/feed concentration and is more often expressed as percent.

Recovery refers to the fraction of water from the feed recovered as desalinated water, and it is mathematically represented by:

Recovery = product (permeate) rate/feed rate. It is also expressed as percent.

Product (permeate) water flux is defined as the water produced per unit area per unit time. Since the membrane area is fixed in an element and hence in a module, sometimes the flux is reported as cubic meters/element.

Module pressure drop indicates the extent of scaling/fouling. Initially, the pressure drop would be minimum but increases with time. Cleaning of the membrane modules would reduce the pressure drop.

Seawater Reverse Osmosis Desalination Reverse osmosis systems consist of a number of modules in parallel depending on the capacity. Each module consists of a number of elements in series contained in a pressure vessel. The membrane elements prepared by different manufacturers have varying internal arrangements with unique hydrodynamic characteristics. Each of them provides software for designing a reverse osmosis system for desalination. Within the design constraints with reference to feed flow rates, concentrate flow rates, and applied pressure, system design is evolved for a targeted capacity and product water quality subject to the fouling/scaling characteristics of the available feed. The number of elements in series governs the recovery (ratio of feed to product rate), while the number of modules in parallel corresponds to the capacity of the plant. In order to work within the membrane element specifications and to have higher recoveries, one may design a second reverse osmosis stage, where the reject from different modules in the first stage is redistributed to a lesser number of modules in the second stage. Depending on the initial pressure, a booster pump may be used for the second stage if required. Similarly, to improve the product quality of first stage, the *permeate* may be processed through one more reverse osmosis system under low pressures, popularly designated as “pass.” The objectives of the design would be to produce product water of a certain quality and quantity at minimum cost or energy consumption. The restraining factor would be the input quality of feed seawater, the scaling potential, and the rigor of pretreatment system. Final evolved design would specify the operating pressure, feed flow rate, arrangement of modules, and expected quality. This has to be supplemented by the specifications of high-pressure pump and the compatible energy recovery system, feed pretreatment, membrane cleaning, and posttreatment system.

A typical seawater reverse osmosis plant consists of the subsystems: intake; pretreatment system consisting of particulate filters, chemical dosing; high pressure pump, and energy recovery; reverse osmosis system; posttreatment; and cleaning systems as shown in Fig. 8.9.

The reverse osmosis performance deteriorates following the slow degradation of the membranes and thus has a life, warranting periodic replacement. The degradation leads to high permeate salinity. By the adoption of two-pass system, it is possible to

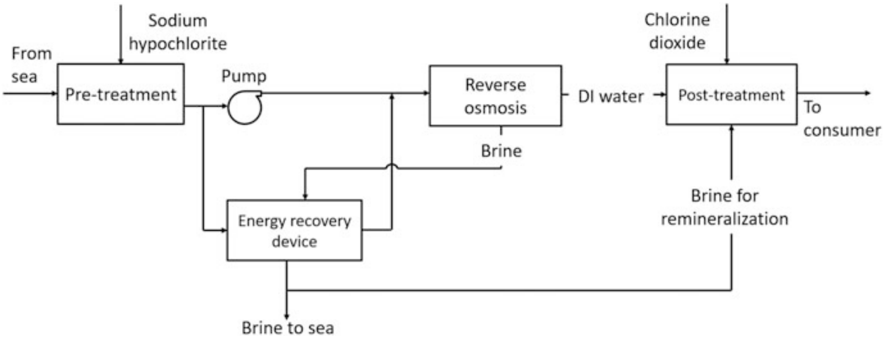


Fig. 8.9 Seawater reverse osmosis desalination plant block diagram. Key components including intake, pretreatment system, chemical dosing, high pressure pump and energy recovery, reverse osmosis system, posttreatment, and cleaning system are represented

achieve consistently high purity levels, wherein permeate from the first pass becomes the feed to the second pass. The concentrated reject water is dispersed into the sea with a diffuser to prevent any sort of salinity shocks to organisms of the sea. Since the process requires strict control of physical, biological, and chemical parameters, operator efficiency plays an important role.

Brackish Water Desalination Brackish water desalination is the viable alternative for remote areas having brackish water as the only source of water. With the dissolved contents being much lower compared to seawater, these plants can be operated at much lower operating pressures. The process is similar to seawater reverse osmosis, but parameters of design and operation are different.

Capacities of brackish water plants are far less compared to seawater desalination plants due to nonavailability of adequate raw water. The composition of the brackish water may vary from source to source, particularly with respect to hardness and trace metals. The raw water may be nearly free of suspended matter and microorganisms. Accordingly, the pretreatment system may be relatively less complicated. Most of the brackish water plants particularly small-capacity plants are located in rural or remote areas, may not operate round the clock, and hence may require protection measures to prevent faster deterioration of the membranes. The reject disposal is a big challenge, as it would find its way to the groundwater resulting in the increase of salinity over time, over and above the increase in salinity in the normal course due to constant withdrawal. Therefore, the design should be directed toward conserving the water resources with dual quality usage. Further, the design should be flexible with a provision for reject recycle so that one can deliver constant quality of product water albeit at different recoveries (Prabhakar et al. 1989; Sarkar et al. 2008). Depending on the salinity of the feed, the withdrawal amount of groundwater may vary, but the plant would operate at constant output quality and capacity. Further, the flexibility would lead to conservation of groundwater to the extent possible.

Water Recovery and Recycle

Reclamation and reuse of water have become quite popular with the advent of membrane technologies because of its cost-effectiveness. Reverse osmosis has been used for the reclamation of water from effluents (Shang et al. 2011). Integrated use of reverse osmosis along with ultrafiltration and microfiltration is common for the tertiary treatment of municipal wastewater to augment water sources as exemplified by 270 MLD plant at the Orange County Water District in Southern California and many other plants in Singapore (Wong 2012). Similar systems have been used in petrochemical industries such as China American Petrochemical Company for recovering 9000 m^3/day at Taiwan and 26,000 m^3/d zero liquid discharge system at PEMEX refinery in Minatitlan, Veracruz, Mexico. Recovery of water from sewage has been in practice in India since the late 19280s, and a number of reverse plants have been established. Currently most of the industries and small residential communities in water stress regions are recovering water for recycle. Virtually all industrial effluent streams including leather (Cassano et al. 1999), paper (Zhang et al. 2009), and textiles (Bottino et al. 2001) can be treated with membrane processes to reclaim water for reuse through reverse osmosis. In all these processes, reclamation of water for reuse is obtained through reverse osmosis, while other membrane processes could be used as a pretreatment or in some cases recovery of valuables.

Reverse osmosis plant follows the primary and secondary treatment in all the effluent treatment systems. One may have to ensure that during the postsecondary treatment, neither chlorine nor microorganisms enter the reverse osmosis system by appropriate treatment. Since the dissolved solid contents are likely to be less, mostly below 3000 ppm, one can achieve high recoveries of about 70–80%. The product water can be further polished or posttreated to suit the end-use quality requirements. Reverse osmosis has been used for the concentration of aqueous radioactive effluents to reduce the volume for further treatment. When cellulose acetate membranes were used, reverse osmosis gave a poor rejection of nitrate species as the concentration increased. This factor was exploited in isolating uranyl species from ammonium nitrate solution (Prabhakar et al. 1992, 1994, 1996).

In general, the role of reverse osmosis process in wastewater treatment is to recover water and concentrate the contaminants to a small volume for further treatment. The *recovery* is limited by the scaling threat and the osmotic pressure of the concentrating feed due to the continuous removal of water through the membrane. The concentrated streams would contain all the contaminants and salts, and their disposal would be a challenge environmentally. For zero liquid discharge, one more unit operation such as evaporator or crystallizers may have to be used. As the water demand and value are in the ascending trend, it is imperative to recover water from any spent stream and in that reverse osmosis has a major role to play.

Applications of Nanofiltration

Nanofiltration is slowly emerging as an alternative to reverse osmosis in some applications and as supplementary technology in some other cases. The nanofiltration membrane elements are available in many average pore sizes designated as NF40, NF90, etc., indicating the approximate solute rejection of sodium chloride. Minor charge on the surface of the membrane coupled with higher pore sizes relative to reverse osmosis enables the separation of monovalent species resulting in the concentration of macromolecules. Because of the passage of some solutes, the effective operating pressure is less due to the net osmotic pressure being lower. Consequently, larger molecules and multivalent ionic species can be separated through nanofiltration, like dyes, as well as uranyl species from the solution. Nanofiltration has potential applications (Astro chemicals and Bio Technologies 2019) in many areas including water softening and removal of natural organic materials. Experimental investigations on using reverse osmosis and nanofiltration (Abid et al. 2012) for the dye removal indicated that nanofiltration system can provide permeate water, meeting the environmental standards by a big margin at 50% electric power relative to reverse osmosis membranes due to reduction in operating pressure. A number of studies have also confirmed the utility of separation of dyes and intermediates (Kelewou et al. 2015; Zhu et al. 2013) using nanofiltration. Review of existing processes for dye removal found that membrane processes have high potential (Ahmad et al. 2015) and require some of the challenges like fouling and sludge production that need to be addressed. Nanofiltration finds use in the separation of low-molecular-weight species from the bulk solution as indicated by studies, where the separation of ammonium nitrate could be achieved from uranyl nitrate (Prabhakar et al. 1996; Zhongwei et al. 2017).

8.4.2 Electro-membrane Process Applications

Electrodialysis process was used for desalination particularly for brackish water desalination in the late 1980s and early 1990s. The following are the limitations of electrodialysis:

1. It is difficult to produce high purity water because of the inherent electrical resistance of water.
2. Polarization near the membrane surface decreases the efficiency of the system leading to increase in power consumption. In addition, power consumption also increases with the concentration of the feed, as more ions have to be transported through the membrane.
3. The efficiency of electrodialysis decreases in the presence of bivalent salts such as calcium, sulfate, magnesium, etc.
4. As on date, no practical energy recovery system is available even though some attempts are made to recover energy using the concept of reverse electrodialysis.

Electrodialysis system can be operated in batch mode for small-scale applications or continuously for large industrial applications. Earliest applications of electrodialysis systems were in brackish desalination. Electrodialysis units have been deployed for desalination up to 15,000 ppm salinity (Burn et al. 2015) with multiple stages. For brackish water desalination up to 3000 ppm feed salinity, electrodialysis can achieve about 80% recovery. Efforts to extend to seawater desalination could not be successful because of very high specific power consumption. Improvements to overcome the challenge through electrodialysis reversal also did not yield desired results due to practical difficulties. Recent innovation of reverse electrodialysis (Mei and Tang 2018) for recovering energy has shown positive results. Perhaps, in the future with further developments, electrodialysis could become a viable alternative for seawater desalination (Galama et al. 2014).

The major challenge of electrodialysis is the power consumption and concentration polarization, both of which increase with concentration of the feed. The challenges were addressed by electrodialysis reversal to some extent, where the polarity of the electrodes was frequently altered. Even though the issues were addressed to some extent, the product water purity was affected due the frequent change of “dilute” and “concentrate” compartments. Moreover, because of the inherent poor conductivity of water, one has to contend with higher salinities of product compared to reverse osmosis. In view of this, electrodialysis is not a preferred alternative for desalination or water treatment applications. Electrodeionization is a minor modification of electrodialysis and is restricted to very low salinity levels. Apart from desalination, electrodialysis has been studied extensively for industrial wastewater treatment for the recovery of chromium (Nataraj et al. 2007), cadmium (Marder et al. 2003), and nickel (Scarazzato et al. 2018) from plating industry effluents and acid mine drainage for recovering water (Cardoso et al. 2013) and to concentrate and recover nutrients from waste streams (Zhang et al. 2013).

8.4.3 Membrane Distillation

Membrane distillation has been demonstrated for its performance in desalination of seawater (Camacho et al. 2013) in a number of studies. The process involves initially the formation of vapor and subsequently its transfer through the membrane. The transfer medium (membrane) and water vapor both are hydrophobic in nature, and the product can be highly pure for an ideal membrane. Since the membrane has pore-size distribution, some contamination is inevitable in condensed water. For large-scale sustainable deployment, the challenges of low-flux and low liquid entry pressure of the membranes have to be addressed.

Apart from desalination, direct contact membrane distillation has been utilized for the recovery of water from pharmaceutical wastewater and radioactive wastewater (Wang and Chung 2015). Studies were conducted to recover water in the crystallization process using membrane distillation crystallization (Chan et al. 2005; Ji et al.

2010). This concept could be quite useful for the recovery of salts and water from the blowdown of thermal desalination plant. One of the potential applications of the membrane distillation in water treatment besides recovering water is to reduce the temperature of return cooling water being disposed into the environment (Jansen et al. 2007). Membrane distillation can be coupled with renewable energy (Blanco Gálvez et al. 2009), particularly solar, for the concentration of solutions including wastewater (Walton et al. 2004). Membrane distillation can be used for de-moisturization of wet steam as moisture can get condensed on the retentate side while dry steam can be sent for appropriate use. Condensation assisted by membrane represents a new source of water (Drioli et al. 2015).

8.4.4 Ultrafiltration

Ultrafiltration membranes were commercially developed later than reverse osmosis membranes. The applications have encompassed many areas including wastewater treatment and water purification. Being a low-pressure technique, the energy consumption is low compared to other pressure-driven processes, and the virtue of ultrafilters is its amenability for backwashing and possibility of dead-end operation mode, which provides nearly 100% recovery of the fluid or solids. The nominal pore size of ultrafilters may be in the range of about 20 nm to 0.1 microns. Commercially ultrafiltration systems are available in different ranges of pore sizes, specified in terms of molecular weight cutoff from 5 kilo Dalton to 1.2 lakh kilo Dalton. Size exclusion is the basic philosophy of separation, and osmotic pressure is normally not a limitation to the process. As the filtration proceeds, the pressure drop across the membrane, i.e., transmembrane pressure drop, would increase leading to reduction in flux. The flux can be nearly restored by backwashing, i.e., by allowing the water to flow from product to feed side for about a minute. The commercially operating system has a backwash cycle for about 1–2 min, for every 40–50 min of service cycle. Most of the seawater reverse osmosis desalination plants use ultrafiltration for the pretreatment as it gives high-quality treated water. After many pilot studies between 1995 and 2005, ultrafiltration has been installed as pretreatment system in many large-scale seawater reverse osmosis plants (Busch et al. 2009).

Size-enhanced ultrafiltration is a technique whereby the size of the desired species is enhanced and separated through ultrafiltration. This method is limited to small concentration of solutes present in bulk solution such as the presence of very small amounts of heavy metal species. Increase in size can be due to complexation, coprecipitation, and adsorption. Because of the size, these species are retained by the ultrafiltration membranes. The advantages of this technique include:

1. Isolation and removal of trace metal species in the presence of bulk component based on size exclusion principle.
2. The process is not limited by osmotic pressure constraints as in reverse osmosis and nanofiltration.

3. Since the concentration of the heavy metal species are so low, the consumption of additives would be very small,
4. Ultrafiltraton is backwashable, and hence the complex can be recovered as such in a backwash cycle.
5. Further, most of the complexation or adsorption processes are sensitive to pH. Hence, after size enhancement and separation of heavy ions, the size enhancement can be reversed by altering pH or other conditions, enabling the separation and recovery of metal ion species as well as the complex for reuse.

   Removal of copper, nickel, and chromium has been extensively studied using a variety of complexing agents such as polyethylenimine (Sarkar et al. 2013; Kadioglu et al. 2010), carboxymethyl cellulose (Kavitha et al. 2018), and chitosan derivative (Kavitha et al. 2019*)*. The removal of cesium and strontium, the radioactive contaminants of nuclear waste from the supernatant solution (after cesium was co-precipitated along with copper ferrocyanide and strontium as phosphate), indicated that s*ize-enhanced ultrafiltration* can be used as a last mile separation process (Rao et al. 2000) because of the fact that even the original waste, before precipitation, would contain less than a ppm even though the radioactivity would be high.

8.4.5 Membrane Contactors

Unlike other membrane processes which are driven by external energy for the separation, membrane contactors do not need external energy for membrane role in the separation process. It enables the conventional techniques of separation in somewhat convenient manner with reference to environment, capacity, and resource requirements. Membrane contactors are porous barriers. The contactors can exhibit different functions: *filters* for the removal of colloids/suspended matter, *interphase contactor* in liquid–liquid extraction, *absorber* for gaseous separation, *barrier* in membrane bioreactors, and immobilizer of solvent in supported liquid membrane. Membrane bioreactors, solvent extraction, gas absorption, and gaseous separation are some of the examples where membrane contactors have been used. With reference to water treatment, membrane bioreactors play a very critical role both in the industrial and domestic wastewater treatments. Membrane solvent extraction is a developing process which can help in recovering the organics or heavy metal species from effluents.

Membrane Bioreactor

A membrane bioreactor combines the activated sludge process with a membrane separation process. The membrane process could be either microfiltration or ultrafiltration. The membrane acts as a barrier filter which enables it to hold the microorganisms and allow the transport of nutrients, oxygen, and degradation products through the pores. The operational range of membrane bioreactors is much higher compared to conventional activated sludge process. The solid retention time for membrane bioreactor can be up to a month compared to about a few days for conventional processes. Membrane bioreactors can operate at high suspended loads usually known as mixed liquor suspended solids unlike conventional systems. The configuration of the membranes in membrane bioreactor can be flat sheet, tubular, or hollow fiber, depending on the design constraints. Ceramic membranes with multiple tubes can also be used. There are two ways by which membrane bioreactors can be deployed, namely, wet (submerged or immersed) installation and dry side stream (outside the activation tank). In wet installation, membrane module is directly submerged into the activation tank, while in dry installation, membrane module is installed outside the tank. Aeration is done for wet installation from the bottom toward the membrane, while for the side-stream design, air is injected along with wastewater. Both of them have their merits and demerits (Dohare and Trivedi 2014). Side-stream installation requires higher power but can be easily cleaned and can handle variations in the feed conditions. On the other hand, the power consumption is less for submerged membrane bioreactor, but cleaning in the membrane is difficult and time-consuming (Gupta et al. 2008). Nowadays more installation follows side-stream installation. The advantages of membrane bioreactor include low footprint area, low hydraulic retention time, and high solid retention time besides high-quality treated water. Membrane bioreactors have been used in the treatment of many industrial effluents having high organic loading such as in food and beverage, petroleum, pharmaceutical, pulp and paper, textiles (Dohare and Trivedi 2014; Mutamim et al. 2012), and municipal wastes. The major challenges include fouling, membrane life, energy consumption, and the overall cost of treatment, particularly due to limited membrane life and energy consumption.

Solvent Extraction Using Membranes

There are two types of membrane contactors used for liquid–liquid extraction, namely, supported liquid membranes and membrane solvent extraction.

Supported Liquid Membrane

Supported liquid membrane technique provides for simultaneous extraction and stripping, less inventory of solvent, and high selectivity. Hollow fiber ultrafiltration membranes are the preferred configuration as it offers high interfacial surface area. In supported liquid membrane, a solvent is immobilized within the pores of the membrane. The feed and the strip solutions are passed through either side of the membranes (tube/shell), and the contact between them is established by the solvent immobilized in the pores. The species, which is being separated, gets transported through the solvent, diffuses through it, and gets stripped by the strip solution. The advantage of this process is its high selectivity and the possibility of uphill transport.

Reviews (Parhi 2013; Dzygiel and Wieczorek 2010) on the supported liquid membrane indicate a variety of laboratory studies including the separation of radioisotopes such as plutonium, cesium-137, europium-154, and ruthenium-106. The liquid–liquid extraction with supported liquid membrane has been shown to have a good potential by a number of studies related to the extraction of metal ions in hydrometallurgical separations as well as from wastewater (Zhang et al. 2010; Ren et al. 2010). Recoveries of copper and uranium from sulfate leach liquors, uranium from wet phosphoric acid, and zinc from the waste liquors were demonstrated on pilot scale (Smith et al. 2014). Many solvents have been used including chelating or acidic extractants for the extraction of various metal ions such as copper, zinc, cobalt, nickel, iron, manganese, and molybdenum (VI). Extractants such as Alamine-336, Aliquat-336, and Alamine-304 based on amines have been used for molybdenum, chromium, and vanadium in the chloride solutions and crown ethers for alkali or alkaline earth metals (Padwal et al. 2018). In spite of all the potentialities including high selectivity, supported liquid membrane is not a commercially viable proposition because of the instability of the immobilized solvent which acts as a membrane and its high cost.

Membrane Solvent Extraction

In membrane solvent extraction, the feed and the solvent are independently circulated through the hollow fiber membrane element, one through the shell side and the other through tube side, depending on the design. Mass transfer occurs between the two streams in contact across the membrane pores. Unlike supported liquid membrane, extraction and stripping are carried out in two independent steps. However, when two sets of membrane elements are assembled together in a loop such that the extracting solvent passes through both the units, extraction and stripping occur continuously. The first unit extracts the species from the feed, while in the second unit, stripping takes place, thus enabling the simultaneous extraction and stripping resulting in the recycling of solvent and recovery of the species (Hemmati et al. 2015).

A number of investigations have been reported on the wastewater treatment for the removal and recovery of contaminants such as acetic acid (Sofiya et al. 2019), phenol (Shen et al. 2009), metal ions such as plutonium (Gupta et al. 2005), and cadmium (Fouad and Bart 2007). The advantage of using membranes includes large interfacial contact area without mixing of the phases and freedom to choose the solvent without density considerations. As the two phases are distinct, the flow rates can be varied independently, and problems of flooding and emulsification do not arise.

8.4.6 *Forward Osmosis*

Forward osmosis is gaining importance as a technology for desalination, concentration of solutions, and energy recovery. Its advantage emanates from being a passive process in nature (not requiring any external source of energy) as the separation is driven osmotic pressure differential between the draw solution and the feed. The challenges to realize the potential require a membrane with good water flux, a less reverse solute transport, and above all a convenient and cost-effective means of recovering pure water from the diluted osmotic sink. No doubt, the literature is replete with novel membranes such as cellulose triacetate (Ong et al. 2015), thin film composite (Ren and McCutcheon 2014), thin film nanofiltration (Ma et al. 2013), biomimetic (Fane and Tang 2012), and draw solute ranging from inorganic solutes, phase change material, low-molecular-weight organic solutes, and volatile solute or dissolved gas solutions (Lutchmiah et al. 2014). Since forward osmosis desalination is a two-step process, many combinations are being investigated using thermal and mechanical energy. Basically, the present methods adopted for forward osmosis desalination includes the combination of forward osmosis and reverse osmosis (Cath et al. 2010), forward osmosis–nanofiltration (Kim et al. 2018), forward osmosis–distillation (McCutcheon et al. 2006), and forward osmosis–phase change material (Kim et al. 2016). Apart from these, *aquaporin-incorporated vesicles* exhibit excellent water permeability and high salt rejection, owing to the superior intrinsic characteristics of the *aquaporin's* as water channels (Li et al. 2017). Double-skinned forward osmosis membranes have also been proposed (Song et al. 2015a).

Forward osmosis as a standalone desalination option is not practical because of the nonavailability suitable draw solute which can be easily regenerated to recover the product water. Forward osmosis has more potential in wastewater treatment (Lutchmiah et al. 2014) as it can be used for the concentration of the waste. Besides, the water that is removed can be recovered by secondary processes such as reverse osmosis/nanofiltration. Alternately, fertilizers can be used as draw solute so that the resulting dilute solution can be directly used in the field. Similarly, if pretreated seawater is used as a draw solution for wastewater, the seawater would get diluted, thereby savings in energy cost for seawater desalination (Akther et al. 2015).

8.4.7 *Diffusion Dialysis*

Because of the low flux, the applications of diffusion dialysis have been limited to the recovery of acids and alkalis from the discharges from steel production, metal-refining, electroplating, cation exchange resin regeneration, nonferrous metal smelting, aluminum etching, and tungsten ore smelting (Jeong et al. 2005). An excellent review by Luo et al. (2011) indicate that many acid recovery systems installed in different industries have made profits suggesting diffusion dialysis is adaptable to industries in a profitable manner even though the process is slow and is limited to acid/base recovery.

8.4.8 *Synergism of Different Membrane Processes in Water Treatment*

Each membrane process has its unique advantages and challenges. The pressure-driven membrane processes, ultrafiltration, nanofiltration, and reverse osmosis, have complementary characteristics. The processes, in pairs or sometimes all together, are used in water treatment applications. The process sequence ultrafiltration–nanofiltration–reverse osmosis may have to be maintained to get the synergism. In fact, ultrafiltration is a standard pretreatment for reverse osmosis in most instances. Ultrafiltration–reverse osmosis and ultrafiltration–nanofiltration–reverse osmosis are combinations which can provide fractionation of the solute species besides recovery of water. Since the operating pressure increases along the sequence, booster pumps are necessary between each membrane operation.

The advantages of using hyphenated membrane systems include satisfactory pretreatment through ultrafiltration to improve the sustainability of the nanofiltration or reverse osmosis systems. The use of nanofiltration in combination with reverse osmosis has the following advantages:

(a) The operating pressure can be reduced because of the poor rejection of monovalent species by nanofiltration and the consequent reduction in net osmotic pressure.
(b) Reverse osmosis can operate at lower pressures due to less concentration of nanofiltration permeate leading to better recovery and better quality of the product (Helal 2009).
(c) Since the reject of reverse osmosis plant would be having mostly monovalent solutes and less in concentration corresponding to the seawater feed, it can be blended with feed to bring down the salinity and hence obtain higher recovery (Song et al. 2015b).
(d) The intangible advantage of nanofiltration–reverse osmosis could possibly be less fouling and less maintenance requirements because of slight charge on nanofiltration membrane surface.

Ahunbay (2019) has indicated that by a combination of reverse osmosis and nanofiltration in a multistage configuration, the specific energy consumption can be brought lower than single-stage seawater desalination system. However, one may have to assess the specific energy consumption of seawater reverse osmosis versus nanofiltration–reverse osmosis system, as the energy recovery component would be less for nanofiltration–reverse osmosis system. For example, in seawater desalination, the combination of nanofiltration and reverse osmosis can lead to recovery of value. The concentrate of reverse osmosis would be rich in sodium chloride with

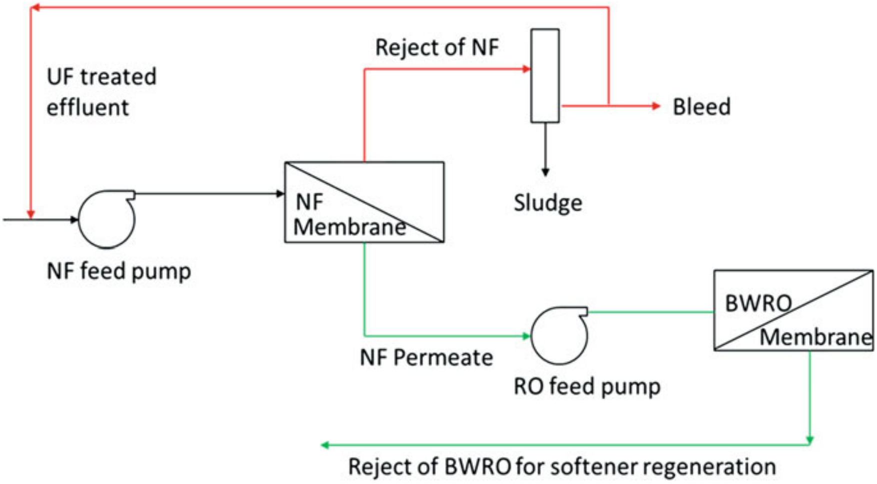


Fig. 8.10 Nanofiltration–reverse osmosis hybrid system for the treatment of mine effluents. Such configuration is useful for the separation of sulfates, chlorides, etc. along with the recovery of water for recycle. (Modified from Sarkar et al. 2011)

relatively less concentration of multivalent solutes and can serve as a feed to electrolytic production of sodium hydroxide at higher efficiencies. Ramaswami et al. (2018) have investigated the removal of water from landfill leachates using nanofiltration–reverse osmosis as well as reverse osmosis–nanofiltration combinations and concluded that nanofiltration–reverse osmosis is advantageous and energy-efficient over reverse osmosis–nanofiltration. Sarkar et al. (2011) have demonstrated that a combination of nanofiltration and reverse osmosis can lead to the separation of sulfates and chlorides, besides recovering water for recycle. The concentrated reverse osmosis stream containing concentrated sodium chloride can be used for the regeneration of the softener being used in the process, as shown in Fig. 8.10. The separation was possible, because of the fact that calcium sulfate requires significant induction period to form the precipitate at reasonable supersaturation level. In wastewater treatment, nanofiltration–reverse osmosis sequence helps in the recovery of nutrients besides water (van Voorthuizen et al. 2005). The use of reverse osmosis–electrodialysis has been suggested for crystallizers (Tanaka et al. 2003). In wastewater treatment and desalination, forward osmosis has a major role to play, and the combination of forward osmosis and reverse osmosis has the potential to reduce energy consumption as percent recovery can be increased provided a wastewater stream is available. A combination of diffusion dialysis and reverse osmosis can recover acid and water from acidic effluents. Removal of organic contaminants and recovery of water can be achieved by using a combination of membrane solvent extraction and reverse osmosis.

8.4.9 Membrane Processes for Point-of-Use Applications

Reverse osmosis water purification systems are easily available in the market across most of the countries which can be fixed in individual apartments for providing point-of-use safe water. Only concern in such plants is the very low recovery which results in wastage of water. Ultrafiltration is used as a final treatment step for the production of ultrapure water for electronic, pharmaceutical, and potable water applications. In places where salinity levels are acceptable, ultrafiltration membranes can be used for obtaining safe water without microbial contaminants. Further ultrafiltration-assisted devices have been developed (Bindal et al. 2011) for the remediation of groundwater contaminants such as arsenic, fluoride, iron, and so on.

8.5 Future Outlook and Prospects

As the society moves toward environmental conservation, membrane processes have more important role to play, particularly in recovering and recycling every component present in the waste stream. Most of waste streams contain value materials but normally not recoverable at an acceptable cost and effort. The availability of a variety of membrane processes and membranes offers plenty of opportunities to realize *wealth from waste*.

The general practice in waste management is to mix all the spent streams (effluents) and treat them as a single batch. Naturally, the whole system becomes complex and complicated, and other than water not much is recoverable.

Membrane processes are modular in nature and the capacity is flexible. Accordingly, small-capacity units can be installed without the requirement of much foot print. In this context, it is possible to decentralize the water treatment operation both in industries and residences. Spent streams emanating from different processes can be isolated and processed which will be easier, and many times value can be recovered. Consequently, each stream will have only one type of contaminant which can be easily separated. The contaminant may be a valuable raw material or product or an intermediate. This is possible even in domestic waste where gray water can be isolated from black water. Water can be recovered from gray water using ultrafiltration and reverse osmosis, while the black water can be bioprocessed to generate energy.

Forward osmosis being a passive process can be used to link the *wastewater–resource* loop. This would help in recovering water from waste without using energy. Membrane distillation also has a bright prospect if it could be used for recovering water from return cooling water of industries or power plants. If the cooling circuit uses less water, the temperature of the cooling water would be higher to provide better yield of a desalinated water which could be a win–win situation. Recovery of values particularly heavy metal species such as in mine discharges and electroplating industries through size-enhanced ultrafiltration looks promising after recovery of acid through diffusion dialysis. It is expected the membranes would have a larger role to play in water treatment in the years to come.

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