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Introduction to Membrane Technology

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1.1 Overview of Membrane Technology

Membrane technology is a general term used for a range of different separation processes. Membrane separation processes have been proven to be well-established technologies in a wide range of water, energy, food, and environmental applications throughout the production, purification, and formulation of useful products [1–4]. Thus, the membrane separation processes have become the leading separation technology over the past two decades. The membrane is defined as a selective thin layer of a semipermeable material that acts as a selective barrier and separates undesired species from a feed solution based on their sizes or affinity by exerting a potential gradient, such as pressure, temperature, electrical, or concentration difference (Figure 1.1). Separation is accomplished if one species of a mixture moves through the membrane faster than another species in the mixture. The main advantage of membrane technology, which differentiates it from traditional separation, purification, and formulation processes, is that it produces stable products without adding chemicals with a relatively low energy consumption with a remarkable potential for an environmental impact. Other benefits include modular and easy to scale-up, well-arranged, compact, and straightforward process in concept and operation, decreased capital and operational cost of technology applications using membrane, and environment friendly.

In general, membranes are classified based on their average pore size, driving force, morphology, and materials. The pore size of the membrane material or surface is a paramount factor in its first differentiation. Nevertheless, membrane materials can be organic and inorganic. All of the membrane separation processes are effective methods of treating the feed mixture, e.g. water, gas, and food that hardly is treated using conventional separation methods.
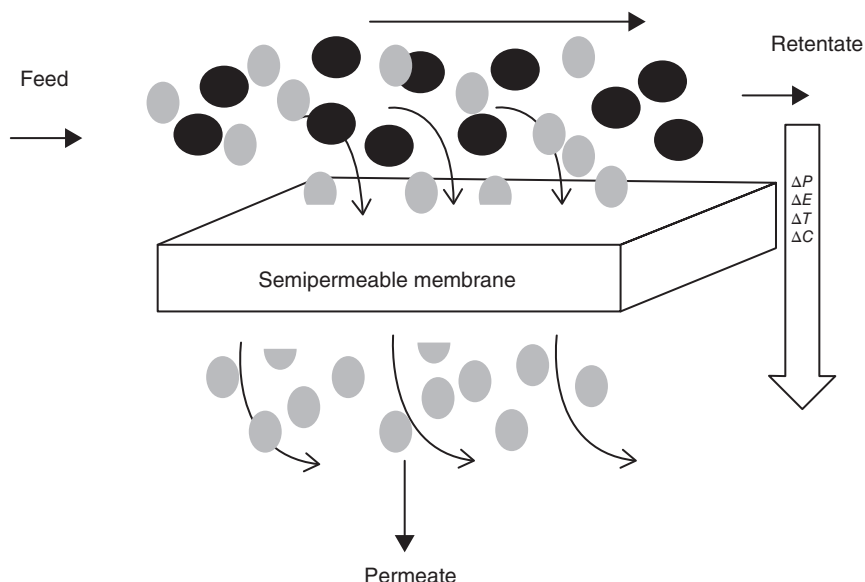
Figure 1.1 Typical membrane separation process.

1.2 Conventional Membrane Separation Processes

1.2.1 Microfiltration (MF)

Microfiltration (MF) is the first classification of membrane separation techniques based on pore size. The MF membrane was first developed to analyze the bacteria in the water. In the 1960s, the first commercial MF membrane was also developed in biological and pharmaceutical applications. Since then, MF membranes have been widely applied in wastewater treatment and juice technology to remove microorganisms, clarify cider and other juices, and sterilize beer and wine. The separation mechanism in MF membranes is governed by the sieving effect or size exclusion technique. Thus, the species are separated according to their size. Large pores of MF remove suspended solids, while even proteins can pass through the MF membrane easily. The MF membranes can also be used to separate sand, clays, algae, and some bacteria from aqueous feed streams. They are recommended to separate species with a diameter larger than 0.1 μm. The applied pressure in MF is low (usually <2 bar), while this is the lowest applied pressure in other pressure-driven membrane separation processes [5, 6].

1.2.2 Ultrafiltration (UF)

Ultrafiltration (UF) is also included in size exclusion-based pressure-driven membrane separation processes. The pore size of UF membranes is around 0.01 μm. These membranes can prevent species in the molecular weight range of 300–500 000 Da to pass through. UF rejects protein and suspended solids. However,

dissolved substances could not be removed by UF unless they are first pretreated in an adsorption column like with activated carbon or coagulated with alum or iron salts. Similarly, UF membranes cannot retain the mono- and disaccharides, salts, amino acids, organics, inorganic acids, or sodium hydroxide. They exhibit small osmotic pressure differentials due to their inability to reject salts, as compared with reverse osmosis (RO). UF processes operate at 2–10 bars. Separation efficiency will further be augmented if the difference in the sizes of the species is high enough. UF is considered nowadays to be the dominant part of membrane separation processes due to its diverse applications in water, energy, food, and the environment. UF processes are considered the most used membrane separation process next to dialysis and MF [7].

1.2.3   Nanofiltration (NF)

Nanofiltration (NF) is another pressure-driven membrane process between RO and UF pore size of around $0.001\,\mu m$. NF membranes remove most organic molecules, viruses, and a range of salts. These membranes are often applied to soften the hard water by removing divalent ions. NF membranes possess a negative charge on the surface. It demonstrates the anion repulsion, which mainly causes the species rejection. Low rejection is witnessed for salts with monovalent anion and nonionized organics with a molecular weight below 150. However, high rejection can be observed for salts with di- and multivalent anions and organics with a molecular weight above 300. NF is advantageous over RO in different aspects, such as being operated at low pressure, giving high permeate flux, retention of multivalent salt and organic solutes, and having low investment and operation and maintenance costs.

   NF membrane is more suitable for ions with more than one negative charge in single charged ions pass, such as sulfate or phosphate. However, NF membranes also reject uncharged and positively charged ions according to the molecule's size and shape. For example, the same rejection of calcium chloride and sodium chloride can be observed while the rejection of sodium sulfate is the same for magnesium sulfate. Instead, the rejection of di- and multivalent anions is high compared with that for monovalent ions. The species rejection decreases with increasing concentration. The Donnan exclusion model can explain this phenomenon. The higher the species concentration, the more cations available to shield the negative charges on the membrane surface, making it easier for the anions to pass through the membrane pores. On the other hand, the charge density of ions also plays an important role in its rejection. For example, the sulfate ion has a higher charge density than the chloride ion and is almost completely repelled by the NF membrane even in a high ionic strength solution such as seawater [8].

1.2.4   Reverse Osmosis (RO)

RO demonstrates, in principle, the least possible pore structure among the membranes. Water is the only species that can pass through the RO membrane;

essentially, all dissolved and suspended species are rejected. RO membranes have a pore size of around 0.0001 μm. The permeate is essentially the pure water because RO also removes most healthy minerals such as calcium, zinc, magnesium, etc. that are present in the water and are useful in a certain quantity for drinking water especially for people with inadequate diets and people living in hot climates. The water can be made healthy bypassing the RO water through calcium and magnesium beds. RO removes monovalent ions to desalinate the saline water. Both NF and RO are also termed as dense membrane separation processes because separation relies to some extent on physicochemical interactions between the permeate (species) and the membrane material. In wastewater treatment and reclamation, RO systems are typically used as the last step for removing total organic carbon (TOC). RO has been proven to remove dissolved species effectively, microbes, and neutral base compounds [9, 10].

To understand the working principle of RO, it is helpful to understand first osmosis. Osmosis refers to the migration of water from a weaker solution to the stronger solution when a semipermeable membrane separates two salt solutions of different concentrations. The migration of salts continues until the two solutions reach the same concentrations, achieving the osmotic equilibrium. The semipermeable membrane allows the water species to pass through naturally, but not the salt. In RO, the two solutions are still separated by a semipermeable membrane, but the pressure is applied to reverse the water's natural flow. This forces the water species to move from the more concentrated solution to the weaker. Thus, the solute aggregate on one side of the semipermeable membrane and the pure water pass through the membrane on the other side. The concept of osmosis and RO is described schematically in Figure 1.2 where (a) and (b) illustrate the process of osmosis and (c) represents the RO. If a certain pressure (ΔP) applied to the concentrated solution equals the osmotic pressure difference between the two solutions ($\Delta \pi$), the system reaches the osmotic equilibrium, and water flow stops. If the applied pressure exceeds osmotic pressure ($\Delta P > \Delta \pi$), water flows from the concentrated solution to the dilute solution. A summary of pressure-driven processes is outlined in Tables 1.1 and 1.2.

1.2.5 Electrodialysis (ED)

Electrodialysis (ED) refers to an electrically driven membrane separation process in which charged ions are separated from a feed solution through selectively
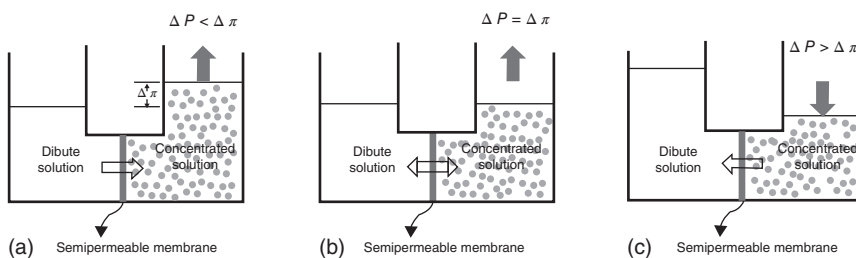

Figure 1.2 Osmotic phenomena: (a) osmosis, (b) equilibrium, and (c) reverse osmosis.

Table 1.1 Pressure driven size-based membrane processes for the removal of typical pollutants.

Feed component	Membrane separation process			
	Microfiltration (MF)	Ultrafiltration (UF)	Nanofiltration (NF)	Reverse osmosis (RO)
Water				
Monovalent ions				
Multivalent ions				
Dissolved substances				
Viruses				
Bacteria, protozoa				
Suspended solids				

ion-permeable membranes. In an ED process configuration, cationic and anionic membranes are alternately arranged between an anode and a cathode plate. By applying an electrical potential, the ions migrate toward the anode and cathode, and consequently, the water molecule is deionized. A typical ED cell consists of electrodes and ion-permeable membranes, as shown in Figure 1.3. When an electric field across the membranes is applied, the cations move toward the cathode, and the anions migrate toward the anode. The cations pass through the cation-selective membrane, while anions pass through the anion-selective membrane. Thus, the feed became diluted in one side and concentrated in the electrolyte on the other side. Best performance in ED membranes could be achieved by selecting the highly permselective, physically strong, and low electrical resistance membranes [5].

1.2.6   Pervaporation (PV)

Pervaporation (PV) is a membrane separation process used to recover more volatile components in liquid mixture through a dense membrane. The PV is governed by a partial pressure difference across the membrane as the driving force by applying a vacuum at the permeate side [11–14]. The solution–diffusion model generally describes the transport of species across nonporous membranes in PV. Because of the negative pressure on permeate side, the osmotic pressure is not a limiting factor, as is the case for RO. The partial pressure difference at feed and permeate sides causes the more volatile liquid to vaporize within the membrane. The vapor passes through the membrane and finally condenses at the permeate side (Figure 1.4). PV

Table 1.2 Comparative analysis of conventional membrane processes.

	Microfiltration (MF)	Ultrafiltration (UF)	Nanofiltration (NF)	Reverse osmosis (RO)	Electrodialysis (ED)	Membrane pervaporation (MPV)
F/P	L/L	L/L, G/L	L/L	L/L	L/L	L/G
Membrane material	Polymeric	Polymeric/ceramic	Polymeric/ceramic/mixed matrix	Polymeric	Polymeric	Polymeric; polyvinyl alcohol composites, silicones, cellulose acetates
Membrane structure	Symmetrical/asymmetrical	Asymmetrical	Asymmetrical	Asymmetrical	Asymmetrical	Asymmetrical
Membrane morphology/thickness	Porous	Porous	Porous/dense	Dense	Dense	Dense
Support layer	10–150 µm	150–250 µm	150 µm	150 µm		
Thin film	1 µm	1 µm	1 µm	1 µm		
Pore size	0.05–10 µm	0.001–0.05 µm	0.5–2 nm	<0.002 µm	MW < 200 Da	Nonporous
Driving force	ΔP	ΔP, activity difference, concentration difference, temperature difference	ΔP	ΔP	ΔE	ΔP vacuum, chemical potential gradient
Separation principle	Sieving mechanism	Sieving mechanism	Donnan exclusion/solution–diffusion/capillary flow	Solution–diffusion	Solution–diffusion/ion migration	Donnan exclusion/solution–diffusion
Operating pressure	<2 bar	2–5 bar	5–15 bar	15–100 bar	Electrical potential	Partial pressure difference
Membrane module type	Tubular, hollow fiber	Plate and frame, spiral wound, tubular, hollow fiber	Plate and frame, spiral wound, tubular	Plate and frame, spiral wound, tubular		Plate and frame, spiral wound, tubular, hollow fiber

MWCO		300–500 000 Da	200–1000 Da	<500 Da	
Applications	Separation of macromolecular to cellular size particles (bacteria, fat, proteins, whey industry)	Fruit juice clarification and concentration, milk separation, food, beverage, and dairy, biotechnology, medical applications	Water softening, removal of color, hardness, TOC, sulfate from water, concentration of organics with molecular weight of 300–1000 in the food and pharmaceutical	Separation of ions mostly in desalination of water	Dehydration of liquid organic, ethanol, isopropyl alcohol, ethylene glycol
Permeate flux		150 l/m²/h	43 l/m²/h/bar	SWRO, BWRO desalination	
Solute rejection (type)	Particles, clay, bacteria	Macromolecules, proteins, polysaccharides, sugars, biomolecules, polymers, colloidal particles	HMWC, mono-, di-, and oligosaccharides, polyvalent ions (−ive), MgSO$_4$, glucose, sucrose	HMWC, LMWC, sodium chloride, glucose, amino acids	
Solute rejection (%)		>90%	Up to 100%	>90%	
Issues and problems		Membrane fouling and concentration polarization			

F/P, feed/permeate; TMP, transmembrane pressure difference; HMWC, high-molecular-weight compounds; LMWC, low-molecular-weight compounds; SWRO, seawater reverse osmosis; BWRO, brackish water reverse osmosis; MWCO: molecular weight cutoff.
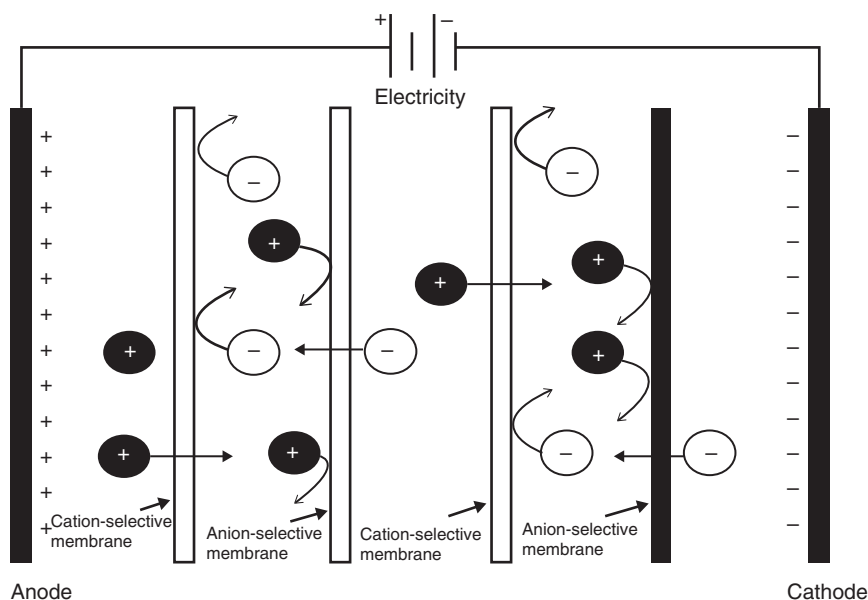
Figure 1.3 A basic electrodialysis system.

is characterized by the imposition of a barrier layer between two phases. Mass transfer occurs selectively across the membrane from one side to the other side of the membrane. The unique phenomenon of PV is the phase change required of the one phase (feed) diffusing across the membrane [17–19]. Since different species present in the feed mixture permeate through the membrane at different rates, a low concentration component in the feed mixture can be highly enriched in the permeate. Thus, the membrane's selectivity becomes the defining factor in the relative flow of the different species. PV has gained more attention from the chemical industry in the past decade due to the effective separation process for recovering volatile components in liquid mixtures. It is currently considered more effective for dehydration of liquid hydrocarbons to yield high-purity organics, most notably ethanol, isopropyl alcohol, and ethylene glycol. PV, due to its simplicity and easy installation, is used as an integrated process with distillation [20, 21].

1.3 Molecular Weight Cutoff (MWCO)

Molecular weight cutoff (MWCO) is a useful tool for characterizing filtration membranes. In early development, UF membranes were used to purify macromolecules in bioseparation processes such as to retain the proteins. Since their molecular weight characterizes macromolecules, the membranes are also characterized by whether the macromolecules up to certain molecular weights are retained. It depends on the size of the pore of the membranes. MWCO is indicated in Dalton that refers to the MWCO of species or solute with 90% rejection. MWCO 500 describes
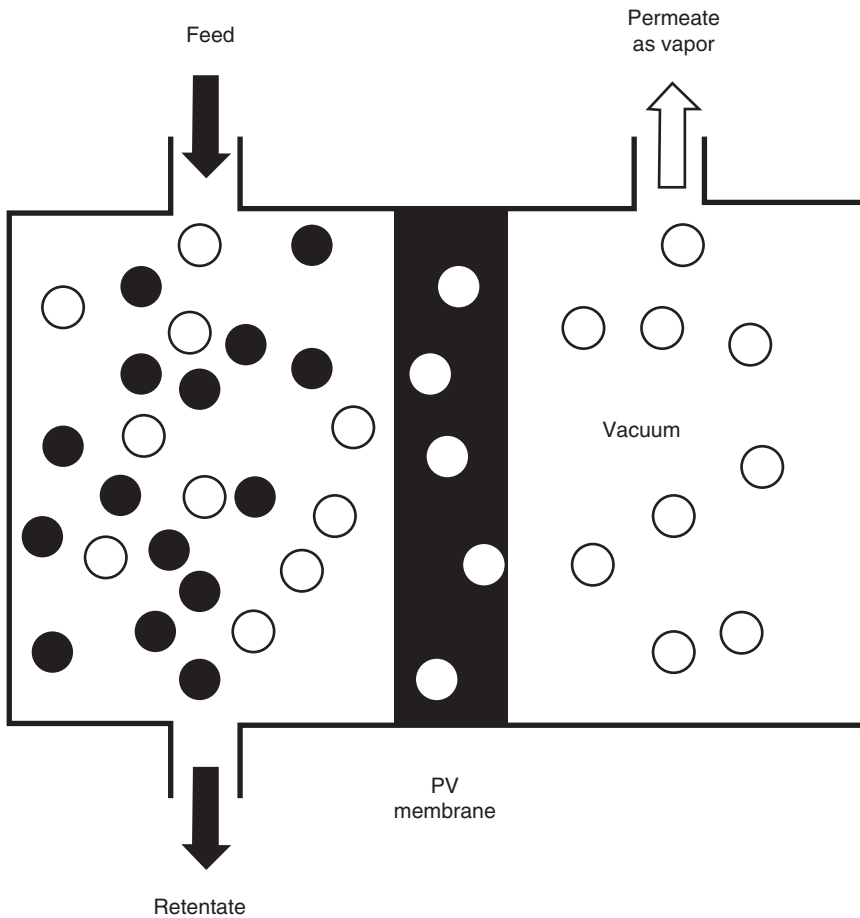
Figure 1.4 Membrane pervaporation process. Source: Based on Winzeler and Belfort [15] and Shirazi et al. [16].

that the molecules with molecular weight (MW) above 500 are rejected, and those with below 500 are passed through the membrane. The MWCO of any membrane can be altered from the chemistry of the solute with membrane interaction, their molecular orientation and configuration, and the operating conditions [22].

1.4 Concentration Polarization

Concentration polarization in membrane filtration is one of the significant problems that hinders the solvent flux and solute rejection. Concentration polarization is an important feature in membrane separation processes. Species rejected by the membrane accumulate at the membrane surface. This accumulation of species on the surface of the membrane is called concentration polarization. It produces a concentration gradient in the zone where the species accumulate. There remains

a balance between species brought to the membrane surface by convective flow of the solvent and back-diffuses to the bulk. At times, however, the balance in species concentration at the membrane surface diminishes. It reaches its solubility limit, which is lower than that predicted by the fluid hydrodynamics of the system.

Consequently, the membrane effectively experiences a higher feed side concentration at its interface, resulting in reduced flux and reduced apparent solute rejection. Often the severity of concentration polarization can be controlled by operating conditions, module geometry, and fluid hydrodynamics. Concentration polarization practices to a smaller increase in transmembrane solvent flux with the rise in operating feed pressure until a gel layer is formed at the membrane's surface. It can also be lessened by increasing the fluid share at the surface of the membrane or producing the turbulence by introducing the channel spacers in the modules. Thus, the transmembrane solvent flux shows no further increase with the pressure and is termed as limiting flux [15, 23].

1.5 Membrane Fouling

Fouling refers to the deposition of solute or any other species in feed on the membrane surface or inside the membrane pores. For example, if the balance in species concentration at the surface due to convective flow and feed bulk concentration reaches the point where species precipitates or forms a thixotropic gel, the situation is termed as fouling. The formed gel layer causes an additional mass transfer resistance in conjunction with the membrane itself. In such cases, increased applied feed pressure may not improve the transmembrane flux; rather it will increase or densify the gel layer [24].

Fouling may be caused by the pore geometry/tortuosity or species–pore wall interactions. Consequently, the pores are blocked entirely or be marginally reduced in diameter, causing a decline in transmembrane flux while the rejection may be either constant or may increase. Proper and scheduled membrane/module cleaning may reverse the fouling; however, irreversible fouling may also occur over time, permanently deteriorating the membrane surface and pores. In such cases, the membrane's replacement becomes indispensable to regain the actual transmembrane flux and the species rejection. Although both concentration polarization and fouling reduce transmembrane solvent flux, they have opposite effects on species rejection. For example, concentration polarization is a function of operating parameters like pressure, temperature, feed concentration, and velocity but is independent of time. In contrast to that, fouling is partially dependent on operating parameters, particularly feed concentration, but is also time dependent. These phenomena have been described schematically in Figure 1.5 [15, 16].

In UF, feed-side mass transfer resistance and resistance due to the gel/cake layer formation on the membrane surface because of fouling play an essential role in transmembrane flux and species rejection. Usually, the proper membrane process and material selection are chosen to decrease the fouling tendencies of the membrane surface. The base polymer surface chemistry can be modified to increase
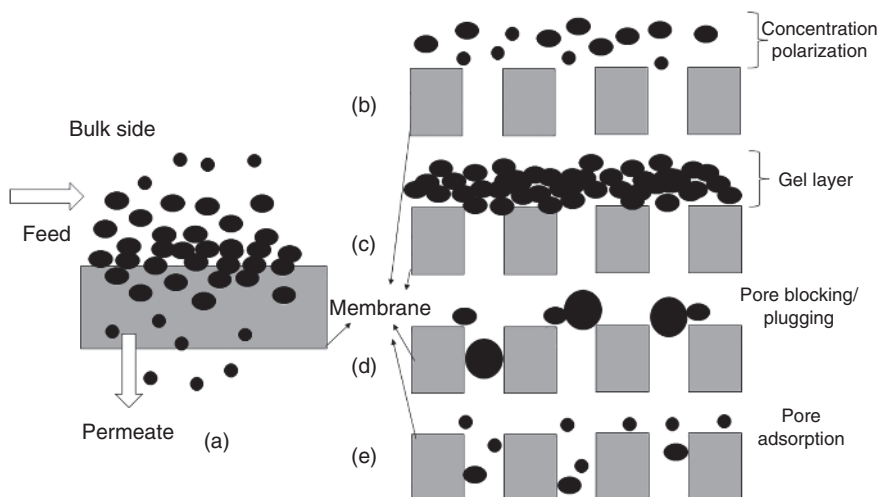
Figure 1.5 Membrane fouling and concentration polarization. (a) Membrane separation process. (b) Concentration polarization. (c) Gel/cake layer. (d) Pore blocking/plugging. (e) Pore adsorption.

hydrophilicity of the membrane with the contacting fluid to increase the flux and reduce the fouling in most aqueous applications. Fouling, scaling, or chemical interaction greatly affects the NF and RO systems while MF and UF are mildly affected in their effective operation. Thus, extensive pretreatment is occasionally made mandatory before NF and RO to avoid conditions leading to fouling, scaling, or chemical interaction [16, 23].

1.6 Diafiltration

In some cases, during filtration, recovery of species may be hindered due to reduced flux, high feed viscosity, solubility limits of nonpermeating solutes, etc. For such cases, the concentrate is diluted by solvent (water) during continuous filtration until satisfactory recovery of the permeable species, which is termed diafiltration.

1.7 Historical Perspective

The history of membrane separation technology dates back to 1748 when the French Abbe Nollet published his observations on osmotic phenomena [25]. The study of UF has been closely associated with that of dialysis. Dialysis experiments through artificial membranes of collodion were recorded by Fick [26]. Similar observations on dialysis were made by Hoppe-Seyler [27] and Schumacher [5]. The pioneering study UF process was reported by Schmidt [28], who investigated the filtration of a solution of protein or gum Arabic through an animal membrane.

In the third decade of twentieth century, membranes were regarded as mechanical sieves, and permeability was considered as the sole dependent on particle and pore dimensions. The concept of semipermeability of the membrane and the theory of partial solubility was also introduced in this decade, which describes membrane's permeability as solvent dissolving in the membrane from one side to the other. For the first time, the membrane was used in seawater desalination to produce sources for freshwater, put forth by Hassler [29]. Later, Reid and Breton introduced the RO membranes when they developed the cellulose diacetate film showing salt rejection up to 96% [30]. However, the breakthrough was achieved when Loeb and Sourirajan developed a cellulose diacetate asymmetric membrane and successfully tested for high flux and salt rejection.

DuPont developed a hollow fiber capillary membrane from aromatic polyamide. However, in 1985, Cadotte prepared high-performance membranes using in situ interfacial polycondensation between poly/monomeric amine and poly/monomeric functional acid halide [31, 32]. This opened a new era for the researchers to explore the polyamide films by crosslinking, which gave high permeate flux that cellulose acetate (CA) membranes [9].

FilmTec introduced the two-layer design membrane modules for water desalination at the industrial scale, which is still dominating the desalination industry. Undoubtedly, the membrane material and the modules have been improved over the years, but the basic concept adopted by FilmTec is still widely accepted. Desalination Systems, Inc. (DSI) introduced three-layer composite membranes for NF and RO. In the twenty-first century, membrane separation processes such as UF, NF, and RO emerged as reliable technology in water, food, environment, and food.

1.8 Concluding Remarks and Future Challenges

Membrane technology has become an important entity of our daily life routine work. Membranes have a potential in the future. Water scarcity and water stress, carbon capture, food security, energy constraints, environmental regulations, and nanotechnology are key drivers to boost the membrane technology further. However, the development in membrane technology would rise exponentially if "engineering aspects" in all membrane separation processes with key attention to "industrialists" and "entrepreneurs" are correctly addressed. Membranes perform the specific task for which they are designed. Each type of membrane filtration, e.g. MF, UF, NF, and RO, has its own role depending upon the pores' size, driving force, operating conditions, membrane material properties, and physicochemical interaction with feed components. However, if a specific membrane was chosen for the particular application and process, it performs well and achieves the required objectives. Two facts should be kept firmly in mind before deciding any membrane process: "Membranes do not lie." The statement describes that membranes do exactly what they can do under the given circumstances. For example, if the membrane material is not compatible with the feed solution or cannot withstand the operating parameters, the membrane will not perform to expectations. In

such cases, this will not be the deficiency of the membrane. The other fact is: "Membranes are designed to reject dissolved solids." This means that if the feed mixture contains substantial and diverse undesired components like suspended solids, then the membrane systems will perform very poorly. So for each membrane separation process, the feed characteristics have also been described, and their protocol should be obeyed. Otherwise, pretreatment of feed should be ensured that the feed solution is free of species that may precipitate or degrade the membrane pores and surface due to their aggregation during the process.

In the twenty-first century, the world is facing more severe challenges than ever toward sustainable development in terms of water quality and sources in developed and developing countries, meeting increasing energy demands, securing the food shortages, and controlling the adverse effects of global warming. Therefore, the demand for the use of novel membranes, innovative processes, and compact modular designs to address these issues in various applications will continue to increase. The conventional membrane separation processes have already emerged as a promising technology in different water food and environment sector applications. Still, there remained a gap to develop the membrane technology to be driven by higher productivity, lower cost of production, and increased development speed. It was learned that several membrane characteristics could determine a membrane's suitability for a specific separation application. These include (i) porosity, (ii) morphology, (iii) surface properties, (iv) mechanical strength, (v) chemical resistance, (vi) selectivity, and (vii) driving force. These characteristics depend on the proper choice of membrane material and the synthesis technique. Further to that, module design is also essential to a great extent to achieve these properties. These characteristics are interrelated; for example, a highly porous membrane structure can be maintained only if the polymer has adequate mechanical strength or the membrane should be operated at low or atmospheric pressure. Surface properties and pore morphology are linked to fouling properties, flux through the membrane, and solute separation. There is a need to reduce or even remove the gas between scientists and industrialists. For example, scientists and engineers' major challenges are as follows: (i) membrane designs should be manufacturer specific, and (ii) application-specific membranes should be developed targeting the specific industry. Membrane system costs and applications are currently materially limited, whereas membrane performance is measured as solvent flux and selectivity which are the limiting factors for scientists and engineers. However, for an efficient and economically feasible industrial application, membranes need to keep their whole lifetime integrity. Unfortunately, the integrity and flux or selectivity is often in the opposite trend. Less integrity will lessen the membrane life and thus is meant for higher replacement costs of the membrane. It is also noted that membrane technology has its own disadvantages. For example, high pressure as a driving force causes high energy consumption and pollution to the environment and uses a range of chemical solvent that could be very harmful to the environment. Thus, the future development of membrane technology and its applications could conform with the sustainable development goals (SDG). Theoretically, $0.7\,\text{kWh/m}^3$ should be the minimum energy required to convert seawater to pure water [33]. Membrane

separation technology is currently considered among the best available technologies (BAT) in the nexus of many processes and applications like food, water, energy, and the environment. However, with the current choice of materials, modules, and technology, the energy consumption still stands between 2 and 5 kWh/m^3 [34]. Thus, the research is focused on increasing the separation efficiency, reducing energy consumption, and making it more environment friendly and fouling resistant. The gap between scientists and industrialists should be removed. Such objectives could be achieved by adopting the membrane contactor technology and switching over to concentration difference as a driving force instead of using pressure difference as the driving force. The successful design and operation of membrane systems lie in a deeper understanding of principles, engineering, and practical aspects such as interfacial phenomena, rheology, material science, and module design of membrane separation processes. The research and development ("R&D") efforts should be focused rather on "engineering applications" such as water, energy, food, and the environment. This would also lead to clear the approach that any membrane module will result in the expected separation.

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