



A Review of Membranes Classifications, Configurations, Surface Modifications, Characteristics and Its Applications in Water Purification

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Abstract: Today, membrane separation technologies are widely used in many areas of water and wastewater treatment. Membrane processes can be used to produce potable water from surface water, groundwater, brackish water, or seawater, or to treat industrial wastewaters before they are discharged or reused. Membrane separation systems have many advantages over traditional water or wastewater treatment processes, lower operating and maintenance costs in comparison to conventional systems consisting of coagulation, clarification, and aerobic and anaerobic treatments. • Membrane separation systems are easy to operate and the performance is more reliable. • Membrane systems give a compact and modular construction, which occupies less floor space in comparison to the conventional treatment systems. In this review, we will introduce fundamental concepts of the membrane and membrane-separation processes, such as membrane definition, membrane classification, membrane formation, module configuration, transport mechanism, system design. Four widely used membrane separation processes in water and wastewater treatment, namely, microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), will be discussed in detail. Some basic requirements for membranes are • high flux of the product, good mechanical strength for supporting the physical structure, good selectivity for the desired substances. Generally, high selectivity is related to membrane properties, such as small pores and high hydraulic resistance or low permeability. The permeability increases with increasing density of pores, and the overall membrane resistance is directly proportional to its thickness. Therefore, a good membrane must have a narrow range of pore sizes, a high porosity, and a thin layer of material. Membranes can be either dense or porous. Separation by dense membranes relies on physicochemical interaction between the permeating components and the membrane material. Porous membranes, on the other hand, achieve separation by size exclusion, where the rejected material may be either dissolved or suspended depending on its size relative to that of the pore. Membranes can be organic (polymeric) or inorganic (ceramic or metallic), according to its composition, and their morphology is dependent on the nature of the material. There is a need for improved membranes that have higher efficiency and are more resistant to the chemical environment, especially chlorine. This article summarizes the art of membrane technology.

Keywords: Membranes, Water Purification, Classifications, Configurations, Surface Modifications, Characteristics, Separation Techniques

1. Introduction

Membranes are an intimate part of being alive. Several examples are simple to cite:

- The skin in all mammals is a very efficient and highly selective type of membrane controlling release of sweat to

cool off the bodies through evaporation of tinny water droplets during hot weather. Skin selectivity as apparent, when its cut the fine blood cells and vessels that runs underneath the skin are broken and releases its blood content. A healthy and intact skin does not release blood. The lungs are also a good example of effective membranes, where fine cells within the lungs allow passage of oxygen from the inhaled air and release carbon dioxide into the same stream. The lungs as a membrane prevents permeation of the nitrogen in the inhaled air, irrespective of its high content. The kidney membranes regulate the water, salt ions, proteins, and other nutrient within the body. The kidneys are extremely efficient that a healthy body can survive with a quarter of both kidneys. On a much smaller scale, membrane walls in single cells within mammals, bacteria, and other microorganisms maintains the cell contents intact and regulate the input/output rates of nutrients or products. Since the early days of civilization mankind have adopted simple forms of membranes. In early agriculture communities, household sieves were invented and developed to separate fin grain ground from coarse grain particles and shells. Similarly, cheesecloth was made from cotton fibers and used to manufacture cheese. Both forms of separation are based on differences in particle size.

However, developments in membrane technology have focused on adoption of other separation mechanisms, such differences in solution and diffusion rates of various species across the membrane material. Other than the sieve type membrane use of artificial membranes is rather new. Major landmarks in use of artificial membranes are summarized in the following points:

In the mid-1970s, cellulose triacetate hollow fiber permeators were introduced by Dow Chemical Company,

followed by Toyobo of Japan. During the same period. Fluid Systems and Film Tec introduced the spiral wound polyamide thin film composite membranes. Throughout the 1980s, improvements were made to these membranes to increase water flux and salt rejection with both brackish water and seawater. Today the predominate membrane materials are still aramids, polyamides, and cellulose acetate and triacetate in spiral wound and hollow fiber configurations. Applications of the RO membranes include potable water production, waste recovery, food applications, kidney dialysis, high-purity water for boiler feed, and ultrapure water electronics applications. In 2000, the RO technology was used to treat more than two billion gallons of water per day, and this market is expected to continue growing during the first half of the 21ST century.

2. Elements of Membrane Separation

A number of membrane-based desalination processes are used on industrial scale. As is shown in Figure 1, the membrane-based processes include reverse osmosis, nanofiltration, ultrafiltration, and microfiltration. Differences among these processes is shown in Figure 1, where Microfiltration operates on a particle size range of 0.15 μm to 0.15 μm, and Ultrafiltration operates on a particle size range of 0.15 μm to 5x10⁻² μm and Nanofiltration operates on a particle size range of 5x10⁻² μm to 5x10⁻³ μm and Reverse osmosis operates on a particle size range of 5x10⁻³ μm to 10⁻⁴ μm. There is an inherent difference in the separation mechanism in all filtration processes and the reverse osmosis process. In filtration, separation is made by a sieving mechanism, where the membrane passes smaller particles and retains larger ones.

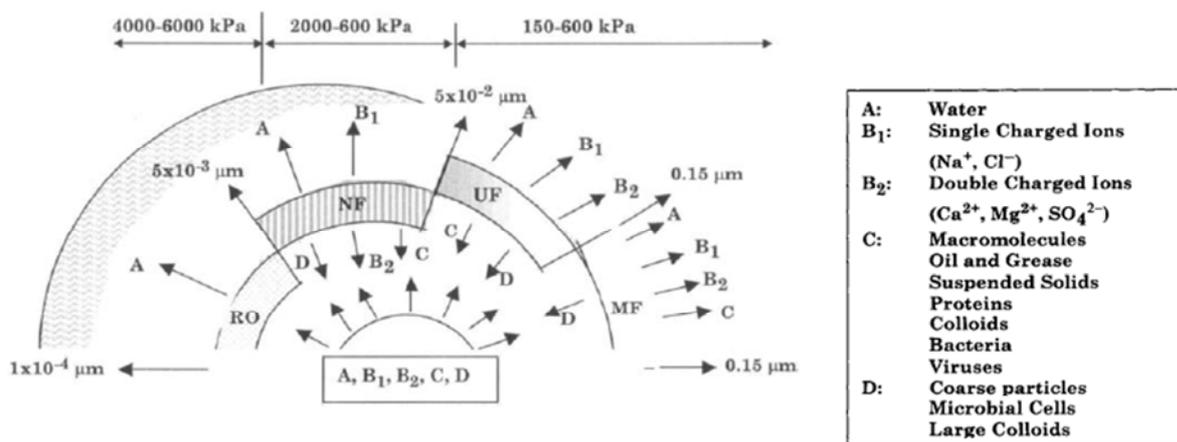


Figure 1. Membrane separation processes and corresponding particle sizes.

In osmosis or reverse osmosis processes the membrane permeates only the solvent and retains the solute. Further distinction of the four membrane processes is shown in Figure 1. As is shown, the microfiltration, ultrafiltration, and nanofiltration processes are used to separate the suspended material. On the other hand, the reverse osmosis process is

used to separate dissolved solids. Nanofiltration is used for partial softening of brackish water. A schematic for the osmosis and reverse osmosis phenomenon are shown in Figure 2. In this configuration, the direction of solvent flow is determined by its chemical potential, which is a function of pressure, temperature, and concentration of dissolved solids.

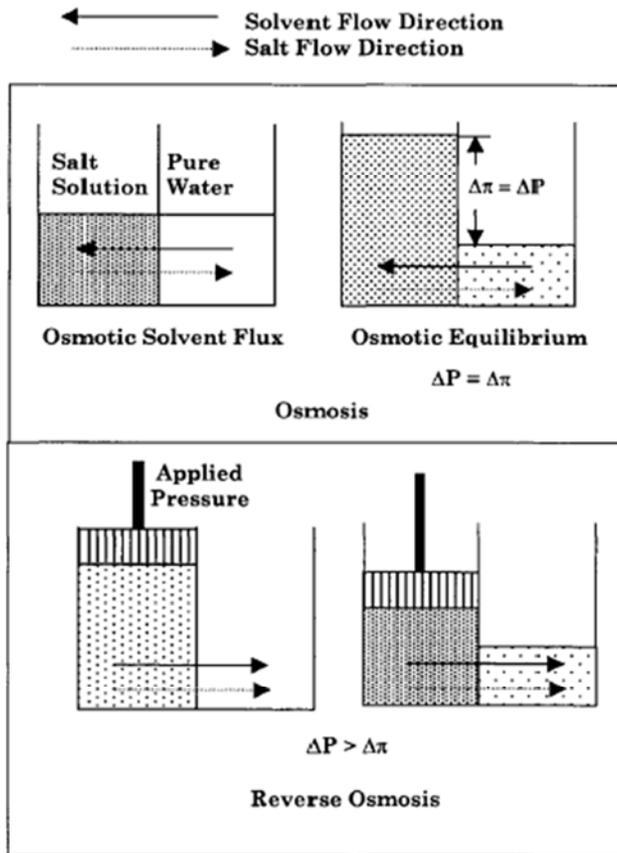


Figure 2. Osmosis and reverse osmosis processes.

Pure water in contact with both sides of an ideal semi-permeable membrane at equal pressure and temperature has no net flow across the membrane because the chemical potential is equal on both sides. If a soluble salt is added on one side, the chemical potential of this salt solution is reduced. Osmotic flow from the pure water side across the membrane to the salt solution side will occur until the equilibrium of chemical potential is restored. Equilibrium occurs when the hydrostatic pressure differential resulting from the volume changes on both sides is equal to the osmotic pressure. This is a solution property independent of the membrane. Application of an external pressure to the salt solution side equal to the osmotic pressure will also cause equilibrium. Additional pressure will raise the chemical potential of the water in the salt solution and cause a solvent flow to the pure water side, because it now has a lower chemical potential.

3. Performance Parameters

The RO process is defined in terms of a number of variables, which includes Osmotic and operating pressure Salt rejection, and Permeate recovery. Membrane manufacturing companies define system specifications in terms of the feed quality, which includes salinity and temperature.

3.1. Osmotic and Operating Pressure

The osmotic pressure, π , of a solution can be determined

experimentally by measuring the concentration of dissolved salts in the solution. The osmotic pressure is obtained from the following equation

$$\pi = R T \sum X_i \quad (1)$$

where π is the osmotic pressure (kPa), T is the temperature (K), R is the universal gas constant $8.314 \text{ kPa m}^3/\text{kg mol K}$ and $\sum X_i$ is the concentration of all constituents in a solution (kg mol/m^3). An approximation for π may be made by assuming that 1000 ppm of Total Dissolved Solids (TDS) equals to 75.84 kPa of osmotic pressure. Operating pressure is adjusted to overcome the adverse effects of the Following: Osmotic pressure, Friction losses, Membrane resistance, and Permeate pressure. If the operating pressure is set equal to the sum of the above resistances the net permeate flow rate across the membrane would be minimal or equal to zero; therefore, the operating pressure is set at higher value in order to maintain economical permeate flow rate.

3.2. Salt Rejection

Salt rejection is defined by

$$SR = 100\% (1 - (X_p/X_f)) \quad (2)$$

where SR is the salt rejection. For example, a feed seawater with 42,000 ppm and a permeate with a salinity of 150 ppm gives a percentage salt passage of 99.64%. Similarly, for a brackish water feed with salinity of 5000 ppm and a permeate salinity of 150 ppm gives a percentage salt passage of 97%. The two cases indicate the dramatic difference between the seawater and brackish water desalination membranes. Current membrane technology provides salt rejection values above 99% for both seawater and brackish water membranes.

3.3. Permeate Recovery

Permeate recovery is another important parameter in the design and operation of RO systems. Recovery or conversion rate of feed water to product (permeate) is defined by

$$R = 100\% (M_p/M_f) \quad (3)$$

where R is recovery rate (in %), M_p is the permeate water flow rate, and M_f is the feed water flow rate. The recovery rate affects salt passage and product flow. As the recovery rate increases, the salt concentration on the feed-brine side of the membrane increases, which causes an increase in salt flow rate across the membrane. Also, a higher salt concentration in the feed-brine solution increases the osmotic pressure, reducing the $(\Delta P - \Delta \pi)$ and consequently reducing the product water flow rate. Membrane recovery for RO systems have increased over the years from lower values of 10-20% to current higher values up to 50%. This is achieved in part by proper system design and use of multiple modules of spiral wound membranes within the same pressure vessel. As for the hollow fiber membranes it common to use a single module within the same pressure vessel [1].

4. Membranes, Membrane Classifications and Membrane Configurations

For a better understanding of the development of membrane technology, the fundamentals of membranes and membrane processes will be briefly reviewed. The word “membrane” is derived from the Latin word “membrana” and was first used in popular English media sometime before 1321 (Webster’s Online Dictionary, “Membrane” has different meanings in different domains. In association with separation, concentration or purification processes, a membrane can be essentially defined as a barrier to separate two phases and be able to restrict the transport of various components in a selective manner, as shown schematically in Figure 3.

A conventional filter also meets the definition of a

membrane; however, the term “filter” is usually limited to structures that separate particulate suspensions larger than 1–10 μm. There are many ways to classify synthetic membranes. They can be classified by the nature of the membrane material, the membrane morphology, geometry, preparation methods, separation regime and processes, etc. For instance, synthetic membranes can be organic (polymeric) or inorganic (ceramic/metal), solid or liquid, electrically charged or neutral in nature; they can be homogeneous or heterogeneous, symmetric or asymmetric in structure. Grouped by membrane geometric shapes, synthetic membranes can be flat, tubular or hollow fiber membranes. There are separation membranes to change the composition of mixtures, packaging membranes to prevent permeation, ion-exchange and biofunctional membranes to physically/chemically modify the permeating components, proton conducting membranes to conduct electric current, or non-selective membranes to control the permeation rate [2].

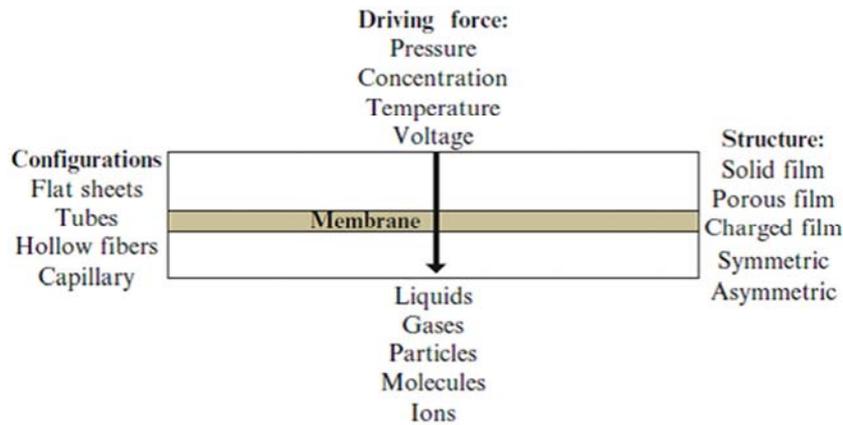


Figure 3. Fundamentals of membrane and membrane processes.

5. Membrane Processes, Operation Modes and Membrane Fouling

Membrane-based processes enjoy numerous industrial

applications as they potentially offer the advantages of highly selective separation, continuous, automatic and economical operation at ambient temperature, and simple integration into existing production processes, as well as appreciable energy savings [2, 3].

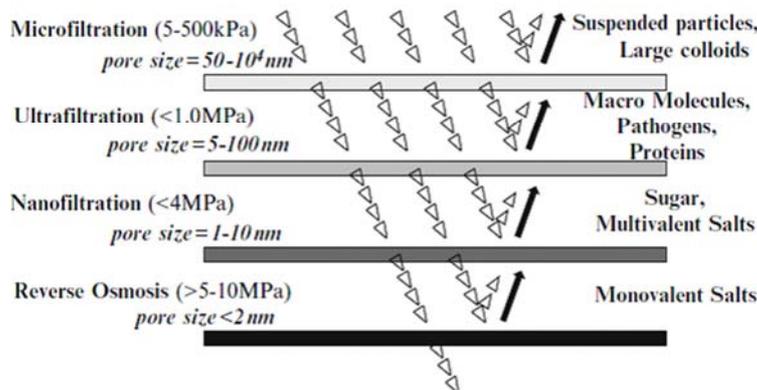


Figure 4. Pressure-driven membranes for water and wastewater treatments.

According to the driving force applied, the membrane processes can be classified as:

- Pressure-driven processes, such as reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), microfiltration

(MF), or gas separation (GS); or partial-pressure-driven processes, such as pervaporation (PV). • Concentration-gradient-driven processes, such as dialysis. • Temperature-driven processes, such as membrane distillation (MD). • Electrical-potential-driven processes, such as electrodialysis (ED). Figure 4 shows the ranges of applications, pore sizes and working pressures for the pressure driven membrane processes for water and wastewater treatments. There are other processes or hybrid processes such as membrane contactors, membrane reactors and membrane bioreactors (MBRs), in which the function of the membrane is integrated with conventional processes to provide highly efficient performance. Different membrane processes can also be combined together to overcome the limitations of individual systems, and to maximize the productivity of the target separation processes. Membrane filtration can be operated basically in two modes: dead-end and cross flow Figure 5. In dead-end mode, the entire feed flow transports towards the membrane perpendicularly so that the retained particles and other components accumulate and deposit on the membrane surface. In a cross-flow operation, the feed stream moves parallel to the membrane surface and only a portion of the feed stream passes through the membranes under the driving pressure. Moving the feed flow tangentially to the membrane surface can result in much higher permeation fluxes as the

stream continuously removes retained material. In addition, back washing, ultrasonic vibration or periodic flow can also be used to remove the deposited material from the membrane surface. The membrane life-span may be prolonged [4]. However, more complex equipment is required by the cross-flow mode compared to the dead-end mode, and also, the operating cost of the cross-flow mode is higher than the dead-end mode because of the energy needed to circulate the feed flow [5]. The dead-end mode tends to be used in the water/wastewater industry for dilute feeds such as surface waters or secondary effluents. Periodic backwash is required to control the cake formation and fouling. In membrane filtration applications, the main concerns are the loss of performance due to membrane fouling and additional costs from membrane cleaning and replacement. Membrane fouling is the deposition of material on or within the structure of membranes that is not readily reversed by simply releasing the pressure or by backwashing. The consequence of membrane fouling is to decrease membrane permeability (flux declines at constant pressure, or pressure rises at constant flux), and to alter solute retention (tends to increase for MF and UF, and decrease for NF and RO). Different fouling mechanisms may occur depending on the specific process, which may include pore blocking, pore narrowing or adsorption, irreversible cake layer formation, etc.

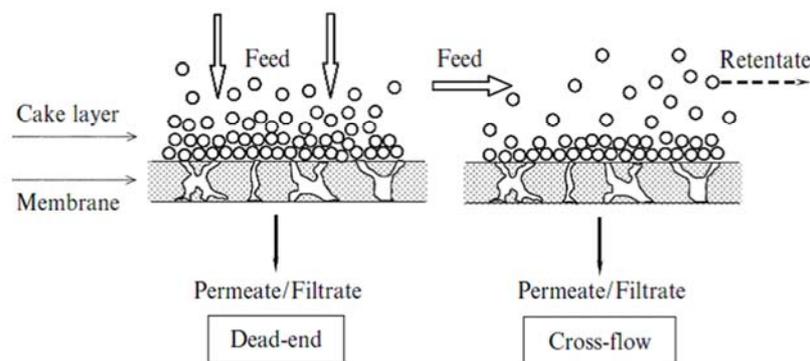


Figure 5. Schematics of dead-end and cross-flow filtrations.

Membrane fouling is a very complex phenomenon, which is related to feed solution properties (concentration, pH, ionic strength and component interactions), the nature of the membrane (hydrophobicity, charge, roughness, pore size, pore size distribution and porosity) and operating conditions (temperature, transmembrane pressure (TMP) and cross-flow velocity). Control of fouling can be achieved, for instance, by modifying the membrane surface and optimizing operating conditions [6, 7]. Pretreatment is frequently used to modify the fouling tendency of the feed.

6. Membrane Characteristics

Membranes are generally classified as isotropic or anisotropic. Isotropic membranes are uniform in composition and physical nature across the cross-section of the membrane. Anisotropic membranes are non-uniform over the membrane cross-section, and they typically consist of layers

which vary in structure and/or chemical composition. Isotropic membranes can be divided into various subcategories. For example, isotropic membranes may be microporous. Microporous membranes are often prepared from rigid polymeric materials with large voids that create interconnected pores [8]. The most common microporous membranes are phase inversion membranes (Figure 6a) [8]. These are produced by casting a film from a solution of polymer and solvent and immersing the cast film in a nonsolvent for the polymer. Most polymers used in such applications are hydrophobic, so water is the most common nonsolvent [9]. Upon contact with water, the polymer precipitates to form the membrane. Another type of microporous membrane is the track-etched membrane (Figure 6b) [8]. This type of membrane is prepared by irradiating a polymer film with charged particles that attack the polymer chains, leaving damaged molecules behind. The film is then passed through an etching solution, and the

damaged molecules dissolve to produce cylindrical pores, many of which are perpendicular to the membrane surface. A less common microporous membrane is an expanded-film membrane (Figure 6c) [8]. Expanded film membranes are oriented crystalline polymers with voids created by an extrusion and stretching process. First, the material is extruded near its melting temperature using a rapid draw-down rate. Then, the extruded material is cooled, annealed,

and stretched up to 300% of its original length. This stretching process creates slit-like pores ranging in size from 200 to 2500 Å. Isotropic membranes can also be dense films which either lack pores or contain pores that are so small as to render the membrane effectively non-porous [8]. These films are prepared by solution casting followed by solvent evaporation or melt extrusion.

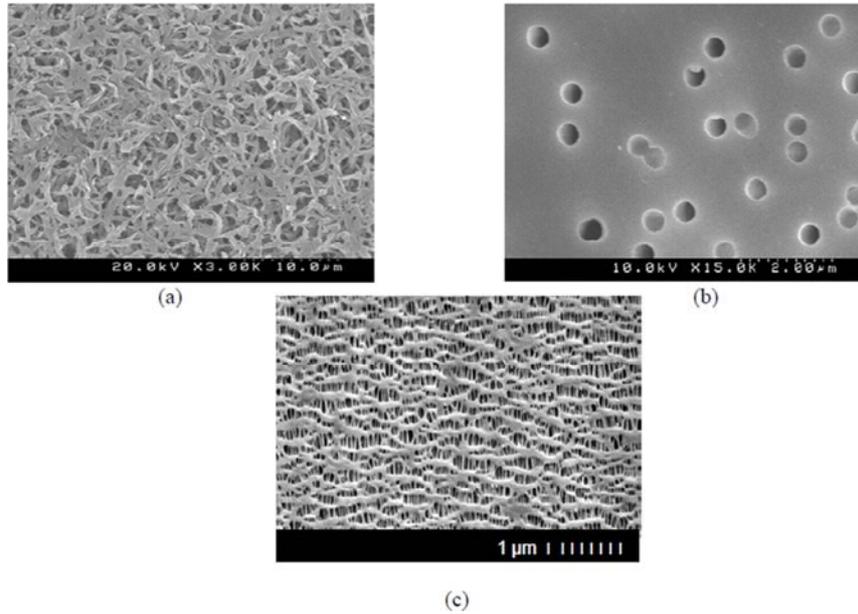


Figure 6. SEM for top surfaces of a) a phase inversion membrane [10], b) a track-etched membrane [10], and c) an expanded film [11].

There are two main types of anisotropic membranes: phase separation membranes and thin film composite membranes. Anisotropic phase separation membranes are often called Loeb-Sourirajan membranes, referring to the people who are credited with initially developing them [8]. These phase-

separated membranes are homogeneous in chemical composition but not in structure. Loeb-Sourirajan membranes are produced via phase inversion techniques such as those described above, except that the pore sizes and porosity vary across the membrane thickness (Figure 7a).

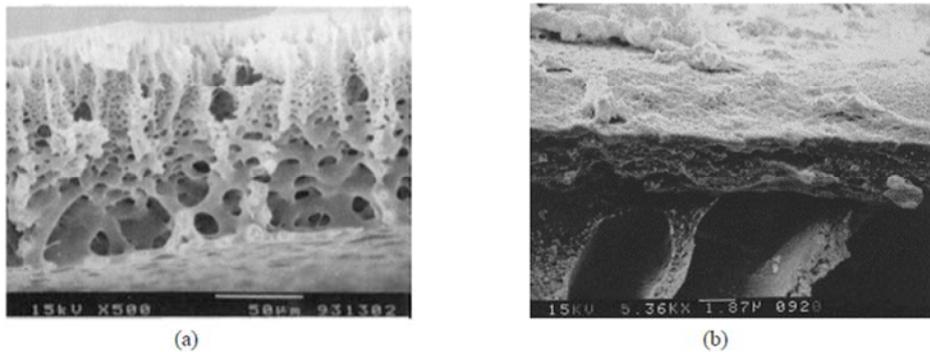


Figure 7. SEM of a) cross-section of an anisotropic microporous membrane [12] and b) cross-section of a thin-film composite [13].

Anisotropic phase separation membranes are often called Loeb-Sourirajan membranes, referring to the people who are credited with initially developing them⁽⁸⁾. These phase-separated membranes are homogeneous in chemical composition but not in structure. Loeb-Sourirajan membranes are produced via phase inversion techniques such as those described above, except that the pore sizes and porosity vary across the membrane thickness (Figure 7a). Loeb-Sourirajan

membranes often consist of a rather dense layer of polymer on the surface of an increasingly porous layer. Thin film composite membranes are both chemically and structurally heterogeneous (Figure 7b) [8]. Thin film composites usually consist of a highly porous substrate coated with a thin dense film of a different polymer. They can be made via several methods including interfacial polymerization, solution coating, plasma polymerization or surface treatment [8]. The descriptions above

of isotropic and anisotropic membranes refer to flat sheet configurations. However, membranes can also be produced as hollow fibers [8]. Like flat sheets, these fibers can either be isotropic or anisotropic. They also can be dense or porous. Common fibers used in industry today are anisotropic with a dense outer layer around a porous tube Figure 8. One advantage of hollow fiber membranes is that they have more surface area per unit volume than flat sheet membranes [8].

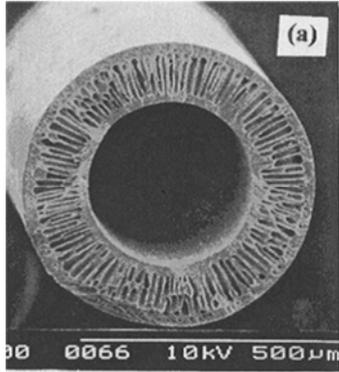


Figure 8. SEM image of hollow fiber cross-section [14].

7. Membrane Materials

Most MF, UF, RO, and NF membranes are synthetic organic polymers. MF and UF membranes are often made from the same materials, but they are prepared under different membrane formation conditions so that different pore sizes are produced [9]. Typical MF and UF polymers include poly (vinylidene fluoride), polysulfone, poly (acrylonitrile) and poly (acrylonitrile)-poly (vinyl chloride) copolymers [8]. Poly (ether sulfone) is also commonly used for UF membranes 3. MF membranes also include cellulose acetate-cellulose nitrate

blends, nylons, and poly (tetrafluoroethylene) [8]. RO membranes are typically either cellulose acetate or polysulfone coated with aromatic polyamides. NF membranes are made from cellulose acetate blends or polyamide composites like the RO membranes, or they could be modified forms of UF membranes such as sulfonated polysulfone [15]. Membranes can also be prepared from inorganic materials such as ceramics or metals [8]. Ceramic membranes are microporous, thermally stable, chemically resistant, and often used for microfiltration [8]. However, disadvantages such as high cost and mechanical fragility have hindered their wide-spread use. Metallic membranes are often made of stainless steel and can be very finely porous. Their main application is in gas separations, but they can also be used for water filtration at high temperatures or as a membrane support [16].

8. Membrane Modules

There are four main types of modules: plate-and-frame, tubular, spiral wound, and hollow fiber Figure 9. The plate-and-frame module is the simplest configuration, consisting of two end plates, the flat sheet membrane, and spacers. In tubular modules, the membrane is often on the inside of a tube, and the feed solution is pumped through the tube. The most popular module in industry for nanofiltration or reverse osmosis membranes is the spiral wound module. This module has a flat sheet membrane wrapped around a perforated permeate collection tube. The feed flows on the other side of the membrane and spirals in towards the center collection tube. Hollow fiber modules used for seawater desalination consist of bundles of hollow fibers in a pressure vessel [8]. They can have a shell-side feed configuration where the feed passes along the outside of the fibers and exits the fiber ends.

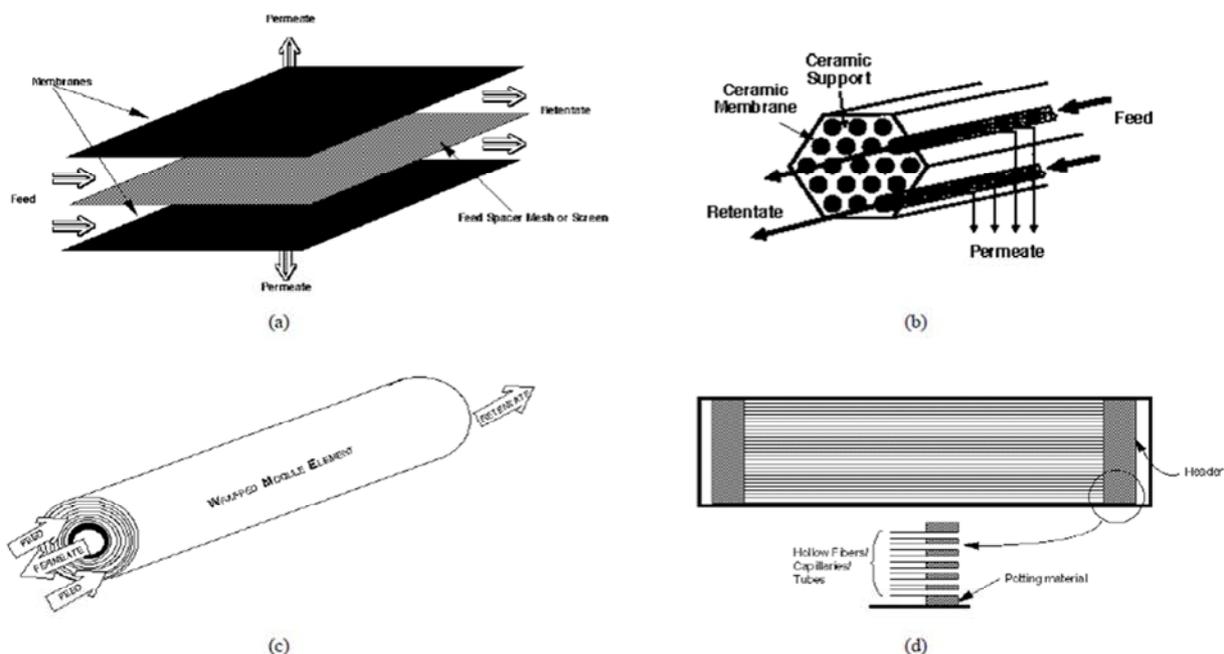


Figure 9. Schematic of a) plate and frame, b) tubular, c) spiral wound and d) hollow fiber modules [17].

Hollow fiber modules can also be used in a bore-side feed configuration where the feed is circulated through the fibers [8]. Hollow fibers employed for waste water treatment and in membrane bioreactors are not always used in pressure vessels. Bundles of fibers can be suspended in the feed solution, and the permeate is collected from one end of the fibers [18]. A useful membrane process requires the development of a membrane module containing large surface areas of membrane. The development of the technology to produce low cost membrane modules was one of the breakthroughs that led to the commercialization of membrane processes in the 1960s and 1970s. The earliest designs were based on simple filtration technology and consisted of flat sheets of membrane held in a type of filter press: these are called plate-and-frame modules. Systems containing a number of membrane tubes were developed at about the same time. Both of these systems are still used, but because of their relatively high cost they have been largely displaced by two other designs—the spiral-wound module and the hollow-fiber module.

Spiral-wound modules were used originally for artificial kidneys, but were fully developed for reverse osmosis systems. This work, carried out by UOP under of the Office of Saline Water (later the Office of Water Research and Technology), resulted in a number of spiral-wound designs [19, 20, 21]. The design shown in Figure 10 is the simplest and most common, and consists of a membrane envelope wound around a perforated central collection tube. The wound module is placed inside a tubular pressure vessel, and feed gas is circulated axially down the module across the membrane envelope. A portion of the feed permeates into the membrane envelope, where it spirals toward the center and exits through the collection tube.

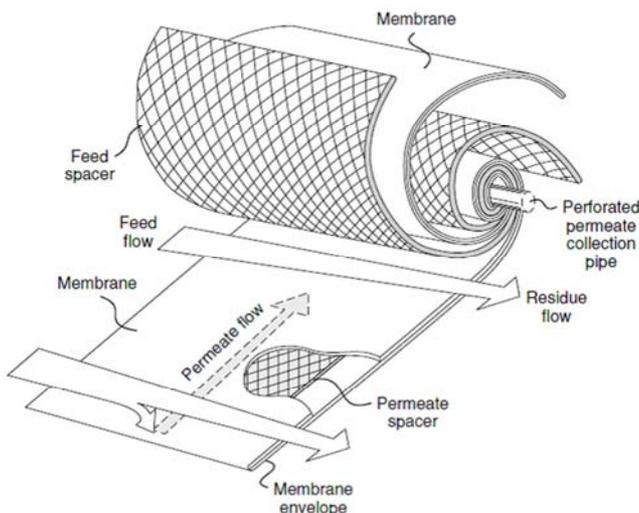


Figure 10. Schematic of a spiral-wound membrane module.

Small laboratory spiral-wound modules consist of a single membrane envelope wrapped around the collection tube. The membrane area of these modules is typically 0.6–1.0 m². Commercial spiral-wound modules are typically 100–150 cm

long and have diameters of 10, 15, 20, and 30 cm. These modules consist of a number of membrane envelopes, each with an area of approximately 2 m², wrapped around the central collection pipe. This type of multi leaf design is illustrated in Figure 11 [20]. Such designs are used to minimize the pressure drop encountered by the permeate fluid traveling toward the central pipe. If a single membrane envelope were used in these large diameter modules, the path taken by the permeate to the central collection pipe would be 5–25 m, depending on the module diameter. This long permeate path would produce a very large pressure drop, especially with high flux membranes. If multiple, smaller envelopes are used in a single module, the pressure drop in any one envelope is reduced to a manageable level.

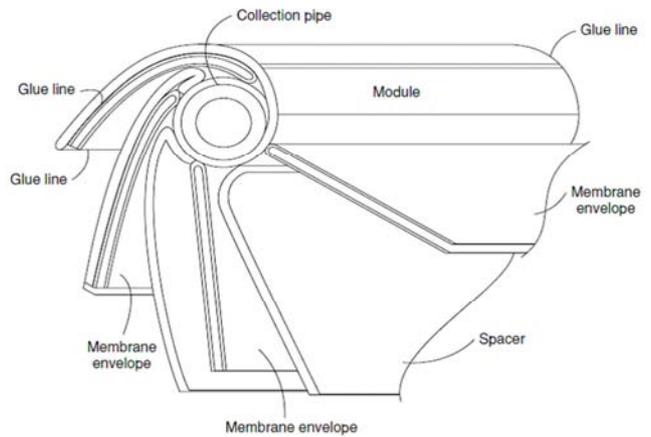


Figure 11. Multileaf spiral-wound module, used to avoid excessive pressure drops on the permeate side of the membrane. Large, 30 cm-diameter modules may have as many as 30 membrane envelopes, each with a membrane area of about 2 m².

Hollow-Fiber Modules are formed in two basic geometries. The first is the shell-side feed design illustrated in Figure 12a and used, for example, by Monsanto in their hydrogen separation systems or by DuPont in their reverse osmosis fiber systems. In such a module, a loop or a closed bundle of fiber is contained in a pressure vessel. The system is pressurized from the shell side; permeate passes through the fiber wall and exits through the open fiber ends. This design is easy to make and allows very large membrane areas to be contained in an economical system. Because the fiber wall must support a considerable hydrostatic pressure, these fibers are usually made by melt spinning and usually have a small diameter, of the order of 100- μ m ID and 150- to 200- μ m OD. The second type of hollow-fiber module is the bore-side feed design illustrated in Figure 12b. The fibers in this type of unit are open at both ends, and the feed fluid is usually circulated through the bore of the fibers. To minimize pressure drops inside the fibers, the fibers often have larger diameters than the very fine fibers used in the shell-side feed system and are generally made by solution spinning. These so-called capillary fibers are used in ultrafiltration, in pervaporation, and in some low to medium pressure gas applications. Feed pressures are usually limited to less than 1

MPa (150 psig) in this type of module. A number of variants on the basic design have been developed and reviewed [22].

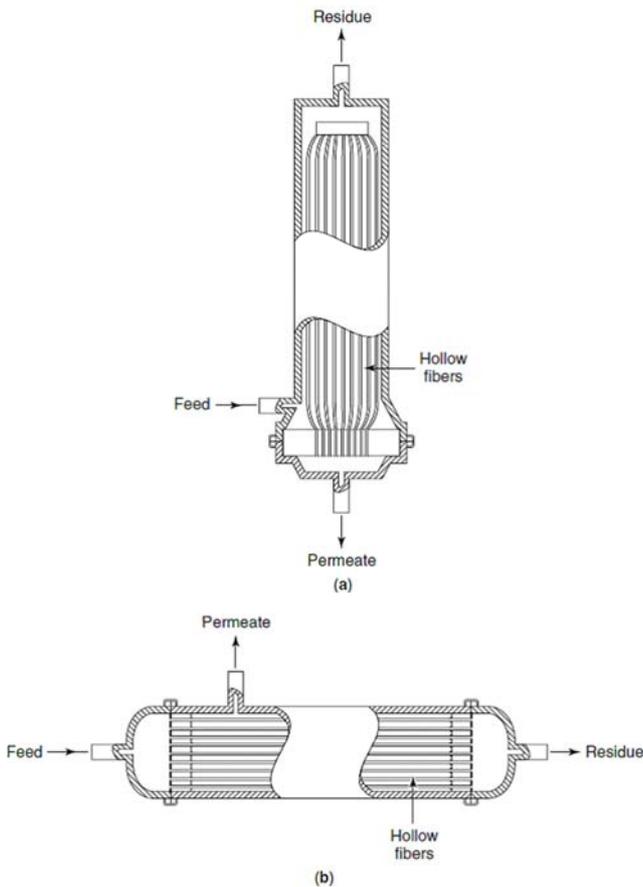


Figure 12. Two types of hollow-fiber modules used for gas separation, reverse osmosis, and ultrafiltration applications. (a) Shell-side feed modules are generally used for high pressure applications up to 7 MPa (1000 psig). Fouling on the feed side of the membrane can be a problem with this design, and pretreatment of the feed stream to remove particulates is required. (b) Bore-side feed modules are generally used for medium pressure feed streams up to 1 MPa (150 psig), where good flow control to minimize fouling and concentration polarization on the feed side of the membrane is desired.

Plate-and-Frame Modules were among the earliest types of membrane system; the design originates from the conventional filterpress. Membrane, feed spacers, and product spacers are layered together between two end plates, as illustrated in Figure 13 [23]. A number of plate-and-frame units have been developed for small-scale applications, but these units are expensive compared to the alternatives, and leaks caused by the many gasket seals are a serious problem. Plate-and-frame modules are now generally limited to electro dialysis and pervaporation systems and a limited number of highly fouling reverse osmosis and ultrafiltration applications.

Tubular Modules are now generally limited to ultrafiltration applications, for which the benefit of resistance to membrane fouling because of good fluid hydrodynamics overcomes the problem of their high capital cost. Typically, the tubes consist of a porous paper or fiberglass support with the membrane formed on the inside of the tubes, as shown in Figure 14.

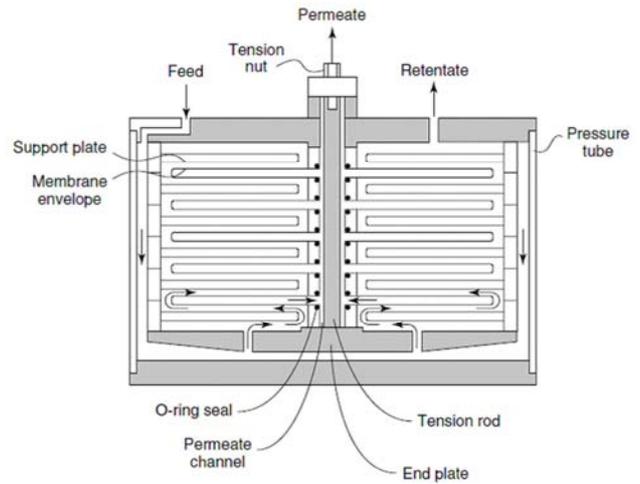


Figure 13. Schematic of plate-and-frame. This design has good flow control, but the large number of spacer and seals leads to high costs.

The first tubular membranes were between 2 and 3 cm in diameter, but more recently, as many as five to seven smaller tubes, each 0.5–1.0 cm in diameter, are nested inside a single, larger tube.

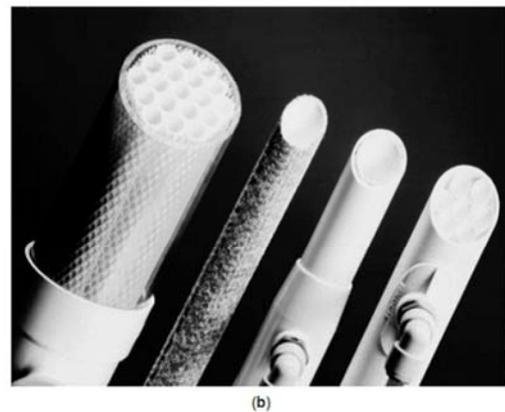
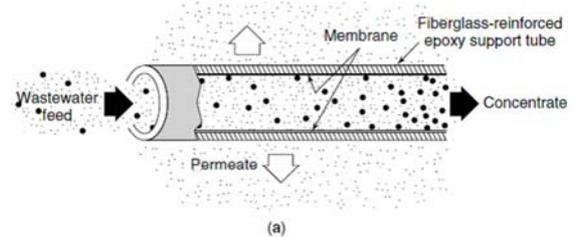


Figure 14. (a) Typical tubular ultrafiltration module design. In the past, modules in the form of 2- to 3-cm-diameter tubes were common; more recently, 0.5- to 1.0-cm diameter tubes, nested inside a simple pipe (b), have been introduced.

9. Module Selection

The choice of the appropriate membrane module for a particular membrane separation balances a number of factors. The principal factors that enter into this decision are listed in Table 1. Cost, although always important, is difficult to quantify because the actual selling price of membrane modules varies widely, depending on the application. Generally, high-pressure modules are more expensive than low-pressure or

vacuum systems. The selling price also depends on the volume of the application and the pricing structure adopted by the industry. For example, spiral-wound modules for reverse osmosis of brackish water are produced by many manufacturers, resulting in severe competition and low prices, whereas similar modules for use in gas separation are much more expensive. Estimates of module manufacturing costs are given in Table 1; the selling price is typically two to five times higher. A second factor determining module selection is

resistance to fouling. Membrane fouling is a particularly important problem in liquid separations such as reverse osmosis and ultrafiltration. In gas separation applications, fouling is more easily controlled. Hollow-fine fibers are notoriously prone to fouling and can only be used in reverse osmosis applications if extensive, costly feed-solution pretreatment is used to remove all particulates. These fibers cannot be used in ultrafiltration applications at all.

Table 1. Characteristics of the Principal Module Designs.

	Hollow - fine fibers	Capillary fibers	Spiral -wound	Plate-and-frame	Tubular
Manufacturing cost \$/ m ²	2 - 10	5 - 50	5 - 50	50 - 200	50 - 200
Resistance to fouling	Very poor	Good	Moderate	Good	Very good
Parasitic Pressure drop	High	Moderate	Moderate	Low	Low
Suitability for high Pressure operation	Yes	No	Yes	Difficult	Difficult
Limitation to specific types of membrane	Yes	Yes	No	No	No

A third factor is the ease with which various membrane materials can be fabricated into a particular module design. Almost all membranes can be formed into plate-and-frame, spiral, and tubular modules, but many membrane materials cannot be fabricated into hollow-fine fibers or capillary fibers. Finally, the suitability of the module design for high pressure operation and the relative magnitude of pressure drops on the feed and permeate sides of the membrane can sometimes be important considerations. In reverse osmosis, most modules are of the hollow-fine-fiber or spiral-wound design; plate-and-frame and tubular modules are limited to a few applications in which membrane fouling is particularly severe, for example, food applications or processing of heavily contaminated industrial wastewater. Currently, hollow-fiber designs are being displaced by spiral-wound modules, which are inherently more fouling resistant, and require less feed pretreatment. Also, thin-film interfacial composite membranes, the best reverse osmosis membranes now available, have not been fabricated in the form of hollow-fine fibers. For ultrafiltration applications, hollow-fine fibers have never been seriously considered because of their susceptibility to fouling. If the feed solution is extremely fouling, tubular or plate-and-frame systems are still used. Recently, however, spiral-wound modules with improved resistance to fouling have been developed, and these modules are increasingly displacing the more expensive plate-and frame and tubular systems. Capillary systems are also used in some ultrafiltration applications. For high-pressure gas separation applications, hollow-fine fibers appear to have a major segment of the market. Hollow-fiber modules are clearly the lowest cost design per unit membrane area, and their poor resistance to fouling is not a problem in many gas separation applications. Also, gas separation membrane materials are often rigid glassy polymers such as polysulfones, polycarbonates, and polyimides, which can be easily formed into hollow-fine fibers. Of the principal companies servicing this area only Separex and GMS use spiral-wound modules. Both companies use these modules to process natural gas streams, which are relatively dirty, often containing oil mist and condensable components that would foul hollow-fine-fiber modules rapidly. Spiral-wound modules

are much more commonly used in low-pressure or vacuum gas separation applications, such as the production of oxygen-enriched air, or the separation of organic vapors from air. In these applications, the feed gas is at close to ambient pressure, and a vacuum is drawn on the permeate side of the membrane. Parasitic pressure drops on the permeate side of the membrane and the difficulty in making high-performance hollow-fine-fiber membranes from the rubbery polymers used to make these membranes both work against hollow-fiber modules for this application. Pervaporation operates under constraints similar to low-pressure gas separation. Pressure drops on the permeate side of the membrane must be small, and many pervaporation membrane materials are rubbery. For this reason, spiral-wound modules and plate-and-frame systems are both in use. Plate-and-frame systems are competitive in this application despite their high cost, primarily because they can be operated at high temperatures with relatively aggressive feed solutions, conditions under which spiral-wound modules might fail [24].

10. Membrane Separation as a Unit Operation

A simplified flow diagram for a membrane-based water purification process is shown as Figure 15 [25]. In this example, there are two membrane separation steps: a membrane pretreatment unit for removal of particulates and other macromolecules followed by a reverse osmosis (RO) unit for salt removal. The flow diagram indicates several other process steps related to microbial control (chlorine addition), pH control, particle flocculation, dechlorination (to protect the reverse osmosis membrane), and scaling control. The membrane technologies of primary interest are pressure-driven processes where a pressurized feed is supplied to the membrane to produce purified permeate (product). Some of these membrane processes use cross-flow geometry whereby a retentate (or concentrate) containing high levels of total dissolved solids (TDS) is also produced.

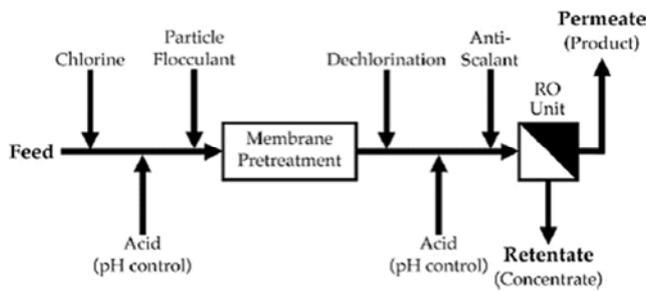


Figure 15. Simplified process flow diagram of a water purification process involving two applications of membrane technology; one for pretreatment and the other for salt removal via reverse osmosis [25].

10.1. Osmotic Pressure

Dissolved solutes in an aqueous feed create an osmotic pressure, π , thermodynamically defined in terms of the activity of the solvent (water) in the solution.

$$\pi = -(RT/V_w)\ln a_w \quad (4)$$

where V_w is the partial molar volume of the solvent, R is the gas constant, T is the absolute temperature, and a_w is the activity of the solvent [26]. For sufficiently dilute solutions, eq. 4 simplifies to the well-known van't Hoff equation

$$\pi \approx C_s RT \quad (5)$$

where C_s is the molar concentration of the solute [26]. To accomplish purification using a semipermeable membrane, the applied trans-membrane pressure difference must be greater than the osmotic pressure difference between the feed and permeate solutions. The flux of water through the

membrane can, therefore, be positive (in the direction of the solution of lower solution concentration) or negative (in the direction of the solution of higher concentration) depending on the applied pressure difference as illustrated in Figure 16. The data in Table 2 represent the reasonable range of osmotic pressures to be expected for water purification applications. It is important to note that the osmotic pressure is highly dependent on the salinity and composition of the solution.

Note that osmotic pressure is sensitive to the total concentration of species (ions and molecules) in solution; [27, 28] therefore, in Table 2, the brackish water sample with a TDS of 2000 mg L⁻¹ has a lower osmotic pressure than a 2000 mg L⁻¹ solution of sodium chloride. This is due to the presence of heavier ions (in terms of molar mass) in the brackish water sample. Particulate matter or polymeric solutes do not make a significant contribution to osmotic pressure.

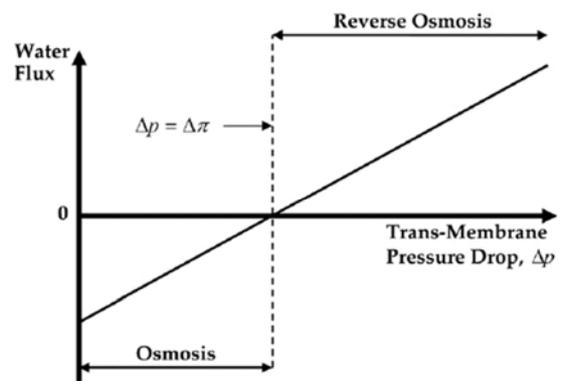


Figure 16. Membrane flux versus an applied trans-membrane pressure difference, Δp , with a given osmotic pressure difference, $\Delta\pi$.

Table 2. Osmotic Pressure for Typical Feed Solutions (25°C) [29].

Solute or Solution	Total Dissolved Solids (mg/L)	Molar Concentration m (mol/L)	Osmotic Pressure (Psi)	Osmotic Pressure (bar)
Brackish Water	2,000 - 5,000	-----	15 - 20	1.0 - 2.7
Sea Water	32,000	-----	340	23.4
NaCl	2,000	34.2	22.8	1.7
NaCl	35,000	598.2	398	27.4
NaHCO ₃	1,000	11.9	12.8	0.883
Na ₂ SO ₄	1,000	7.1	6	0.41
MgSO ₄	1,000	8.3	3.6	0.25
MgCl ₂	1,000	10.5	9.7	0.67
CaCl ₂	1,000	9.0	8.3	0.57
Sucrose	1,000	2.9	1.05	0.0724
Dextrose	1,000	5.5	2	0.14

10.2. Two Membrane Transport Mechanisms

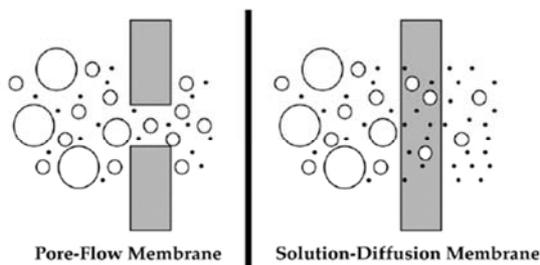


Figure 17. Pore-flow membrane transport contrasted with solution-diffusion membrane transport.

Membranes of interest here can function by two fundamentally different mechanisms: pore flow or solution-diffusion as depicted schematically in Figure 17 [25, 30, 31]. Simple filtration involves pore flow where separation is predominantly accomplished via a size-sieving mechanism. However, when the pore size is small enough, such as in nanofiltration (NF) membranes, polymer surface charge may cause pore flow membranes to exhibit low to moderate rejection of higher valent ions whereas they exhibit low rejection of monovalent ions [25, 32, 33, 34–37]. These membranes typically have a molecular weight cutoff for organic solutes in the range of 200–1000 Daltons as

nanofiltration membranes have a “loose” structure whereby some transport occurs via pore flow [25, 32, 35–37]. The mass flux, n , of a solution of density, ρ , and viscosity, μ , through pore flow membranes with a porosity, ϵ , can be modeled as flow through a circular tube of radius, R , and length, L , using the well-known Hagen-Poiseuille equation [38].

$$n = \frac{\epsilon \rho R^2}{8 \mu L} [P^o - P_L] \tag{6}$$

where the pressure difference between the entrance of the pore and the exit of the pore [$p_0 - p_L$] drives the flow. On the other hand, in the solution-diffusion case, penetrants molecularly dissolve in the polymer matrix of the membrane, diffuse through the thickness of the membrane, and desorb from the polymer matrix at the downstream side of the membrane [39–41]. In desalination, the water flux results from a concentration gradient of water in the membrane established by the applied pressure difference across the membrane [42–44]. In the practice of reverse osmosis, the flux of water and salt are often described by the following phenomenological equations [39-41].

$$\text{Water Flux} = A [\Delta p - \Delta \pi] \tag{7}$$

$$\text{Salt Flux} = B \Delta C_s \tag{8}$$

The salt flux is driven by a difference in salt concentration between the feed side and the permeate side of the membrane and is essentially independent of the driving pressure. The parameters A and B are useful for describing the performance of a membrane but they are not material properties of the membrane and offer no insight about the structure of the membrane or the mechanism by which it operates.

10.3. Filtration (Porous) Membranes and Processes

Molecules pass through RO membranes primarily by a solution- diffusion mechanism as discussed in a later section. Microfiltration (MF) and ultrafiltration (UF) membranes operate exclusively by pore-flow, whereas NF membranes show a combination of solution-diffusion and pore-flow character. This section will discuss MF, UF, and NF membranes. The four major types of polymer membranes and conventional filtration (CF) materials effectively remove particles of sizes that are shown in Figure 18 [45].

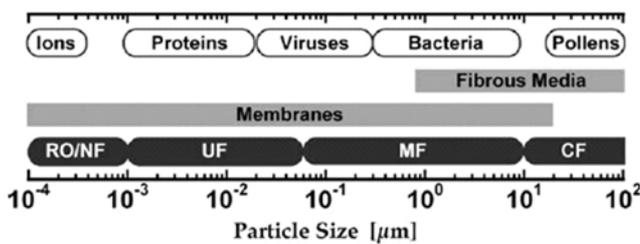


Figure 18. Size of particles removed by RO, NF, UF, and MF membranes along with conventional filtration [45].

Filtration membranes may have a relatively uniform pore

structure throughout the thickness; such symmetrical structures act as depth filters. Alternatively, the membrane may consist of a thin layer with fine pores (active layer or “skin”) overlaying a thicker layer with larger pores to provide mechanical support but little resistance to water flow; such asymmetric membranes are sometimes called screen filters because the separation of particulates occurs at the surface of the membrane in a very thin, selective layer. Unlike screen filters, where rejection of large solutes takes place on the membrane surface, depth filters capture solute particles within the membrane. Depth filters may capture particles by several mechanisms, including size sieving, adsorption, diffusion, and electrostatic adsorption. Sieving typically accounts for only a small fraction of the membrane’s rejection [46, 47]

10.4. Formation of a Pore-Flow Membrane

The oldest and most common technique for forming porous polymeric membranes consists of forming a concentrated solution of the polymer in a solvent with subsequent immersion into a liquid bath, typically water or a mixture with the solvent, in which the solvent is miscible but the polymer is not. Water vapor adsorption from a humid atmosphere, solvent evaporation, or some combination of techniques may be used in place of immersion in the liquid bath [25]. Methods were summarized by Pinnau and Koros [48].

Under proper conditions, a film is formed comprised of a continuous phase of solid polymer and an interconnecting phase of voids, chambers, or pores through which liquids can flow. The distribution of phases during solvent exchange dictates the physical structure of the solid membrane. Anisotropic membranes are created by contacting the top surface of the cast film with the non solvent first, creating a finely porous selective skin layer. The precipitated skin layer slows the penetration of non solvent into the film, causing polymer below the skin layer to precipitate more slowly. As a result, the substructure is more porous than the skin layer. In the membrane literature, this process has been called “phase inversion”. structures of this type were being studied more than a century ago. An analogous procedure is used to make fibers by wet spinning where the solidification step is called “coagulation.” The pore structure, that is, pore size, shape, and volume, is affected by many factors.

There is a sizable body of literature devoted to analysis of the phase inversion or coagulation process; [48] however, the practice is still largely an empirical art. Early membranes made in this way consisted of a similar pore structure through the entire membrane, and because of their thickness such membranes had low fluxes. Loeb and Sourirajan [69] introduced a solvent evaporation step prior to precipitating the polymer; the polymer concentration gradient in the nascent film leads to a gradation of pore size upon phase inversion. This effectively gives a “thin skin” with very fine pores, that is, the separating layer, overlaying a substrate consisting of much larger pores that provide mechanical support but relatively little resistance to water flow. With a wet annealing step, Loeb and Sourirajan were able to make the first practical reverse osmosis membrane. The polymer solution can be cast in batch mode to make laboratory membranes or in a

continuous fashion and used to form commercial membranes. The solution can be cast on a fabric or other porous substrate for additional support. An analogous process with an evaporation step, known as dry-jet wet spinning, is used to make hollow fiber membranes [48]. One of the most important membrane preparation methods is the Loeb-Sourirajan process described in 1963 [48]. The Loeb-Sourirajan process uses water as the phase inversion non solvent and was originally used to produce cellulose acetate reverse osmosis membranes. Today, reverse osmosis and nanofiltration membranes are usually of the polyamide thin-film composite type which will be discussed later. The Loeb-Sourirajan process is, however, still the predominant method of making ultrafiltration and microfiltration membranes. Common ultrafiltration membrane materials include cellulose acetate, polyacrylonitrile, poly (ether imides), aromatic polyamides, polysulfone, poly (ether sulfone) [25, 48], poly (vinylidene fluoride), and poly (vinyl pyrrolidone). Early microfiltration membranes were nitrocellulose and cellulose acetate; materials used more recently are poly (vinylidene fluoride), polysulfone, polyamide, poly (tetrafluoroethylene) [25, 48], and polyethylene. Several other methods of producing pore-flow membranes have been reported. Thermally induced phase separation (TIPS) bears some similarity to the phase inversion process but uses a temperature decrease rather than a non solvent to coagulate the polymer. A polymer solution is spread on a support and one face of the film is cooled, initiating phase separation. The rest of the film is gradually cooled and phase inversion gradually propagates to form an isotropic or anisotropic porous membrane. To create the selective surface layer in the case of anisotropic membranes, solvent evaporation at the selective surface is sometimes used to enhance the phase inversion process rather than only a simple thermal gradient in the solvent. TIPS also makes a number of polymers accessible for membrane formation that cannot be used in the traditional phase inversion technique. TIPS has been carried out on a number of different polymers including homopolymers such as polypropylene and diphenyl ether and copolymers such as poly (ethylene-co-acrylic acid). Connected pore structures form at low polymer concentrations; as polymer concentration and cooling rate increased, pore size is found to decrease. When evaporation is used to create anisotropic membranes, the polymer molecular weight does not significantly affect the cell size of the selective layer and, therefore, does not greatly influence the membrane performance. Pore flow membranes have also been created without solvent by stretching melt-cast polymer films. This process was developed extensively by Celanese to produce the product CelgardVR based on polypropylene and is described in several patents. These patents are directed at medical dressings and battery separators and cover a wide range of polymers. Gore also applied the stretching technique to production of porous fabrics made of polytetrafluoroethylene. The process begins with a precursor film which shows rownucleated lamellar morphology. The precursor film is typically annealed to eliminate any inconsistencies in the crystal structure. Stretching is then carried out at low

temperature to introduce voids and subsequently at high temperature to enlarge those voids. The morphology of the precursor film is of utmost importance for the success of the stretching technique. The crystals form as a result of stress and elongation induced during the extrusion process and their formation is a strong function of processing conditions and most importantly polymer molecular weight. A critical molecular weight for crystal formation is known to exist which is dependent on shear rate and temperature up to a particular shear rate after which it is independent of process conditions. High molecular weights were found to increase pore size and pore uniformity, leading to high water vapor transmission in polypropylene membranes. In the case of poly (vinylidene fluoride) membranes, the necessary crystalline structure in the precursor film was found to form most readily when a blend of low- and high-molecular weight polymer was used. Another type of solvent-less membrane formation is track etching. By this technique, a polymer film is bombarded with α -particles to create "tracks" through the film. The film is then immersed in a chemical etchant to create straight through circular pores. Polycarbonate membranes have been formed by this technique. Unlike membranes prepared by the other methods described here, track-etch membranes are typically of a very uniform thickness and have precisely defined pore diameters. As a result of the unity tortuosity and the uniform thickness (which allows the membrane to be exceedingly thin everywhere), the porosity of a track-etch membrane may be significantly lower than that of a solvent cast membrane but both membranes may show similar permeability. Semiporous nanofiltration membranes bear a strong compositional similarity to reverse osmosis membranes. Both reverse osmosis and nanofiltration membranes, though formerly produced by the Loeb-Sourirajan process from cellulose acetate, are today thin-film composite membranes. Soon after, Loeb and Sourirajan published their phase inversion method, Francis' developed composite membranes. Petersen provided an extensive review of composite reverse osmosis and nanofiltration membranes [32]. Composite membranes consist of an ultra-thin selective layer atop a porous support backing. These two components are almost always of differing chemical compositions (unlike Loeb-Sourirajan integrally skinned membranes) and may, therefore, be optimized for their particular roles. Cellulose acetate was initially used as the support material; polysulfone and polyethersulfone (PES) are the backings of choice now. The composite structure may be formed in a number of ways, including laminating together separately formed backing and selective layers, but the vast majority of nanofiltration membranes are produced by interfacial polymerization of a set of monomers on the support surface. Linear aromatic polyamides are one of the few polymers with the necessary solute rejection and flux characteristics for the selective layer [32, 48].

10.5. Applications of Pore-Flow Membranes

Membranes are used for sterilization in a variety of applications. Microfiltration membranes are often assembled into disposable cartridges which are typically used for short

periods of time before being replaced. The pharmaceutical and microelectronics industries have been extensive users of microfilters over the past several decades. Microfiltration cartridges are typically used to sterilize injectable drug solutions because 200 nm microfilters are able to remove virtually all bacteria. Filters are sterilized by autoclaving or other means after manufacture and immediately before use. In the electronics industry, microfilters are used to polish ultrapure water before use. Filters with 100 nm pores are used to remove any contamination from piping between the water treatment facility and end-use point [25]. The food and beverage industry extensively uses MF and UF membranes. In wine and beer purification applications, microfilters remove yeast and bacterial cells to clarify the final product [48]. Because of the low cost of wine and beer relative to products such as pharmaceuticals, prefilters are often used to extend the lives of the MF membranes [25]. Drinking water treatment is an ever-growing application for microfilters. MF/UF plants have been in use for ~2 decades in bringing surface water into compliance with USA EPA drinking water guidelines [25, 48]. Similar guidelines exist in Europe.

Hollow fiber membrane modules which are backflushed frequently are typically found in these applications [25]. Cheese production is another well-known application of membranes. Instead of traditional coagulation processes, which results in significant difficult-to-dispose whey production, MF or UF is used to concentrate proteins in milk for the direct production of yogurt and soft cheeses or for further processing in the production of hard cheeses [48]. When traditional coagulation is used, UF membranes are used to concentrate whey proteins and remove lactose concentrate and salts. The whey proteins are valuable and can be reused where they used to be discharged prior to ultrafiltration development. Fruit juices, including apple, pear, orange, and grape, are all clarified using ultrafiltration. Crude filtration is performed immediately after crushing the fruit; ultrafiltration produces a perfectly clear, nearly sterile product [25, 48]. The first industrial UF application was the recovery of electrocoating automotive paint. Automotive paint is an emulsion of charged paint particles. Metal parts are coated by applying a charge opposite that of the paint particles. After electrocoating, the pieces are rinsed to remove excess paint. The rinse water becomes contaminated with otherwise reusable paint particles. In addition, the quality of the paint emulsion is degraded by ionic species which migrate from the metal cleaning process prior to painting. The electrostatic nature and high solids content of the paint emulsions make for difficult filtration as significant fouling layers readily develop on the membrane, resulting in low fluxes. Unlike MF, UF tends to be expensive, but the high value of the paint makes the ultrafiltration process worthwhile [25]. Industrial UF systems are used to separate oil/water emulsions and to recover process water. Machining operations often use oil/water emulsions for lubrication and cooling. Ultrafiltration is used to separate water from the oil for safe disposal after use. Cleaning process water in-house and recycling it leads to reduced municipal water costs. Ultrafiltration has the added benefit of effectively

operating at elevated temperatures. As many industrial process streams are hot, ultrafiltration provides a means of cleaning streams without the energetic expense of cooling and re-heating. NF membranes have been developed to fill market niches between RO and UF membranes. The polymeric matrix of NF membranes is more open than that of their RO counterparts, affording them some degree of porous flow while maintaining some salt selectivity. Reverse osmosis membranes provide very high salt rejections but low fluxes; nanofiltration membranes do not reject as much salt but do provide much higher fluxes. NF membranes typically reject of 20–80% of sodium chloride present, but reject much more of the large divalent salt ions. Molecular weight cutoffs for organic solutes are 200–1000 Da. The looser structure of the NF membranes allows them to operate at trans-membrane pressures that are much lower than those of RO systems. Most applications of NF membranes are in final polishing of already clean water. Low levels of contaminants may be readily removed from drinking water as a final step at a water treatment plant or at the end-use facility. Municipal water may be softened by removal of multivalent cations such as sulfate [25].

10.6. Challenges Facing Pore-Flow Membranes

A significant hurdle to the widespread implementation of membranes for liquid purification is fouling. Fouling is the deposition of colloidal or particulate matter in a membrane's pores or on its surface that leads to changes in membrane transport characteristics [Figure 19(a)]. As water containing particulates, colloids, macromolecules, or microbes is filtered through a membrane, the foreign material deposits inside the porous structure and onto the surface of the membrane, creating a cake layer which drastically reduces water flux and affects overall membrane rejection performance [Figure 19(b)]. Because of fouling, the flux declines, which results in significant increases in the cost of membrane operation due to required membrane cleaning, periodic membrane replacement, and increased energy input to achieve high flux. Pore-flow membranes may experience two kinds of fouling: surface and internal, [48] as shown in Figure 19(a).

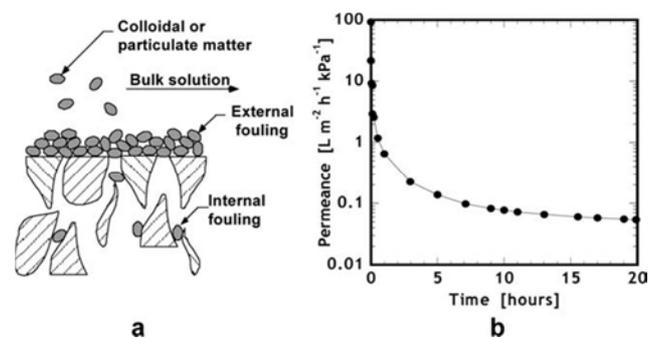


Figure 19. (a) Schematic of particulate fouling in porous water purification membranes (Reproduced from ref. 94, with permission from *Advanced Materials for Membrane Separations*, ACS Symposium Series 876. Copyright 2004 American Chemical Society). (b) Conventional MF membrane in crossflow protein filtration with $1 g L^{-1}$ bovine serum albumin in pH 7.4, phosphate-buffered solution, $25 cm s^{-1}$ crossflow, $\Delta P = 1000 kPa$ (145 psi), $0.2 \mu m$ nominal pore size poly (vinylidene fluoride) membrane.

Surface fouling is caused by particulate adsorption to the membrane surface while internal fouling is the result of foulant entrainment in the membrane pores. Nonporous reverse osmosis membranes, in contrast, undergo surface fouling only. Internal fouling is largely irreversible because the particles entrained in the membrane cannot be easily removed, even with harsh chemical or mechanical cleaning. Surface fouling may be either reversible or irreversible. Reversible surface fouling consists of foulants that may be removed by cleaning. Some particulates, especially after extended exposure to the membrane surface, are so strongly adsorbed to the membrane surface that they cannot be removed, constituting irreversible surface fouling. Surface modification has developed as a popular means of reducing the fouling propensity of many types of membranes [48]. Surface modification aims to change the surface properties of the membrane while maintaining its selective structure. By reducing fouling, flux is maintained at a high level. Resistance to fouling also lessens the need to clean the membranes. Cleaning can be accomplished in many ways, such as through backpulsing, gas sparging, increasing shear at the membrane surface, or UV radiation. Chemical agents such as ozone, acids, bases, or chlorine may be used, but these compounds may pose deleterious environmental consequences or even degrade the membrane structure, such as in the case of chlorine compounds and polyamide membranes. To maximize output and minimize the need for membrane cleaning, membrane modifications aim to alter the surface properties of membranes to make fouling less likely. Surface properties such as surface hydrophilicity, charge, and roughness are known to affect membrane fouling. Hydrophilic and smooth surfaces typically show the best resistance to fouling. Negatively charged membrane surfaces may reduce some forms of fouling by electro-statically repelling negatively charged foulants. However, negatively charged membrane surfaces may attract positively charged foulants; thus, un-charged membranes may exhibit a reduced tendency toward fouling. In measuring and quantifying surface properties, it is important to consider the effect of feed composition on surface properties as these properties are often measured under ideal and low TDS conditions [48]. In water treatment, hydrophilic membranes show reduced fouling because of their affinity for water. Water is strongly bound to a highly hydrophilic membrane surface; foulants interact only with this water layer and not with the membrane surface. If the membrane surface is hydrophobic, water near the membrane can be easily displaced by foulants and hydrophobic-hydrophobic interactions bind the foulant to the membrane surface. To increase the surface hydrophilicity of a membrane, two types of surface modifications have appeared in the literature. Hydrophilic moieties may be coated or grafted to the membrane surface as shown in Figure 20.

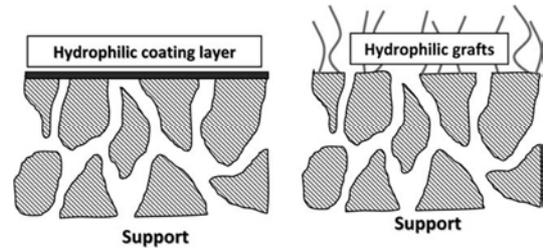


Figure 20. Membrane surface modification by hydrophilic coating or grafting.

In either case, additional mass transfer resistance is introduced to the membrane surface, so highly hydrophilic polymers (to permit high water uptake into the surface layer) are typically used. The hydrophilic coating layer is nonporous and, therefore, must be very thin to avoid introducing catastrophic mass transfer limitations. Dense coatings, however, eliminate entrainment of foulants inside the membrane. Grafting of hydrophilic chains may be used as an alternative to the dense coating layer. The mass transfer limitations imposed by grafting modification are typically less than in the case of the coating layer, but foulants may still be able to find their way inside the membrane structure. Hydrophilic polymers can be grafted directly to membranes surfaces by a variety of methods. Chemical grafting to the surface provide a more stable structure than simple adsorption of hydrophilic polymers to the membrane, which has shown some prevention of protein fouling in microfiltration and ultrafiltration. Grafting can be achieved by inducing polymerization from the membrane surface or by tethering polymer chains to the surface. Plasma-induced polymerization techniques have been used to graft polyamides or poly (acrylic acid) to porous membrane surfaces. This technique has also been reported on polyethylene surfaces, polycarbonate and poly (vinylidene fluoride) microfilters, and poly (vinyl chloride), poly (acrylonitrile), and polysulfone ultrafilters. Photo-initiated graft polymerization has been used to attach a variety of monomers to polyethersulfone membranes by inducing radical formation in the PES backbone. Photo-induced graft polymerization and subsequent crosslinking has been used to attach epoxy diacrylates to ultrafilters. Photo-grafting acrylic acid, 2-hydroxyethyl methacrylate, and poly (ethylene glycol) methacrylate derivatives have also seen use in photo-induced polymerization onto poly (acrylonitrile) flat-sheet membranes. Grafting by photo-polymerization has been carried out on membrane architectures other than flat sheets such as microporous hollow fibers. Polymer chains may also be tethered to the surface to form a graft structure. Dextran derivatives were grafted to ultrafiltration membranes to reduce protein fouling. Poly (ethylene glycol) (PEG) has proven to be extremely popular for use with this technique. Photo-induced grafting requires surface or PEG functionalization to achieve a covalent link between the surface and the polymer chain. Dense hydrophilic coating layers have also been used to induce fouling resistance. Because of their notorious propensity for fouling, ultrafiltration membranes have been a popular substrate for such coating layers. Composite ultrafiltration membranes have been formed by crosslinking thin layers of poly (vinyl alcohol) on the

membrane surfaces. Poly (ethylene glycol) has also been used in the same manner. Crosslink density in the coating layer may be manipulated by varying the polymer/solvent ratio in the thin-film casting solution. Membrane surface modifications explored to date, however, are not without limitations. Many modification techniques are membrane-specific. For example, photo-grafting induces radical formation on the backbone of PES to which hydrophilic moieties may be grafted, as noted previously [48].

Unfortunately, photo-grafting is not effective on other common membrane materials such as poly (vinylidene fluoride) (PVDF), poly (tetrafluoroethylene) (PTFE), and polyamides since, unlike PES, these polymers do not readily form surface radicals under UV irradiation. Other modification strategies such as plasma treatment and multi-step organic reactions may be difficult or expensive to apply in a manufacturing environment. Measurement of the zeta potential is becoming a popular means of characterizing the surface of modified membranes. The zeta potential describes the potential induced between the membrane surface and the shear plane of fluid moving past the surface. As noted previously, uncharged surfaces typically show good fouling resistance. The zeta potential, therefore, can be used to predict the fouling resistance of a membrane. Surfaces become charged by ionization of chemical functionalities on the surface or by adsorption of charged particles. The pK, isoelectric point, and charge density all affect the zeta potential of a surface. The zeta potential has also been found, however, to depend on membrane pore diameter and surface roughness. Interaction of membrane surface with foulants, therefore, can only be compared among well-defined membranes [48].

10.7. Reverse Osmosis Membranes

There are at least four requirements for a commercially viable reverse osmosis membrane system for desalination. First, the membrane must be made from a polymer whose intrinsic characteristics are capable of giving adequately high water permeation and low salt permeation rates. The high salt rejections required can be achieved by a solution-diffusion mechanism but not by pore flow. Second, to achieve the high fluxes needed, the membrane layer that does the separation must be made very thin, about 100 nm in thickness. However, the membrane needs to have sufficient mechanical integrity to be assembled into a module and to withstand the driving pressures imposed, that is, several times the osmotic pressure of the salt solution to be purified. A thin dense layer (or skin) overlaying a porous support structure has proven to be the ideal way to meet these opposing requirements (see Figure 21). Third, these membranes must be assembled in a way that provides a high membrane area per unit volume of the pressure vessel. There are four types of membrane modules that have found some commercial utility: tubular, plate and frame, hollow fibers and spiral wound (see illustration in Figure 22) systems; these are described in detail elsewhere [25, 30]. Finally, the membrane needs to be chemically and physically robust enough to perform at specification for years in the environment of the reverse osmosis process. One of the more difficult of these is to resist

the chlorination used to disinfect the feed water.

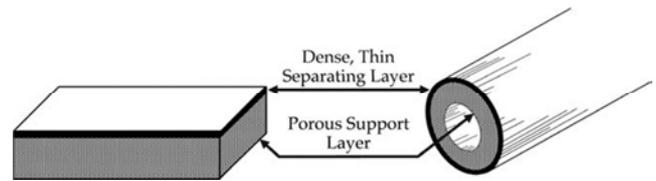


Figure 21. Schematics for flat-sheet (left) and hollow-fiber (right) membranes where each has a dense, thin selective separating layer supported by a porous layer.

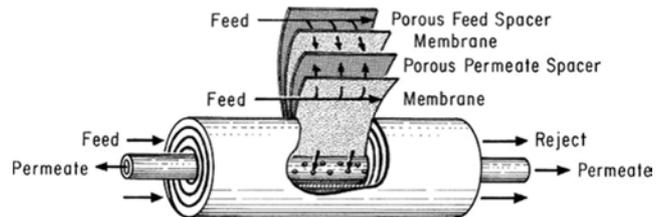


Figure 22. Illustration of a spiral wound module.

The following subsections review the development of membranes that meet most of the above requirements, the current state of the art, and some of the possibilities for next generation membranes. The last half-century has seen a remarkable evolution of membrane technology for this purpose. The rapidly growing need for water purification throughout much of the world will likely drive an even more accelerated evolution of better membranes in the coming years. The next section describes in more detailed mathematical terms the basis of transport by the solution-diffusion mechanism and point to areas where better understanding of these processes in polymers is needed. Desalination of seawater and brackish water requires membranes with high levels of NaCl rejection, > 98%.13, For example, seawater typically contains about 35,000 mg L⁻¹ TDS [31, 49-51]. In a reverse osmosis plant run at 50% recovery, [49, 50] the average upstream concentration would be 52,000 mg L⁻¹ TDS. The World Health Organization does not publish a health related specification for sodium, chloride, or TDS in drinking water [49]. However, a typical TDS target for an RO desalination permeate is <500 mg L⁻¹ [31, 49-51]. To meet this specification, the membrane must have a salt rejection of 99.1%. This analysis neglects the effects of concentration polarization. If concentration polarization is considered, the required salt rejection will increase. Depending on the severity of concentration polarization, salt rejection greater than 99.7% may be required to make potable water from seawater [52]. There are applications where such high rejections are not needed but higher fluxes are. "Nanofiltration" membranes have been developed for this market niche [25, 32]. They have poor rejection of single valence ions, which results in much higher permeate ion concentrations relative to RO membranes and, therefore, higher permeate osmotic pressure difference across the membrane, so the water flux is inherently higher at the same Δp . Such membranes can achieve high flux at low Δp values.

10.8. Asymmetric Membrane Structures

The first commercially useful reverse osmosis membranes

were made from cellulose acetate. Interest in these materials for desalination stemmed from the pioneering work of Reid and coworkers [53, 54] published in 1959, showing that cellulose acetate films were capable of much higher salt rejection than other polymers considered. However, because these films were relatively thick, 4–22 μm , fluxes were unacceptably low. The breakthrough that made reverse osmosis a viable process, and ultimately membrane separation of gases, was the discovery by Loeb and Sourirajan [48]. They developed a procedure for casting a complex solution of cellulose acetate followed by an evaporation period, immersion in cold water, and then wet annealing. Their membranes had fluxes orders of magnitude greater than those reported by Reid and Breton while maintaining equivalent salt rejection. The wet annealing step is essential for achieving high salt rejection; without this step, the membrane skin is porous. Riley et al [55]. examined the structure of the Loeb-Sourirajan membranes by transmission electron microscopy and found they had an “asymmetric” morphology comprised of a very thin dense skin, $\approx 100\text{--}200$ nm in thickness, supported on an open cell porous substructure like that shown schematically in Figure 21. The wet annealing step closes the pores in the skin to make it dense. Merten and coworkers [39, 41, 56, 63] developed a simple solution-diffusion model to describe the reverse osmosis process and did extensive experiments to characterize the equilibrium and transport behavior of the CA/water/salt system and verified the solution-diffusion mechanism. Their equations for flux and rejection will be presented later in the context of a broader analysis of the solution-diffusion mechanism for reverse osmosis [43]. An essential teaching of this simple model is the need for a sufficient level of swelling of the membrane by water to have adequate water permeation while not sorbing water to such an extent that high salt permeation rates destroy salt rejection. For example, the equilibrium water sorption by cellulose acetate materials is generally in the range of 15–30 wt % [39, 57, 63]. Figure 23 shows the flux and rejection characteristics of experimental asymmetric cellulose acetate membranes [39, 63]. The flux was measured for two different NaCl feed concentrations to show the effect of osmotic pressure. The flux plots are somewhat nonlinear; this plus some degree of hysteresis on decreasing the pressure has been attributed to compaction of the porous substructures but this feature can be significantly reduced by an optimized casting process. In the plot of rejection versus pressure, the points represent measurements for a feed containing 1000 mg L^{-1} NaCl using an experimental asymmetric membrane while the solid lines were calculated from separately determined water and salt permeabilities from the same cellulose acetate in film form. The points fall somewhat below the theoretical prediction presumably because of slight defects in the asymmetric membrane [39, 148]. As the degree of acetylation of the cellulose acetate increases, membranes made from them exhibit higher salt rejection but the flux decreases [25, 41]. Some of the best membranes reported consist of blends of a 39.8 wt % acetylated polymer with

small amounts of cellulose triacetate (44.2% acetate) or cellulose acetate butyrate; [25, 58] seawater salt rejections of 99.0–99.5%, which is close to the theoretical limit, were achieved but fluxes were modest [25]. Most commercial cellulose acetate membranes have been optimized to give higher fluxes and lower salt rejection.

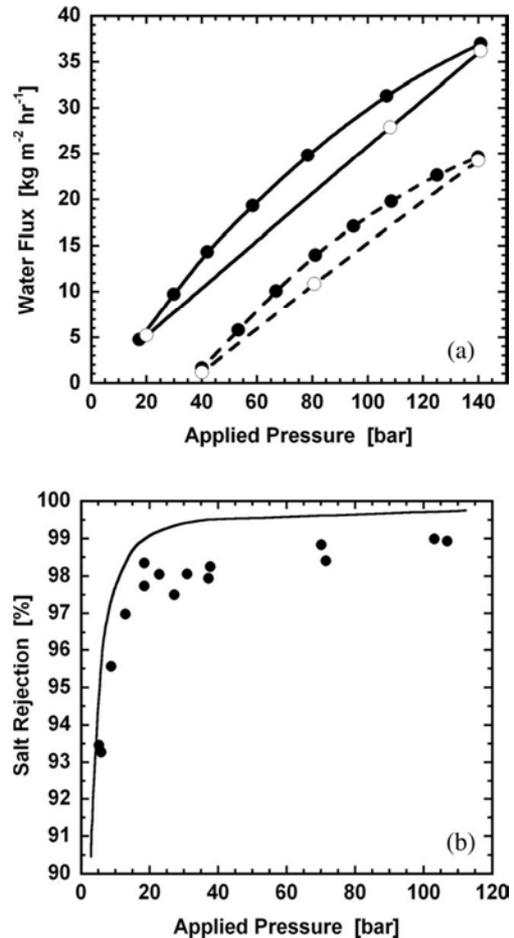


Figure 23. (a) Water flux versus applied pressure for a cellulose acetate membrane (solid lines indicate 0.13 wt % NaCl feed and dashed lines indicate 4.5 wt % NaCl feed) showing hysteresis between increasing (●) and decreasing (○) pressure. (b) Predicted salt rejection based on water and salt permeability measurements (lines) and experimental data (●) [65].

Cellulose acetate membranes are resistant to the chlorine added to disinfect the feed water, which is advantageous for applications with significant bacterial content. However, cellulose acetate membranes do hydrolyze over time; the rate is at a minimum in the pH range of 4–6 [41]. During the 1960–1970s, cellulose acetate and other polymers were made into hollow fiber membranes having an asymmetric structure as illustrated in Figure 21 [59–62]. DuPont commercialized a polyamide hollow fiber membrane for RO; [59] however, by the year 2000, hollow fiber polyamide membranes were no longer being sold for reverse osmosis. Nevertheless, a successful cellulose triacetate hollow fiber membrane is still being sold for reverse osmosis. Hollow fiber technology has been successfully translated, with different polymers and some modifications, into a significant commercial business for gas separations. The DuPont hollow fibers were not

resistant to chlorine, which is the case for all polyamides including the very successful thin film composites that now dominate the reverse osmosis market. A few other polymers like poly (vinyl alcohol), post polymerization sulfonated polysulfone, etc., have found niche applications.

11. Surface Modification of Synthetic Polymeric Membranes

At present the demand of membrane technology in the field of gas separation (GS), medicine, waste water treatment, production of drinking water by desalination, and other methods is increasing day by day. The use of synthetic materials in biomedical applications has increased dramatically during the past few decades. Surface properties of polymers are of fundamental importance in many branches of industrial applications (e.g., separation of gasses, liquid mixtures, bonding, coating, adhesion, etc.). Performances of membranes also depend on the properties of their surfaces, since membrane may be considered as one of the surface phenomena. Hence, it is very natural that much attention has been paid to the membrane surface modification. Surface contamination which may lead to deterioration in membrane performance is also known to be governed by the membrane surface properties. According to Zeman and Zydney, [66] almost 50% of all MF and UF membranes marketed by 1996 were surface modified. However, the additive used and procedures followed in commercial membrane manufacture are industrial secret. It is well known that, in polymer blends, thermodynamic incompatibility usually causes demixing of polymers. Polymer blend surfaces have been studied by many different groups using theoretical calculations [67-70] and various surface-sensitive techniques, including X-ray photoelectron spectroscopy (XPS), 6-8 secondary ion mass spectroscopy (SIMS), [70, 71, 74] atomic force microscopy (AFM), [71, 72, 74] contact angle goniometry, [75] Sum-Frequency spectroscopy, and neutron reflectivity [77]. Ulbricht [20] wrote a comprehensive overview on the development of polymeric membranes or novel functions in various membrane separation processes for liquid and gaseous mixtures (GS, RO, pervaporation, NF, UF, and MF) and in other important applications of membranes such as biomaterials, catalysis (including fuel cell systems), or lab-on-chip technologies. In his article, Ulbricht [78] discussed novel processing technologies of polymers for membranes, the synthesis of novel polymers with well-defined structure as “designed” membrane materials, advanced surface functionalization of membranes, the use of templates for creating “tailored” barrier or surface structures of membranes and preparation of composite membranes for the synergistic combination of different functions by different (mainly polymeric) materials, and the developments for the future of membrane technology. Many of the surface modifications were done to improve the selectivity and permeability. Plasma treatment, grafting reaction, etc., [79] were applied for this purpose. For example, surface oxidation

by plasma treatment (e.g., O₂ and water) improved the wettability of polymers such as polyethylene (PE), polysulfone (PSf), poly (methyl methacrylate), etc [80, 81]. Many new methods have also been developed such as the introduction of active additives [82, 83] and ion implantation on the surface, either physically or chemically. The most important purpose of membrane surface treatment is, however, the improvement in fouling reduction, since in spite of its remarkable achievement, membrane separation technology suffers from a serious problem: the membrane fouling. Membrane fouling is caused mainly by two following reasons [84-86]. i. Plugging the pore openings at the porous membrane surface by the suspended solid particles or large solutes in the feed. ii. The attachment of bacteria and subsequently colonization on the membrane surface (biofouling). Generally, proteins are adsorbed more strongly at hydrophobic surfaces than hydrophilic surfaces [85, 86]. Initial biofilm is achieved by bacteria attachment through copolymer synthesis at the membrane surface, and this would be avoided if the membrane surface be hydrophilic in nature. Most of the hydrophilic UF membranes have fixed negative charges at the membrane surface; this negative surface charge prevents the negatively charged colloidal particles to settle on the membrane surface, and, therefore, it slows down the membrane fouling process [85]. The reduction in membrane fouling can be done by increasing the negative surface density of the membrane and the hydrophilic nature of the neutral membrane. The membranes with the hydrophilic surface are less susceptible to fouling than hydrophobic membranes, whereas the ability to recover the performance upon washing is higher for the membrane with a chemically neutral surface than the charged membranes. It was also reported that the susceptibility of membranes of microbiological fouling decreases with a decrease in the roughness of the membrane surface [87]. Thus, surface charge, hydrophilicity, and roughness were identified as three important factors that govern the membrane fouling, and attempts are made to control these factors by surface modification. It is well known that casting solvent affects the surface properties of the membrane [88].

11.1. Modification of Polymeric Membrane Surfaces by Additives

A number of factors have been noticed to affect surface composition of a homopolymer blend system. Clarke et al., [89] studied poly (ε-caprolactone)/poly (vinyl chloride) (PCL/PVC) blends and found that the surface composition was dependent on molecular weight and degree of crystallinity. It was noticed that the surface behavior of poly (propylene oxide)/ polystyrene (PPO/PS) blends was strongly dependent on the casting solvent used. In fact, solvent cast films may not be equilibrated thermodynamically due to the rapid solvent evaporation during the film formation process, and the resulting surface could be predominantly due to solvent effect. PVC/PMMA {poly (methyl methacrylate)} blends were found that the surface was enriched with PMMA if blends were cast from tetrahydrofuran (THF), whereas surface composition was

equivalent to bulk if blends were cast from methylethylketone. Moreover, it has been shown that the phase morphology depends on polymer molecular structure, composition, and the method of blend preparation. Surface morphology can also be influenced by a suitable choice of the substrate surface free energy. The film surface segregation and morphology may also be modified by film thickness. Moreover, annealing at a temperature higher than the glass transition temperatures (T_g) of the polymer components of the blend films is believed to produce a different structure than that prepared at temperatures below the T_g of the polymer components. Wang et al modified the surface of phenolphthalein poly (ether sulfone) UF membranes by blending with acrylonitrile based copolymer containing ionic groups for imparting surface electrical properties. It is hence interesting to use the phenomena of polymer demixing for the surface modification. In this context, the simplest method seems blending hydrophilic polyvinyl pyrrolidone (PVP) or poly (ethylene glycol) (PEG) into polysulfone (PSf) or polyethersulfone (PES) host polymers, which have been exercised for a long time for casting flat sheet (FS) membranes or hollow fibers, without knowing that the additives were indeed modifying the surface. For example, Lafrenie' re et al. made a thorough study of PVP blended PES membranes revealing the effect of PVP content on the pore size and pore sizes distribution. The highest product permeation rate was obtained at a PVP/PES weight ratio of unity when the PES concentration in the casting solution was 15–30 wt %. It was later found by Miyano et al. that PVP, although soluble in water, remained in the polysulfone (PSf) membrane for a long time under the UF operating conditions.

As well, PVP molecules were more concentrated at the surface than in the bulk. Therefore, addition of PVP can make the surface of the membrane made of PSf or other polymers more hydrophilic. Much attention was paid therefore the surface properties of PVP blended PES or PSf membrane.

A small amount of PVP in the casting solution of PES resulted in an increase in permeability without significant changes in selectivity. From AFM parameters it was concluded that the addition of PVP changed mainly the surface porous structure, along with little change in bulk parameters such as porosity, thickness, and/or tortuosity. These changes gave increasing permeability's without changing the manufacturing process. Hollow fibers subjected to removal of natural organic matter (NOM) prepared from PES/PVP exhibited a much lower fouling tendency than the commercial PSf membrane. Xu and Xu prepared PVC hollow-fiber UF membranes by using PVP or PEG with different molecular weight as additive and DMAc as a solvent. It was found that using PVP or PEG as additives can increase the membrane porosity and enhance the permeation flux by changing the membrane morphology. To make the modified surface properties more permanent, surface-modifying macromolecules (SMMs) were developed. SMM has an amphiphatic structure consisting theoretically of a main polyurethane chain terminated with two low polarity polymer chains (i.e., fluorine segments) (Fig. 24). Because of the low polarity and high hydrophobicity of the fluorine segments, this type of SMM is called hydrophobic surface modification molecule (BSMM).

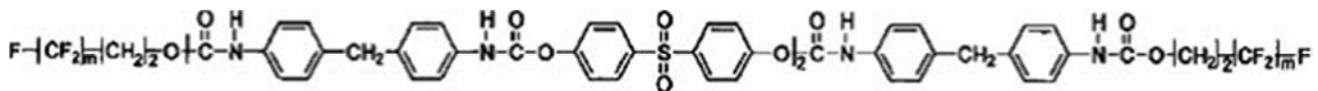


Figure 24. Molecular structure of a hydrophobic BSMM.

When BSMM is added to a solution of a more hydrophilic host polymer, for example, PSf or PES, and a solution film is cast, BSMM will migrate to the air/solution interface to reduce the system's surface tension (Fig. 25).

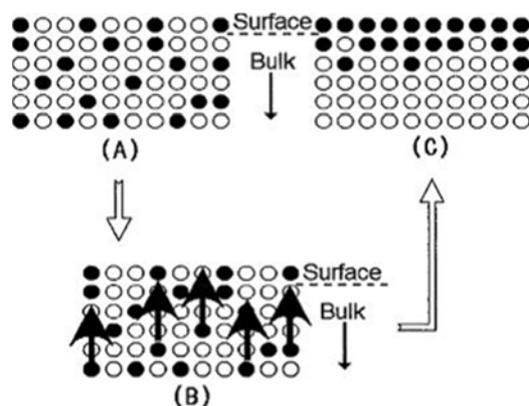


Figure 25. Schematic diagram illustrating BSMM migration: ● BSMM; ○ host polymer (PSf, PES) Case A: time zero; Case B: time in between; Case C: time infinite. The migration of BSMM onto surface was confirmed by the change of contact angle and surface fluorine content as a function of evaporation time (Figures 26 and 27).

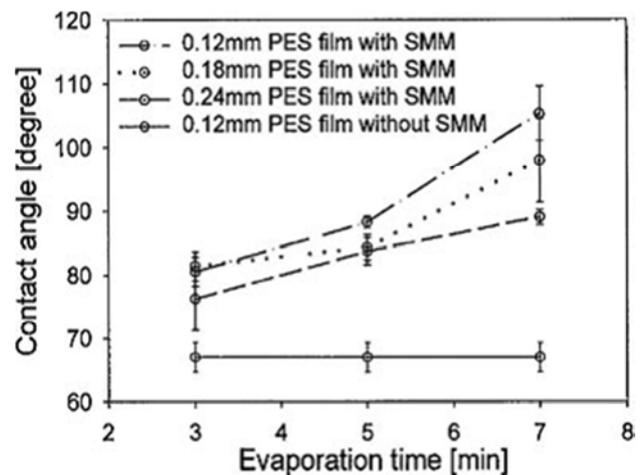


Figure 26. Contact angle versus evaporation time.

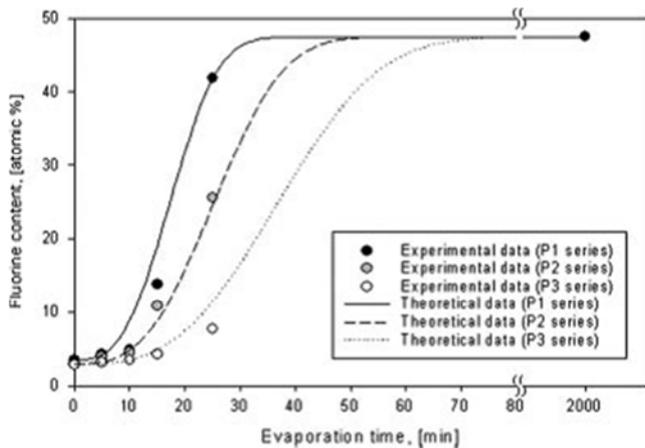


Figure 27. Surface fluorine content versus evaporation time.

The preferential adsorption of a polymer of lower surface tension at the surface was confirmed by a number of researchers for a miscible blend of two different polymers, as well. Later, hydrophilic SMMs (LSMM) and charged SMMs (CSMM) were developed by replacing the fluorocarbon end caps of BSMM with polyols. One of a typical BSMM's structures is shown in Figure 28. Depending on whether SMM is BSMM or LMSS, the membrane surface becomes either more hydrophobic or more hydrophilic than the host polymer. One of the most important features of SMMs is, however, that the central polyurethane part is miscible with

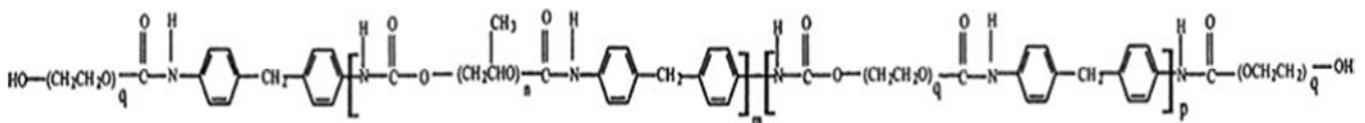


Figure 28. Molecular structure of a hydrophilic SMM.

Membrane fouling tests with humic acid as the foulant indicated that the permeate flux reduction of the BSMM modified membranes was much less than that of the unmodified ones. In pervaporation, PES-BSMM membranes showed that it is water selective as a significant depletion of chloroform in the permeate was observed. Suk et al. studied the kinetics of surface migration of surface-modifying macromolecules in membrane (subjected to UF) preparation. BSMMs were blended into the casting solution of PSf. The cast films were placed in an oven with a forced air circulation for 3–2000 min range to remove the solvent before being immersed in water at 4°C for gelation. According to the XPS analysis, after an initial time lag the surface fluorine content increased as the evaporation time increased and finally leveled off. During the process of casting the polymer solution into a film and the removal of solvent by evaporation, BSMMs migrate to the membrane surface, rendering the surface of the membrane ultimately obtained more hydrophobic than the bulk membrane. Similar migration of BSMMs toward the surface of the membrane is reported in the PEI/BSMMs, and PES/BSMMs membrane preparation. On evaporation of the modified membranes, it was noticed that more of BSMMs migrated toward the

the host PSf or PES polymer and holds the SMM secure to the membrane surface. Thus, SMMs stay at the membrane surface semipermanently. Several works of surface modification by SMMs are highlighted below. Pham et al. blended eight types of BSMMs into PES membranes and characterized the membranes for surface and physical properties. The BSMMs were synthesized with a diisocyanate, polypropylene oxide (PPO), and a fluoro alcohol as the reactants. Water droplet contact angle measurements and X-ray photoelectron spectroscopy data revealed that BSMMs migrated to the surface and rendered the PES material more hydrophobic. Although advancing contact angle data were equivalent to those of pure Teflon™, the highest average values of receding angles of these systems were less than those of commercial Teflon™. The opaqueness of PES/BSMMs films and data from differential scanning calorimetric experiments showed that the BSMMs were either immiscible or only partially miscible with PES.

The modified PES/BSMMs UF membranes had a superior performance, reflected in their higher flux when treating oil/water emulsions, than the control unmodified membrane. Both the mean pore size and pore size distribution and MWCO of the BSMM-modified membranes were lower than those of the corresponding unmodified ones.

membrane surface as the evaporation time increased. The mean pore size and the MWCO of the BSMM modified PEI membranes were lower than those corresponding to the unmodified membranes, whereas the sizes of the macromolecular nodules observed by AFM were larger. The membrane surface became smoother by the addition of the BSMM in the PEI polymer casting solution and with an increase in the PEI polymer concentration. The mean roughness of the unmodified membrane was higher than that of the PEI/BSMM membranes and decreased as the solvent evaporation time increased. The reduction in surface roughness may be attributed in part to the reduction of the pore size due to migration of BSMM toward the PEI membrane surface. Modified with LSMMs, PES membranes were used for water treatment (concentrated Ottawa River water). The addition of LSMM significantly affected the membrane performance. TOC removal was higher when compared with the results reported in the literature for UF membranes. Mosqueda-Jimenez et al. modified the PES UF membranes by adjusting three membrane manufacturing variables: addition of LSMMs, the solvent evaporation time and PES concentration in casting solution. The impact of membrane surface modification with hydrophilic LSMMs

was not as high as expected. The performance of these membranes was exceptionally good in terms of NOM (natural organic matter) removal, and their permeate flux was within the range of tight commercial membranes. The use of 18 wt % PES and PPOX (LSMM synthesized using polypropylene diol as polyol) in the casting solution proved to be the most suitable combination of manufacturing conditions to maximize the TOC (total organic carbon) removal and final flux, and to minimize fouling. It was reported that LSMM blended membrane showed higher fouling resistance and long-term stability than the PES membrane without LSMM. However, Nguyen et al. studied PES UF membranes modified by three different tailor-made hydrophilic surface-modifying macromolecules, and reported that no clear correlation between membrane hydrophilicity and fouling reduction was observed. Khulbe et al. modified the surfaces of hollow fibers prepared at different air gaps, by adding SMM to the dope (PES in DMAc). From the AFM, XPS, and UF results, it was observed that the membranes could be put into two groups: i) the membranes fabricated between 10 and 10 cm air gap and ii) fabricated at higher than 50 cm air gap. Suk et al. designed and synthesized a new type of surface-modifying macromolecules (nSMM) by incorporating polydimethylsiloxane (PDMS) component in its structure. Membranes of nSMM+PES were prepared with different compositions, evaporation temperature and evaporation period. It was reported that nSMM migrated to the surface and effectively increased the surface hydrophobicity of PES membrane when blended. The cast film was kept at room temperature for a designated period before immersion in water.

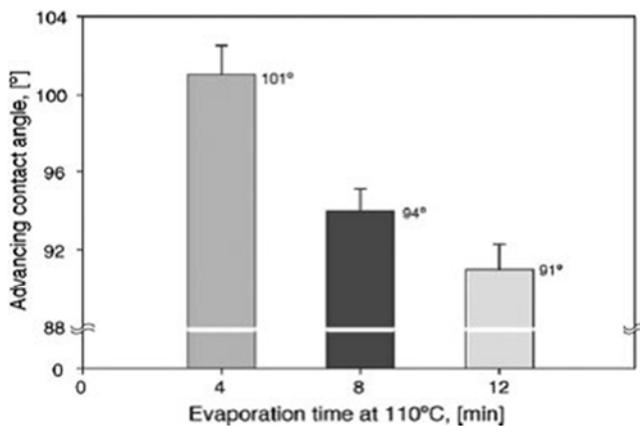


Figure 29. Contact angle vs. evaporation time. Evaporation temperature, 100°C; Composition of casting solution, PES/ nSMM1/NMP % 15/0.9/84.1.76.

Figure 29 shows that the contact angle decreased as the evaporation period increased. The hydrophobicity of nSMM blended PES membranes changed depending on the conditions of membrane preparation. Kwak et al. explored the role of dimethyl sulfoxide (DMSO) used as an additive to modify the morphological as well as the molecular nature of aromatic polyamide during the formation of thinfilm-composite (TFC) membranes. DMSO enhanced the flux in

RO. The combined results of AFM, XPS and solid-state NMR provided a robust explanation for the mechanism of flux enhancement of the aromatic polyamide. It is well known that PS dialysis membranes hydrophilized by blending PVP have excellent biocompatibility in clinical use. Khayet et al. studied the effect of concentration of ethylene glycol (EG) in the PVDF spinning solution as well as the effect of ethanol either in the internal or the external coagulant on the morphology of the hollow fibers subjected to UF. Pore sizes increased as the concentration of EG in the spinning solution increased and when ethanol was added to either the internal or the external coagulant or both. The effective porosity decreased with the addition of ethanol in either the bore liquid or in the coagulation bath or both. Similar effect was observed on the surface porosity [89].

11.2. Coating

The membrane surface can be modified by contacting the surface of one side of the polymeric (A) membrane with a solution of a different polymer (B). A thin layer of polymer (B) is left on top of the membrane of polymer (A) after solvent evaporation. Some post-treatment can also be applied. The following reports are based on these techniques. The Hilal School investigated the surface structure of molecularly imprinted (MIP) PES (UF) membrane by AFM. Molecularly imprinted polymeric membranes were developed using photoinitiated copolymerization of 2-hydroxyethyl methacrylate (HEMA) as functional monomer and trimethylpropane trimethacrylate as crosslinker in presence of adenosine 3'0.5'-cyclic monophosphate as template, followed by deposition of a MIP layer on the surface of PES microfiltration membranes. For producing the MIP layer, membranes were coated with photo initiator by soaking in a 0.25 M solution of benzoin ethyl ether/methanol and then immersing in a solution of 80 mM TRIM (trimethylpropane trimethacrylate), 40 mM HEMA, and 2 mM Adenosine 3', 5'-cyclic monophosphate (cAMP) (adenosine 3'0.5'-cyclic monophosphate) in an ethanol water mixture (70: 30 vol %). Thereafter, samples were exposed to B-100 lamp of relative radiation intensity 21.7 mW cm⁻² at 355 nm. Membranes with different modification were obtained using various UV exposure time. AFM images of these membranes revealed that a consistent increase in the degree of modification led to a systematic decrease in pore size and an increase in surface roughness. The AFM characteristics of imprinted membranes were in good correlation with the filtration data. PES UF membrane surface was modified by self assembly of TiO₂ nanoparticles (40 nm or less) via dip coating. The neat PES membrane was dipped in the transparent TiO₂ colloidal solution, stirred for 1 minute by ultrasonic method and placed for 1 h to deposit TiO₂ nanoparticles. The contact angle test of the composite membrane showed that the hydrophilicity of the membrane surface improved remarkably. The fouling experiment verified a substantial prevention of the dip-coated membrane against the fouling by hydrophobic substances, suggesting a possible use as a new type of antifouling composite membrane. Song et al. used hydrophobic PP hollow

fibers with a porous fluoro-silicone coating on the outside surface for the direct contact membrane distillation (DCMD)-based desalination. As the brine temperature was increased from 40 to 90°C, water-vapor flux increased almost exponentially. Increasing the distillate temperature to 60 from 32°C yielded reasonable fluxes.

11.3. Interfacial Polymerization / Copolymerization

When reactive monomers are dissolved in two different solvent phases and these two phases are brought into contact, rapid reaction occurs only at the interface between the two phases, creating a thin polymer film. This is a technique well established for the fabrication of RO and NF membrane. Some of recent studies are for the through understanding of this technique and also the application of the technique for fouling reduction. Nanofiltration (NF) composite membranes were prepared by the interfacial polymerization (IP) technique. The membrane support was made from a mixture of polysulfone (PSf) and PVP. The top active layer was obtained through IP between trimesoyl chlorides (TMC) in hexane with aqueous phase containing bisphenol. The variation of reaction time as well as monomer concentrations could affect the properties of the membrane produced. Increasing the reaction time resulted in decreasing water permeabilities. However, based on AFM data, the pore sizes were of similar values. Increasing the monomer concentration also resulted in decreasing water permeabilities. Based on AFM imaging the pore sizes differed considerably. Chu et al. reported a simple and effective route for the hydrophilic surface modification of ceramic supported PES membranes by synthesizing a poly (vinyl alcohol)/polyamide composite thin surface layer with an IP method. The fabricated membranes were characterized with XPS, SEM, and contact angle measurements, and the effects of hydrophilic surface modification on the membrane flux and oil rejection in the treatment of oil-in-water (O/W) microemulsions were experimentally studied. All the characterizations and filtration results showed that, the hydrophilic surface modification was achieved successfully and consequently reduced the membrane fouling effectively. The route of modification presented by Chu et al. is valuable for developing robust membranes with a low level of membrane fouling in the separation of Oil/Water microemulsions. Susanto et al. prepared low-fouling UF membranes by simultaneous photograft copolymerization of PEG methacrylate (PEGMA) onto a PES UF membrane with a nominal cut-off of 50 kg/mol. The effects of UV irradiation and monomer concentration on membrane characteristics as well as performance were studied. The results showed that UV irradiation time was the most important parameter with monomer concentration as another parameter to adjust the degree of functionalization. All modified membranes showed more resistance to fouling and higher rejection than unmodified membrane for both BSA solution and sugarcane juice. This study provides valuable information for the development of low-fouling UF membranes for sugarcane juice clarification. Kim and Lee fabricated organic inorganic

hybrids of poly (amide-6-b-ethylene oxide) (PEBAXVR) and silica via in situ polymerization of tetraethoxysilane (TEOS) using the sol-gel process, and their gas-transport properties were studied.

Gas permeation measurements were accomplished at various temperatures with He, CO₂, O₂, and N₂. These hybrid membranes exhibited higher gas permeability coefficients and permselectivities than PEBAX[®], particularly at an elevated temperature. Lu et al. reported high performance NF membranes prepared by IP, using UF membranes (SPES and PVDF UF membranes). Bisphenol-A (BPA) and isophthaloyl chloride, amine, and/or piperazine were used to form three reaction systems for IP. The results showed that NF series membranes all exhibited high rejection of electrolytes including divalent ions [89].

11.4. Plasma Treatment

Plasma polymerization process is a technique that allows us to obtain highly crosslinked polymers from nonfunctional monomers that are not utilized in conventional polymer synthesis. Plasma surface modification can improve biocompatibility and biofunctionality. In the plasma surface modification process, glow discharge plasma is created by evacuating a plasma reactor, usually made of quartz because of its inertness, and then refilling it with a low pressure gas. The gas is then energized using techniques such as radio-frequency energy, microwaves, alternating current, or direct current. The energetic species in gas plasma include ions, electrons, radicals, metastables, and photons in the shortwave ultraviolet (UV) range. When membrane surfaces are brought into contact with gas plasmas the surfaces are bombarded by these energetic species, and their energy is transferred from the plasma to the solid. As a result, the surface of the membrane is etched leaving many reactive sites (mostly radicals) on the surface. When an organic vapor or a monomer is introduced into the plasma reactor, polymerization takes place at the reactive sites. This is called plasma polymerization. Plasma polymers were prepared from three different organosilicon monomers: diethoxydimethyl silane, hexamethyldisiloxane (HMDSO), and octamethyltrisiloxane (OMTMO). Films were deposited upon silicon wafers and different porous substrates. Silicon-containing polymers are well known as polymers excelling in gas permeation. When they are synthesized by the plasma process, they also exhibit high selectivities because of high cross-linking compared with conventional polymers. Roualdes et al. studied the gas (N₂, H₂, O₂, CO₂, and CH₄) separation properties of organosilicon plasma polymerized membranes. Acrylamide (AAm)-plasma graft-aromatic polyamide (AAm-p-aramide) membrane was prepared by plasma polymerization. The membrane was subjected to pervaporation (water/ethanol mixtures). The effects of degree of grafting, feed composition, feed temperature, and surface properties on the pervaporation performances were studied. The separation factor and permeation rate of AAm-p-aramide membranes were higher than those of the unmodified aramide membrane. Optimum pervaporation was obtained by

a AAm-p-aramide membrane with a degree of grafting of 20.5% for a 90 wt % ethanol feed concentration, giving a separation factor of 200 and permeation rate of 325 g/m² h. A commercial PSf membrane was modified by grafting a positively-charged polymer onto it using low plasma treatment. The effects of the plasma treatment time, plasma generating power, and polymerization time on the pore structure, chemical composition, and f -potential of the membrane surface were examined. The static adsorption of BSA and lysozyme on a DMAEMA {2-(dimethylamino) ethyl methacrylate}- or C₄ monomer- modified HT (commercial hydrophilic PSf membrane) and filtration of BSA through an acrylic acid modified HT membrane showed that the enhancement of the repulsive electrostatic force was effective in reducing protein adsorption on the membrane surface. The results show the role of electrostatic forces in membrane fouling and can be used to guide membrane synthesis and membrane surface modification. Cyclohexane plasma was also used to modify the poly (ethylene terephthalate) track-etched membrane (Particle track-etched membrane, PTM, applications as in sensors, virus detection or removal, high quality water production). Surface of polypropylene (PP) membrane was modified by dichloromethane (CH₂Cl₂) plasma to induce hydrophilic and hydrophobic modifications. It was revealed that the surface had a thin crosslinked network, which was verified by solubility test. On the other hand, film treated in CCl₄ and CHCl₃ plasma gave greater hydrophilic modifications. Modification of PP film in CH₂Cl₂ plasma showed good durability and bond ability when compared with that in CCl₄ and CHCl₃ plasmas. Chitosan membranes were modified by alkane (petroleum ether) vapor plasma technique. Water contact angles of chitosan surface increased from 13° to 23° after plasma treatment at 93 W for 60 min and from 13° to 26° after plasma treatment at 119 W for 30 min. It indicated that the hydrophilicity of the membrane surface decreased. Mechanical properties such as tensile strength and elongation-at-break of the chitosan membranes were also improved. Permeation coefficients through the chitosan membrane plasma treated at 93 W for 30 min for urea, creatinine, uric acid, and cis-DDP decreased by 54.0, 83.3, 64.7 and 47.6%, respectively.

Inorganic gas plasma is known to promote the implantation of atoms, radical generation, and etching reactions, and is called a nonpolymer forming plasma. It is reported that highly reactive particles from gas plasma can etch a surface very gradually. Van't Hoff et al., Fritzsche et al. and Weigel et al. performed etching experiments with oxygen plasma on PES GS HFMs and on asymmetric PSf hollow fibers, respectively. They noticed that it was possible to determine the sublayer resistance after etching the fiber. Plasma etching is a technique that also allows the measurement of the thickness of the top layer in asymmetric and composite membranes. The uniformity of the structure in the top layer as well as the properties of the layer just beneath the top layer and those of the sublayer can also be determined. By measuring the gas-transport properties as a

function of the etching time, information can be obtained about the morphology and the thickness of the thin nonporous top layer. Hydrophilic modification of porous PES membranes was achieved by Ar-plasma treatment followed by graft copolymerization with acrylamide (AAm) in the vapor phase. Both surfaces of the modified membranes were found to be highly hydrophilic (ungrafted and grafted). Microporous polyethersulfone membranes were modified by nitrogen based plasma systems such as N₂, NH₃, Ar/NH₃, and O₂/NH₃.

Treatments were designed to alter the surface chemistry of the membranes to create permanently hydrophilic surfaces. Analyses by FTIR and XPS established the incorporation of NH_x and OH species in the PES membrane. The plasma treatment modified the entire cross-section of the membrane as the plasma penetrated the thickness of the membrane. Optical emission spectroscopy revealed the presence of OH* when the membrane was modified with gaseous plasma, which was not in 100% ammonia plasma, suggesting OH* must play a critical role in the membrane modification process. The usefulness of plasma treatment was revealed by increased water flux, reduced protein fouling, and greater flux recovery after gentle cleaning when compared with an untreated membrane.

11.5. Surface Modification by Irradiation of High Energy Particles

It is known that the polymer surfaces can be modified both chemically and physically when they are exposed to high energy particles. This method has been applied for the membrane surface modification [89].

11.5.1. UV Irradiation

Treatment with UV-ozone has been used as a means of removing organic contaminants from different polymer surfaces. However, UV/ozone treatment has also been used to increase the wettability of poly (ethylene terephthalate) (PET), polyethylene (PE), polypropylene, different rubbers (vulcanized styrene-butadiene-SBR, unvulcanized styrene-butadiene- SBS. This UV/ozone treatment results in an increase in the surface energy of the polymer through oxidation of the polymer. The photons produced by UV/ozone irradiation have sufficient energy to break most CAC bonds and also can induce chain scission and cross-linking on polymer surface. Both ozone and atomic oxygen radicals can react with polymer surfaces to remove low weight contaminants and to modify surfaces. Recently, Landete-Ruiz and Martin-Martinez reported that the UV treatment for 5 min gave the highest increase in the adhesion of ethylene vinyl acetate (EVA) copolymer to polychloroprene adhesive due to improved wettability, the creation of surface roughness (cracks), and the formation of carbon-oxygen moieties. Exposing PP to ozone in the presence of UV light is simple and effective way of modifying its surface to improve its wettability and adhesion. Berdichevsky et al. investigated the conversion of bulk poly (dimethylsiloxane) by deep penetration and complete

oxidation of thick-film by UV/ozone treatment. UV/ozone treatment resulted, improved wettability, enhanced electro-osmotic flow, and reduced adsorption properties in the modified PDMS channels.

11.5.2. Ion-beam Irradiation

Xu and Coleman modified the 6FDA-pMDA (polyimide) films by irradiating ion-beam and studied the structure and morphology by AFM. Detailed roughness and bearing analyses of the AFM images indicted that free-standing polyimide films have deep surface valleys which could extend to a depth of several micrometers. Ion-beam irradiation, even at a small dose, alters the microstructure of the surface layer of the polymer, and high fluence irradiation resulted in a large number of small-size microvoids in the surface. All of these changes had effects on the gas permeation properties as well as on iodine diffusion. Surfaces of polyimide and PSf membranes were modified by carbonization using ion-beam. To control the structure of membrane skin and to improve gas-transport properties, the irradiation conditions, such as the dosage and the source of ion beams, have been varied. The ideal separation factor of CO₂ over N₂ through the surface modified PI and PSf membranes increased three-fold compared with those of the untreated, pristine membranes, whereas the permeability decreased by almost two orders of magnitude. This could be due to the fact that the structure of the membrane skin had changed to a barrier layer.

11.6. Surface Modification by Heat Treatment

Membrane surfaces can also be modified by heat treatment. The PES HFMs were prepared by dry-wet-spinning method and heated in an oven at 120, 150, and 180°C. The membrane shrank by heating. It was noticed that pore size decreased from 8.16 nm for untreated hollow fiber to 3.8 nm with 1-minute heating and then increased to about 6 nm with 5 min heating at 150°C. With an increase in heating temperature, the pore size of the membrane decreases. By using a coextrusion and dry jet wet spinning phase-inversion technique with the aid of heat treatment at 75°C, Li et al. fabricated a dual-layer PES HFMs (GS) with an ultra-thin dense-selective layer of 407 Å. The dual-layer hollow fibers had an O₂ permeance of 10.8 GPU and O₂/N₂ selectivity of 6.0 at 25°C. It was observed that heat treatment at 75°C improved the gas permeation and ideal selectivity, whereas heat treatment at 150°C resulted in a significant reduction in both permeation and selectivity due to enhanced substructure resistance. SEM pictures confirmed that higher heat-treatment temperature can significantly reduce pore sizes and the amount of pores in substructure immediately underneath the dense-selective layer. Ton-That et al. studied the effects of annealing on the surface composition and morphology of PS (polystyrene)/PMMA blend. The PS/PMMA film was annealed at a temperature above their glass transition temperatures for up to 48 h. The polymer with a lower surface free energy, PS, was shown to aggregate to the surface upon annealing. The surface enrichment and

morphology changes upon annealing were explained by dewetting of PMMA relative to PS.

11.7. Graft Polymerization / Grafting

Grafting can also be applied for the surface modification of the membrane. Although the method should work for any polymeric materials, most of the recent works on membrane surface graft polymerization were on polyamide thin-film composite (TFC) membranes or porous polypropylene membranes. The reports on the grafting on the surface of polyamide TFC membranes are as follows. Hydrophilic PEG chains were grafted onto the surface of a thin-film composite (TFC) polyamide RO membrane. Aminopolyethylene glycol monomethylether (MPEG-NH₂) was used as the grafting monomer.

The membranes were characterized by ATR-FTIR, XPS, and AFM. A preliminary experiment confirmed that the grafting of PEG chains improved membrane antifouling property. Gilron et al. modified the commercial RO polyamide membranes, ranging from ultra low pressure to seawater desalination membrane, using redox generation of monomer radicals. Base membranes were thin-film composite aromatic polyamides membranes. A redox system composed of potassium persulfate and potassium metabisulfate was used to generate radicals. These attack the polymer backbone, thus initiating the graft polymerization by attachment of monomers to the membrane surface. The following monomers were used to generate grafted polymers on the membrane surface: glycol ester of methacrylic acid (PEGMA)—uncharged, sulfopropyl methacrylate (SPM)—anionic, and 2 acrylamido- 2-methyl propane sulfonate (AMPS)—anionic. Modification of membrane significantly reduced both receding and advancing contact angles. Modified membranes adsorbed less organic material and were more easily cleaned than unmodified membranes. Specific fluxes were not changed by more than 0–25%, and NaCl rejection was unchanged or increased slightly [89].

11.8. Surface Modification by Chemical Reaction

The membrane surface can also be modified by chemical reaction. Maekawa et al. examined the chemical modification of the internal surface of the pores of poly (ethylene terephthalate) (PET) membranes using the alkylation reaction of the carboxylic acids on the surfaces. The chemical incorporation of the reagent on the surfaces was confirmed by the fluorescence microscope images of the membranes reacting with the alkylation reagent bearing a pyrene fluorophore [89].

11.9. Other Techniques for Modification

Several surface modification techniques that do not belong to any of the above methods are summarized below. Molecular Imprinting Technology (MIT) allows preparing polymeric materials with selectivity toward specific molecules through polymerization or phase inversion in

presence of template. Ion implantation on the surface of the membranes affects the surface properties. The surfaces of a composite polyamide NF membrane (NF 90 Filmetec) and a cellulose acetate NF membrane (SP 28 Osmonics) were modified by implanting with F-ions at two different intensities. Zeta potential measurements of unmodified membranes and modified membranes showed higher negativity with an increased intensity of ion implantation. Multi-component salt permeation experiments were performed. A decrease of solute flux for all the ions through the modified membranes was observed when compared with the unmodified membrane. It was suggested that ion implantation on NF surface is a novel technique to increase salt rejection property of membrane [89].

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