CHAPTER 1

An Overview of Membrane Science and Technology

CONTENTS

MEMBRANE DEFINITION

A *membrane* is defined as a thin sheet, film, or layer, which works as a selective barrier between two phases that can be liquid, gas, or vapor. In other words, a membrane is an interface between two adjacent phases acting as a selective barrier, regulating the transport of species between the two compartments (Ulbricht 2006).

The membrane itself can be a solid, a liquid, or a gel. The membrane is considered as a molecular sieve constructed in the form of a film from more than one layered material with fine mesh or small pores to enable the separation of tiny particles and molecules. It acts as a selective barrier, allowing specific substances to pass through while retaining others. The ability of membranes to differentiate among species is called *selectivity*. Membranes are used for the separation of solute–solvent, solute–solute, particle–solute, and particles–solvents.

According to the European Membrane Society, a membrane is an intervening phase separating two phases and acting as an active or a passive barrier to the transport of matter between the phases adjacent to it.

Membranes can be porous or nonporous. In the porous membrane, the separation process of a mixture of components is achieved by passing one or more components through the membrane (permeate fractions) and rejecting the other components of the membrane (retentate fractions). Retentate is called *concentrate*, as it is a concentrated media of rejected substances. For example, a mixture of A, B, C, and D components can be separated by a porous membrane by rejecting C and D as retentate fractions and passing the A and B component permeate fractions through the pores of the membrane as shown in Fig. 1.1. The word *membrane* is used to indicate an interface or region of discontinuity between two phases. The membrane controls the zone at which compounds permeate through it. Thus the membrane can be also defined as a barrier, the purpose of which is to prevent the permeation of all compounds. The membrane is able to control the rate at which compounds permeate (Mulder 1996).

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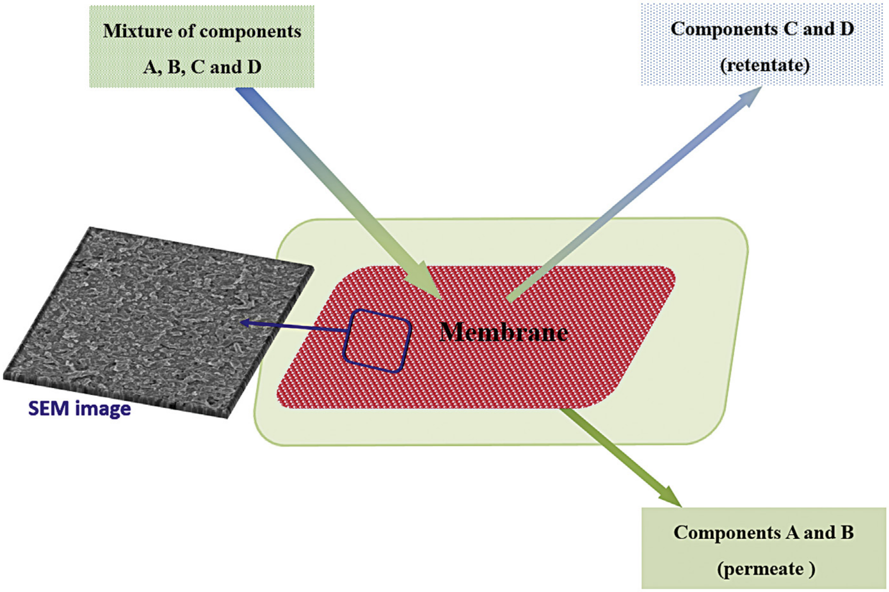

FIGURE 1.1 Ideal principle of porous membrane process.

Thus the membrane can also be considered as a permeable medium. A specific amount of energy is required to accomplish the separation of substances or components. The minimum amount of energy, W_{min}, required to accomplish the separation is larger than the free enthalpy of mixing as shown by $W_{min} \geq \Delta G_m = \Delta H_m - T\Delta S_m$.

Membrane processes are operations where the feed stream is divided into two streams: a permeate and a retentate. A membrane, as applied to water treatment, is a material that allows some physical or chemical components to pass more readily through it than others. It is thus perm-selective, because it is more permeable to those components passing through it—the permeate—than those that are rejected by it—the retentate (Judd 2011). The retentate, also called *concentrate*, is usually enriched with substances retained by the membrane, whereas the permeate or filtrate is a stream passing through the membrane, devoid of substances retained by the membrane. The membrane's role is to change the composition of a solution based on relative permeation rates and to physically or chemically modify the permeating to regulate the rate of permeation. From the other side, it is to conduct electric current, to prevent permeation—to retentate. Depending on the membrane's ability to alter the chemical nature of the permeating species, membranes can be either passive or reactive. Therefore, based on their ionic nature, membranes can be classified into neutral or charged membranes.

HISTORICAL AND KEY DEVELOPMENTS OF MEMBRANE TECHNOLOGY

The history of the membrane started with the development of several materials as natural or synthetic membranes for the separation of gases and vapors.

Membrane Research Contributions before 1900

Thomas Graham reported on the use of flat rubber membranes to study the diffusion of gases and vapor species (Graham 1829; 1833). He reported the solution-diffusion mechanism, which he observed using rubber as a liquid in which the gas dissolves and diffuses to a concentration gradient. Before that in 1748, French cleric, Abbé Jean-Antoine Nollet discovered the phenomena of water transport (Nollet 1748; 1779). Nollet placed spirit of wine in a vessel. The mouth of the vessel was closed with an animal bladder, and then he immersed the vessel in the water. Because it was more permeable to water than to wine, the bladder swelled and sometimes even burst, demonstrating semipermeability for the first time. Eighty years after that, the term *osmosis* was coined by the French physiologist Henri du Trochet (du Trochet 1828).

Mitchell reported on gas permeation through natural rubbers (Mitchell 1831). Schoenbein reported on the synthesis of cellulose nitrate, the first synthetic (or semisynthetic) polymer (Schoenbein 1846). The frog battery is an example of a class of biobatteries, which can be made from any number of animals. The general term for an example of this class is the *muscular pile*. The first well-known frog battery was created by Carlo Matteucci in 1845, but there had been others before him. Matteucci also created batteries out of other animals, and Giovanni Aldini created a battery from ox heads.

Fick made a synthetic membrane of cellulose nitrate coated onto a ceramic thimble in his classic study “Ueber Diffusion” to dialyze biological fluids (Fick 1855). Fick worked on the dialysis of solutions through artificial membranes formed from collodion. Based on his experiments, he published his law of diffusion, which is still in use. Graham worked with isolated bacteria and “colloids from crystalloids.” Graham is credited with the use of the term *dialysis* as he reported the dialysis experiments with synthetic membranes. He also demonstrated that rubber films exhibited different permeabilities to different gases. A device consisting of flat membranes with a vacuum on one side was reported for permeability rate measuring (Graham 1866). Graham postulated mechanisms for the permeation process (Graham 1861; 1866). Table 1.1 summarizes the achievements in the field of membrane technology made before 1900.

Membrane Research Contributions after 1900

John William Strutt (1900) determined the relative permeability of oxygen, nitrogen, and argon in rubber (John William Strutt 1900). Later on, polymer

Table 1.1 Membrane Research Contributions before 1900

Development	Contributor	Year
Discovery of osmosis phenomenon in natural membranes	Nollet	1748
Research on anisotropy of natural membranes	Matteucci	1845
Laws of diffusion	Fick	1855
Dialysis, gas permeation	Graham	1861
Synthetic membrane from nitrocellulosis	Fick	1865
Solution-diffusion transport mechanism	Graham	1866
Research on gas separation on rubber membranes	Graham	1866
Research on osmosis on synthetic membranes	Traube	1867
Research on osmosis on ceramic membranes	Pfeffer	1877
Research on osmosis phenomena	Gibbs; van't Hoff	1897;1888
Theory of osmosis phenomena	Gibbs; van't Hoff	1897;1888
Osmotic pressure	Pfeffer; Traube; van't Hoff	1860–1887

membranes were used for the separation of gases, and so forth (Glater 1998; Matthes 1944). Traube and Pfeffer prepared artificial membranes, and they developed the van't Hoff osmotic pressure relationship as a result of their work with osmotic phenomena. Bechold coined the term *ultrafiltration* in 1906 (Bechold 1907, Bechold & Schlesinger 1931). Michaels (1968) further developed ultrafiltration. Zigmondy developed asymmetric microporous filters made with a fine porous skin on the feed side and open structure on the permeate side (Zsigmondy 1922). The tightest of the ultrafiltration membranes were made from cellophane or cellulose.

Reverse osmosis was initiated and studied in the 1920s. It was rediscovered by Reid and his coworkers in the 1950s. The practical phenomenon of hemodialysis was developed by Kolff (Kolff & Berk 1944). Reverse osmosis, also called *hyperfiltration*, for desalinating seawater was initiated by the Office of Saline Water to meet future water demands. Because of their large pore size, microporous membranes were not suitable for desalination (Sing, Hoffman & Judd 2006).

Reid and Berton discovered polymeric membranes that could show high salt rejections. Their challenge was that the membranes were too thick and required casting a thin film without imperfections. Because the thickness was about 6.0 μm, which is not enough to provide high flux, the water flux was nonpractical. This problem was relatively solved when Loeb and Sourirajan, during 1958 to 1962, discovered how to make asymmetric membranes of small thickness and with controlled pore sizes (Loeb 1981; Loeb & Sourirajan 1963). The membrane was made of very thin cellulose acetate film, supported by a fine cellulose acetate porous substrate, using the phase-inversion method, and it was called *L-S membrane* (Loeb & Sourirajan 1963). This development was a great breakthrough in membrane technique, and especially in the pressure-driven

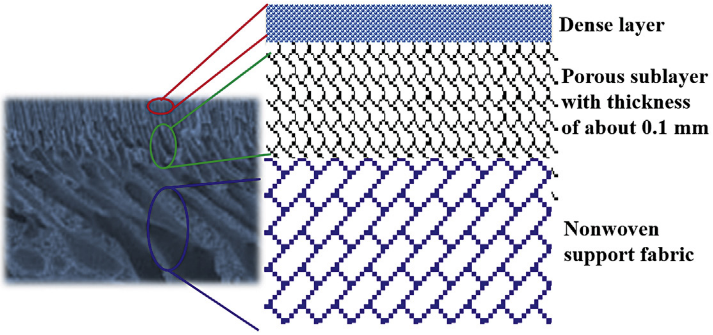

FIGURE 1.2 A representation of an asymmetric, skinned membrane.

separation process used for the purification of water. When characterized under an electron microscope by Riley in 1964, the membranes were found to be skinned with a thickness of about 0.1 mm (Lonsdale 1982). The skinned (asymmetric) membrane has a top layer that is skinlike and a bottom side that has large pores over a nonwoven support fabric, which provides mechanical strength to the membrane, as illustrated in Fig. 1.2. They were capable of producing a flux of 5 to 11 gallons per square foot per day of 0.05% NaC1 water, under a pressure of 100 to 135 bar(g).

Westmoreland and later Bray invented the spiral-wound module, which was more efficient than the tube-in-shell module. The spiral-wound membrane can be viewed as a plate-and-frame arrangement that has been rolled up. The original module had a single leaf of membrane, whereas modern spiral-wound modules contain multileaf membranes.

After that, cellulose triacetate hollow-fiber membranes and the means to modularize these fibers were developed by Mahon, McLain and others (Mahon 1966; McLain 1969; McLain and Mahon 1969). However, a quite competitive development with the L-S type membrane, the hollow-fiber aromatic polyamide membranes, was prepared by Henry Hoehn and George Milford at DuPont in the late 1960s. These membranes were prepared with a solution which was spun into hollow fibers with a 42 μm inside diameter and an 85 μm outside diameter with a skinned structure on the shell side. Although the water flux was well below that exhibited by cellulose acetate membranes, the salt rejection was higher. Therefore, to enhance the flux, several hundred thousand of the fibers are required to be incorporated into modules containing several thousand square feet of membrane area. This development was key to the development of hollow-fiber ultrafiltration and microfiltration. Tables 1.2 and 1.3 summarize the achievement in the field of membrane technology after 1900 (Ferry 1936; Kołtuniewicz 2006; Koros 2004; Loeb & Sourirajan 1963; Loeb 1981; Lonsdale 1982; 1987; Michaels 1968; Petersen 1993; Strathmann 2001).

Table 1.2 Membrane Research Contributions during 1900–1950

Development	Contributor	Year
Affinity effects in ultrafiltration	Bechold	1907
Distribution of ions law (Distribution law)	Donnan	1911
Pervaporation	Kober	1916
Microporous membrane	Zigmondy	1907–1918
Research on dialysis	Abel	1926
Research on reverse osmosis	Manegold; McBain; Michaels	1926–1931
Description of hemodialysis procedure	Abel; Haas	1913
Research on electrodialysis	Elder I in	1934
Membrane potential	Meyer; Teorell; Sievers	1930s
Hemodialysis	Kolff	1944

Table 1.3 Membrane Research Contributions after 1950

Development	Contributor	Year
Gas separation on silicone rubber	Kammermeyer	1957
Pervaporation of azeotropic mixtures	Kammermeyer	1957
Skinned membrane	Loeb & Sourirajan	1959
Research on composite membranes	Lonsdale	1960
Synthesis of asymmetric membranes and controlling pore size in membranes	Loeb & Sourirajan	1962
Capillary membranes	Mahon	1963
Concentration polarization	Merten	1963
Hollow-fiber membranes	Mahon	1966
Membrane transport models	Katachalsky; Kedem; Loeb & Sourirajan; Lonsdale; Merten; Pusch	1960–1970
Spiral-wound membrane element	Bray; Westmoreland	1965–1970
Hollow-fiber RO membranes	Hoehn; Mahon; Milford	1965–1970
Thin-film composite membrane	Cadotte & Rozelle	1977
Classification of pressure-driven processes	Porter	1975
Models of facilitated transport	Goddard	1977
Membranes with immobilized carriers	LeBlanc	1980
Description of facilitated transport in membranes	LeBlanc	1980
Membranes with active centers	Yoshikawa	1986
Chain model of facilitated transport	Aris; Brown; Cussler	1989
Membrane hybrid processes	Rautenbach	1990

In the 1970s, Cadotte and Rozelle developed thin-film composite membranes for reverse osmosis applications. These membranes were made of polyamide polymer deposited on a support of polysulphone membrane by interfacial polymerization reaction (Schafer, Fane & Waite 2004). In 1984, Petersen developed another application using such membranes, which he called *nanofiltration*

Table 1.4 Some Membrane Modules and Their Applications in the Market

Membrane or Module	Applications
Cellulose acetate spiral-wound membranes	Industrial and municipal water treatment
Thin-film composite spiral-wound reverse osmosis membranes	Water desalination and high-purity water production
Hollow-fiber reverse osmosis membranes	Seawater desalination
Hollow-fiber ultrafiltration and microfiltration membranes	Industrial applications

(Petersen 1993). Stimulating from this technology, Henis and Tripodi made industrial gas separation economical by drawing on the experience of developments in revers osmosis membranes and modules. This also led to the development of several membrane modules and their applications in the marketplace, such as spiral-wound modules with cellulose acetate and thin-film composite polyamide membranes, polyamide hollow-fiber membranes, and ultrafiltration polysulphone hallow fiber membranes (Lonsdale 1987; Table 1.4).

Understanding the mechanism of water transport through the membranes was a key point for the development in reverse osmosis. In the 1960s, Sourirajan developed a preferential sorption-capillary flow model based on the assumption that the membrane surface has pores. Another mechanism is a model called the *solution-diffusion flow model*, which is based on the assumption of a pore-free membrane surface. It was first used by Ferry in 1936, to explain the permeation of gases, vapors, and organic liquids through dense, nonporous, homogeneous, and defect-free membranes (Ferry 1936). It is based on the assumption that species is sorbed by the membrane at one interface, transported by diffusion across the membrane through the voids between the polymeric chains, and desorbed at the other interface. It involves molecular scale interactions of the permeating solutes with the membrane surface (Ferry 1936; Matsuura 1994).

MEMBRANE SCIENCE

Membrane science is a field that deals with materials development for membrane design and its process performance. Therefore, membrane science can be simply categorized into material selection, material characterization and evaluation, membrane preparation, membrane characterization and evaluation, membrane transport phenomena, membrane module design, and process performance (Meares 1976; Turbak 1981; Starzak 1984). Each one of these categories deals to some extent with the study of permeation and permeable media, which is the membrane (Lloyd 1985). The basic categories of material science are illustrated in Fig. 1.3.

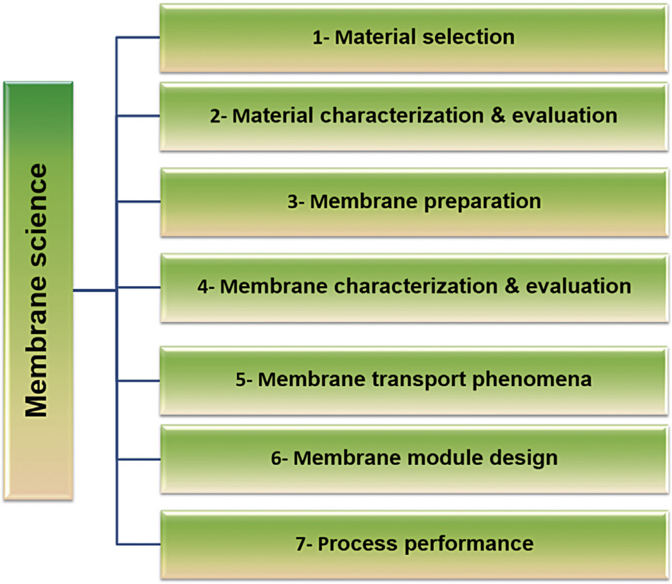

FIGURE 1.3 Basic categories of material science.

MEMBRANE TECHNOLOGY

Membrane technology encompasses the related scientific and engineering approaches for the transport or rejection of components, species, or substances through or by the membranes. Membrane technology is used to explain the mechanical separation processes for separating gas or liquid streams (Baker 2004; Nunes & Peinemann 2001). Some major steps in the development of membrane technology are listed in Fig. 1.4.

Because of its multidisciplinary character, membrane technology is used in several industries, including water treatment for domestic and industrial water supply, chemical, pharmaceutical, biotechnological, beverages, food, metallurgy, and other separation processes. A schematic representation of the applications of membrane processes is depicted in Fig. 1.5.

The wider industrial and environmental applications are because of the advantages of membrane separation as a clean technology; saving energy; and its ability to replace conventional processes, such as filtration, distillation, ion exchange, and chemical treatment systems. Other advantages are its ability to produce high-quality products and flexibility in system design. The main advantages of membrane technology are listed in Fig. 1.6.

Using membrane technology, the separation can be carried out continuously under mild conditions with relatively low energy consumption and without

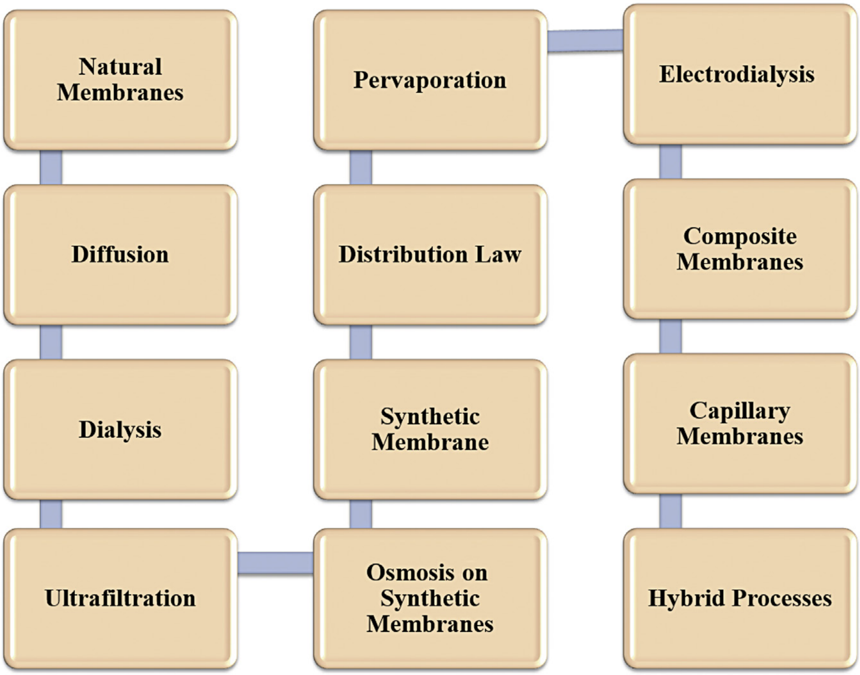

FIGURE 1.4 Some major steps in development of membrane technology.

the need for additives. Moreover, the technology can be combined with other separation processes, forming hybrid processes. However, this technology has some obstacles, such as concentration polarization and membrane fouling, low membrane lifetime, and low selectivity and flux. Fig. 1.6. illustrates the benefits and drawbacks of membrane technology. Although membrane fouling and concentration polarization are disadvantages, they are part of the separation process.

MEMBRANE SEPARATION PROCESSES

Membrane separation process is a process where a membrane is used to separate the components in a solution by rejecting unwanted substances and allowing the others to pass through the membrane. The role of the membrane is also to change the composition of a solution on the basis of relative permeation rates. Membrane performance can be measured by the ability of the membrane to prevent, regulate, or enhance the permeation. Several factors control the rate of permeation and the transport mechanism. These include the magnitude of the driving force and the size of the permeating molecule relative to the size

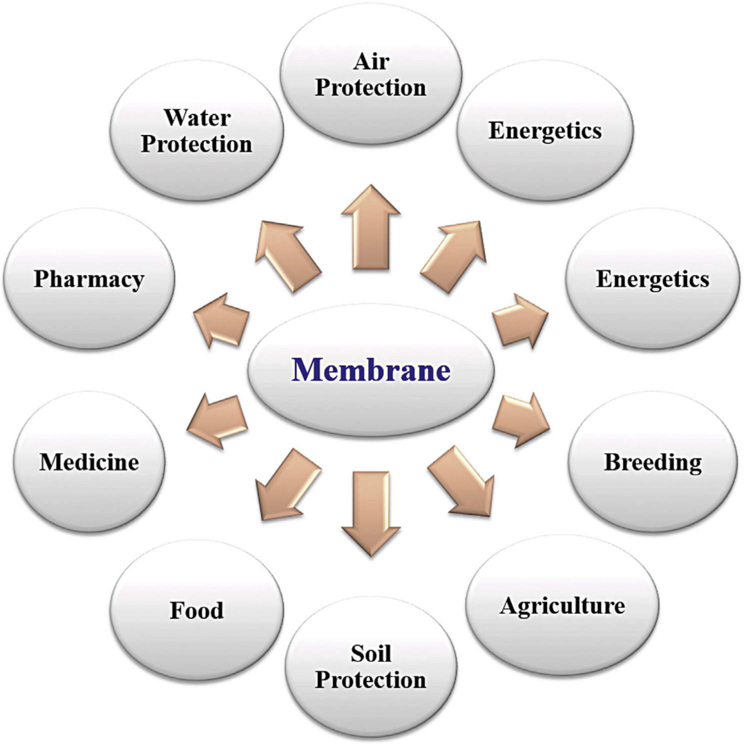

FIGURE 1.5 A schematic representation of the applications of membrane processes.

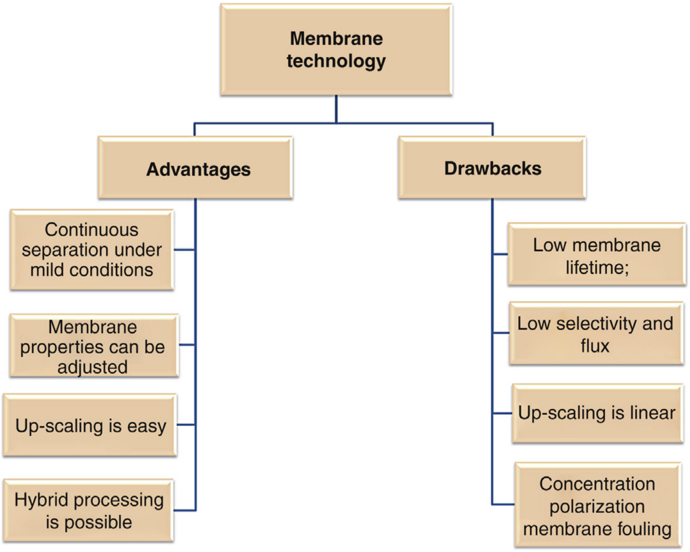

FIGURE 1.6 Benefits and drawbacks of membrane technology.

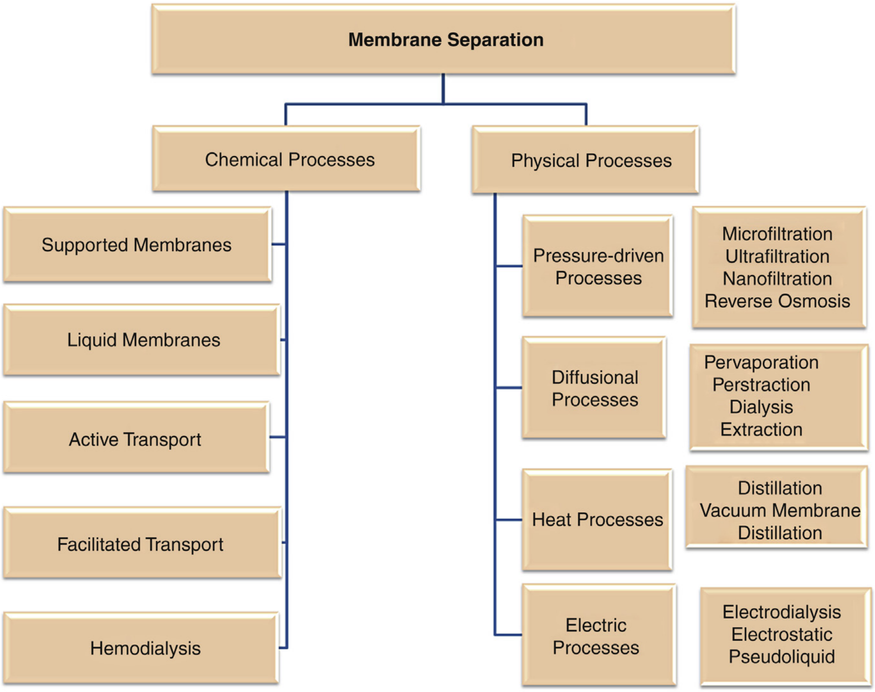

FIGURE 1.7 Simple classification of membrane separation processes into physical and chemical processes.

of the available permanent. The chemical nature—dispersive, polar, ionic, and so forth—of both the permeant and the material used to make the membrane may also effect on the separation. The membrane process conditions must be engineered carefully, however, the performance limits are determined by the membrane properties. Membrane separation processes are used in numerous industrial and environmental applications. Membrane separation processes can simply be classified into physical and chemical processes, as shown in Fig. 1.7. A variety of membrane separation processes can be categorized according to either driving force, membrane type and configuration, or removal capabilities and mechanisms. Transport of selected substances through the membrane can be achieved by applying a driving force (pressure, temperature, concentration, electrical potential) across the membrane.

MEMBRANE MATERIALS

The selection of the materials suitable to make a membrane for a specific application is a key factor that requires more investigation. The selection of membrane material allows control over the nature and magnitude of the interactions between permeants and membranes. It determines the packing density and the

Table 1.5 Organic Materials for Fabricating Membranes for Separation Processes

Serial No.	Separation Process	Examples of the used materials
1	Microfiltration	Cellulose nitrate, cellulose acetate, polyamide, polysulfone, poly(ether sulfone), polycarbonate, poly(ether imide), poly(vinylidene fluoride), polytetrafluoroethylene, polypropylene, polyacrylonitrile, regenerated cellulose
2	Ultrafiltration	Cellulose acetate, polyamide, polysulfone, poly(ether sulfone), polycarbonate, poly(ether imide), poly(vinylidene fluoride), polyacrylonitrile, poly(methyl methacrylate), regenerated cellulose
3	Nanofiltration	Polyamide
4	Dialysis	Cellulose acetate, polyamide, polycarbonate, polyacrylonitrile, poly(methyl methacrylate), regenerated cellulose
5	Pervaporation	Polyvinyl alcohol), polydimethylsiloxane
6	Gas separation	Cellulose acetate, polysulfone, polycarbonate, poly(2,6-dimethyl-1,4-phenylene oxide), polyimide, polydimethylsiloxane
7	Reverse osmosis	Cellulose acetate

segment mobility of the polymer chains that comprise the solid regions of the membrane. Although both material selection and membrane preparation procedures influence the mechanism of transport, membrane stability, and membrane performance, the latter determines the membrane morphology, which influences the rate of permeation by physical properties, such as steric hindrance.

Membranes are fabricated from a wide variety of organic and inorganic materials. Examples of inorganic materials are carbons, alumina, and zeolites. However, the majority of commercial membranes are fabricated from polymers and liquids. Examples of organic materials are listed in Table 1.5. These materials are used to fabricate membranes with high mechanical strength, thermal stability, and chemical resistance, in addition to stable long-term separation properties.

Inorganic Membrane Materials

Inorganic membranes are used for gas separation, microfiltration, and nanofiltration. These membranes vary greatly in pore size, support material, and configuration (De Vos & Verweij 1998). Examples of this type are glass, metal, alumina, zirconia, zeolite, and carbon membranes. However, other inorganic materials such as silica, silicon carbide, silicon nitride, titania, cordierite, tin oxide, and mica can be used to produce porous membranes. Generally, inorganic membranes covering a wide range of materials can be classified into dense (nonporous) or porous (symmetric and asymmetric). Each of these inorganic materials has advantages for a specific use in membrane technology.

Dense membranes can be made of palladium and its alloys, silver, nickel, and stabilized zirconia. They are used for the purpose of gas separation. For example, ceramic dense membranes are used in the separation of oxygen from the air or the separation of hydrogen gas from a mixture. The limitation in their industrial applications is caused by their low permeability.

Conversely, porous membranes are used in industrial applications because of their molecular sieving properties, such as high permeabilities and selectivities. They have high chemical stability, which makes them usable in separations where aggressive media, such as acids and strong solvents, are present. They also have high thermal tolerance, which makes them usable in high-temperature membrane operations. They are highly resistant to corrosive chemicals. Special attention is given to the porous membranes, such as silica, zeolites, and carbons, which appear to be promising in separation of gases in real applications (Chen & Yang 1994; Fuertes & Centeno 1995).

For example, silica-based membranes selectively separate hydrogen from other gases (Hayashi et al. 1997) however; permselectivity between similar-sized molecules, such as oxygen and nitrogen, seems insufficient and invisible for real applications. Carbon molecular sieves produced from the pyrolysis of thermosetting polymers, such as polyacrylonitrile, poly(vinylidene chloride), perfluoroalkoxy polymer (PFA), cellulose, cellulose triacetate, saran copolymer, and phenol formaldehyde resins, or from coals such as coconut shell, are promising to be effective for gas separation in adsorption applications. Several parameters influence the size and pore dimensions of carbon, and thus the molecular sieving effect. These are (1) morphology of the organic precursor, (2) the chemistry of pyrolysis, (3) mild activation, and (4) sintering steps (Koresh & Soffer 1981; 1983;1986;1987).

Organic Membrane Materials: Polymers

A polymer can be defined as a very long chain (molecule or macromolecule) made up of small molecules or units called *monomers*. Polymers can be naturally occurring or synthetic. Synthetic and natural polymers play an essential and ubiquitous role in membrane science because of their broad range of properties (McCrum et al. 1997; Painter & Coleman 1997; Roiter & Minko 2005). Membranes fabricated from polymers are use more in industrial application because of their high performance and ease of design (Osada & Nakagawa 1992; Pinnau & Freeman 1999). There are a number of polymers, but choosing a membrane polymer is not an easy task because the polymer has to have appropriate characteristics for the intended application (Zeaman & Zydney 1996). In addition to chemical and mechanical stability and with good separation

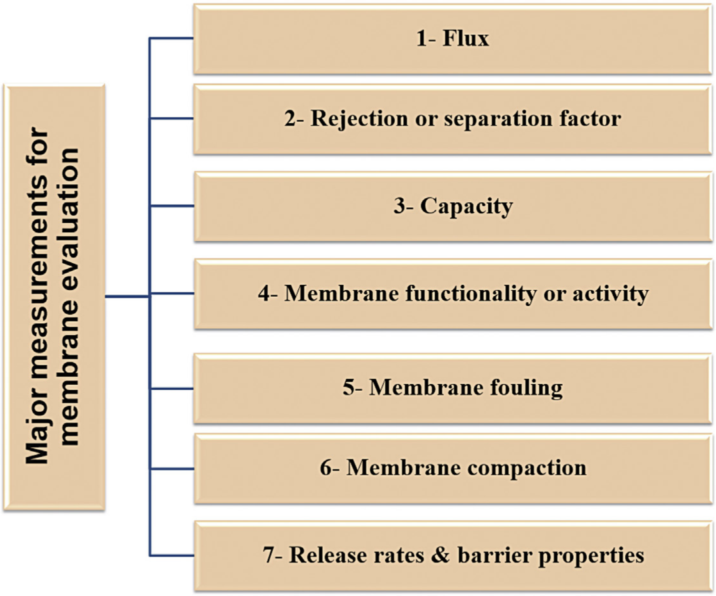

FIGURE 1.8 Major measurements for membrane evaluation.

properties, the polymer has to offer a low binding affinity for separated molecules and has to withstand harsh cleaning conditions. Moreover, it has to be compatible with membrane fabrication technology (Zeaman & Zydney 1996). The polymer has to be suitable in terms of its chain rigidity and interaction and the polarity of its functional groups (Zeaman & Zydney 1996). It should be obtainable at a good price. Some of the common polymers used in membranes are listed in Table 1.5 (Madaeni 2001; Martinez et al. 2000; Palacio et al. 1998; Templin et al. 2006; Zydney & Ho 2003).

Membrane Evaluation

It is important to evaluate the performance of the membrane, using essential parameters, before employing it in real applications. There are some measures used to evaluate the membrane performance. These include measurements of flux, rejection factor, separation factor, capacity, membrane activity, membrane fouling, membrane compaction, release rates, and barrier property (listed in Fig. 1.8). These measures are directly related to materials selection and membrane preparation methods.

Membrane Evaluation Characteristics

The membrane can be used in industrial and environmental separation process if it exhibits the required characteristics. These include high flux, high selectivity with required rejection, mechanical stability, tolerance to feed stream components, fouling resistance, tolerance to temperature variations, manufacturing reproducibility, cost- effectiveness, and the ability to be packaged into high-surface-area modules (Baker et al. 1991; Kesting 1971; Koros et al. 1988). The selectivity determines the extent of separation toward a specific application because a higher product purity can be achieved if the membrane is of higher selectivity.

Filtration Flux

The rate of membrane surface fouling is a function of the permeate flux rate, measured as gallons per square foot of membrane area per day (GFD). The lower the flux rate, the lower the rate of fouling. With higher filtration flux, solutes are dragged more in the direction of the pores, and result in pore blocking and a cake layer on top of the membrane surface. The optimum flux is a flux that is *low* enough to make sure that no deposition takes place on top of the membrane. Selection is made using the critical flux hypothesis, which is that on start-up there exists a flux below which a decline of flux with time does not occur; above it, fouling is observed (Field et al. 1995). This flux is the critical flux and its value depends on the hydrodynamics and probably other variables. The level of the critical flux depends, among others, on cross-flow velocity, membrane type, type of solute, and bulk concentration of the solute.

NANOMATERIALS

An Overview of Nanomaterials

Nanomaterial is defined as a substance or a set of substances where the external dimensions or at least one dimension is in the range of 1 to 100 nanometers. The word *nano* is derived from the Greek "nanos" meaning "dwarf. (Boholm and Boholm 2012)" Nanoscience is the study of phenomena and manipulation of material at the nanoscale, where properties differ significantly from those at bulk. The nanomaterials that have the same composition as known materials in bulk form may have different physical, mechanical, and chemical properties than the same materials in bulk form. Nanomaterials can be in the form of particles, tubes, rods, or fibers. Nanomaterials are an increasingly important product of nanotechnologies.

Nanotechnology is the science and technology of small things. It is the study and application of extremely small things and can be used across all the other scientific fields, such as chemistry, physics, materials science, and engineering. It is a science, engineering, and technology conducted at the nanoscale; it is a multidisciplinary field, meaning that it involves ideas integrated from many traditional disciplines, such as solid-state physics, chemistry, electrical and chemical engineering, biochemistry and biophysics, and materials science. Nanotechnology includes materials with at least the following three properties:

1. They are of small size, measured in hundreds of nanometers or less.
2. They have unique properties because of their small size.
3. The properties are controlled by regulating the structure and composition on the nanometer scale.

Historical and Key Developments of Nanotechnology

The physicist Richard Feynman at an American Physical Society meeting at the California Institute of Technology in December 1959, delivered a talk titled "There's Plenty of Room at the Bottom" and described a process in which scientists would be able to manipulate and control individual atoms and molecules. However, the first one to use the term *nanotechnology* was Professor Norio Taniguchi (Taniguchi 1974). With the development of the scanning tunneling microscope in 1984, and the great microelectronics revolution, the techniques of micro- and nanolithography and etching, nanotechnology-based research has been significantly developed.

Although some nanomaterials occur naturally, engineered nanomaterials are of particular interest and can be designed for many commercial products and processes. Nanomaterials have a much greater surface-area-to-volume ratio than their conventional forms, which can lead to greater chemical reactivity and affect their strength. Also at the nanoscale, quantum effects can become much more important in determining the material's properties and characteristics, leading to novel optical, electrical, and magnetic behaviors. Table 1.6 illustrates the milestones in nanotechnology developments achieved before 1990 (Klein et al. 2011; U.S. National Nanotechnology Initiative, n.d.). Table 1.7 and Table 1.8 illustrate the milestones in nanotechnology developments achieved during 1990 to 2000 and after 2000, respectively.

General Properties of Nanomaterials

Nanomaterials combine distinctive physical, chemical, and biological properties compared to their bulk, which endow them with their beneficial characteristics. These properties are mainly caused by their structure and higher surface-area-to-volume ratio. These unique properties of nanomaterials are promising for applications in water and wastewater treatments. Carbon structures, such as carbon nanotubes and graphene, can be used as adsorbents because of their properties, such as high specific surface area and assessable adsorption sites, selective and more adsorption sites, short intraparticle diffusion distance, and tunable surface chemistry. Titania and zinc oxides are used in photocatalysis degradation of organic pollutants in waters because of their photocatalytic activity in the solar spectrum, high stability and selectivity, and low cost (Amin et al. 2014).

Table 1.6 The Milestones in Nanotechnology Developments Achieved before 1990

Contributions	Contributor	Year
Colloidal ruby gold discovered: nanostructured gold under certain lighting conditions produces different-colored solutions	Faraday	1847
Field emission microscope invented, allowing near-atomic-resolution images of materials	Müller	1936
Semiconductor transistor invented: greatly expanded scientific knowledge of semiconductor interfaces, laying the foundation for electronic devices and the Information Age	Bardeen, Shockley & Brattain	1947
Theory and process for growing monodisperse colloidal materials to fabricate colloids for industrial uses (papers, paints, thin films, dialysis) developed	La Mer & Dinegar	1950
Field ion microscope developed	Müller	1951
Concepts of molecular engineering introduced as applied to dielectrics, ferroelectrics, and piezoelectrics	von Hippel	1956
Technology and engineering at the atomic scale presented: "There's Plenty of Room at the Bottom" at an American Physical Society meeting at Caltech	Feynman	1960
Moore's Law developed by Intel cofounder; described the density of transistors on an integrated chip, increasing reliance on nanotechnology as chip and transistors approach atomic dimensions	Moore	1965
Nanocrystals produced by inert gas evaporation technique	Granqvist & Buhrman	1976
Scanning tunneling microscope invented; Nobel Prize awarded in 1986	Binnig & Rohrer	1981
Nanocrystalline, semiconducting quantum dots discovered in a glass matrix with electronic and optical properties	Ekimov	1981
Buckyball fullerene (C60) discovered; awarded 1996 Nobel Prize in Chemistry	Kroto, O'Brien, Curl & Smalley	1985
Colloidal semiconductor nanocrystals (quantum dots) discovered	Brus	1985
Atomic force microscope invented	Binnig, Quate & Gerber	1986
Manipulated individual xenon atoms to spell out IBM logo; ability to precisely manipulate atoms	Eigler & Schweizer	1989

In addition to direct contribution of nanomaterials to water purification, nanomaterials could be used for the modification of membrane characteristics to improve resistance to fouling or for specific pollutant types. For example, nanoparticles of silver, titania, zeolites, and other metal and metal oxides are used as fillers in membrane technology because of their strong antimi-

Table 1.7 Milestones in Nanotechnology Developments Achieved during 1990s

Contributions	Contributor	Year
Nanotechnology began to operate: in 1989 by Nanophase Technologies; in 1990 by Helix Energy Solutions Group; in 1997 by Zyvex; in 1998 by Nano-Tex	Klein et al.	2011
Carbon nanotube (CNT) discovered: Iijima shared the Kavli Prize in Nanoscience in 2008 for this advance and other advances in the field.	Iijima	1991
Nanostructured catalytic materials MCM-41 and MCM-48 discovered at Mobil Oil; now used heavily in refining crude oil as well as for drug delivery, water treatment, and others	Kresge et al.	1992
Method for controlled synthesis of nanocrystals (quantum dots) for biology and high-efficiency photovoltaics and lighting invented	Murray et al.	1993
Molecule [iron carbonyl $Fe(CO)_2$] from constituent components [iron (Fe) and carbon monoxide (CO)] assembled with a scanning tunneling microscope to prove chemical bonding	Lee & Ho	1999
Dip-pen nanolithography invented, leading to writing of electronic circuits and patterning of biomaterials for cell biology research, and nanoencryption	Ginger et al.	2004

crobial activity, hydrophilicity low toxicity, high mechanical and chemical stability, high permeability and selectivity, and/or photocatalytic activity. The synthesis of nanomaterials will be discussed in Chapter 4, while the synthesis of nanomaterials/polymer membranes will be discussed in Chapters 5 and 6. The characterization of the nanomaterials/polymer membranes will be discussed in Chapters 7 and 8 followed by discussion in other chapters for their applications.

CONCLUSION

In this chapter, basic concepts related to the historical overview of membranes, membrane technology, and membrane separation processes were discussed. These include membrane definition, history, and contributions in membrane science and technology. Membrane separation processes and methods for membrane evaluation were also highlighted and we attempted to provide a complete overview. Various major types of membrane materials were classified. An overview of nanomaterials and the history of their development was also discussed. Accelerate the development of membrane materials with high filtration flux and low membrane blocking, may further promote membrane application in different fields including water treatment.

Table 1.8 The Milestones in Nanotechnology Developments Achieved after 2000

Contributions	Contributor	Year
Gold nanoshells developed, which when tuned in size to absorb near-infrared light, serve as a platform for the integrated discovery, diagnosis, and treatment of breast cancer without invasive biopsies, surgery, or systemically destructive radiation or chemotherapy	Halas, West, Drezek & Pasqualin	2003
First college-level education program in nanotechnology in the United States launched: the College of Nanoscale Science and Engineering	SUNY Albany	2004
DNA-based computation and algorithmic self-assembly theories developed in which computations are embedded in the process of nanocrystal growth	Winfree & Rothemund	2005
Nanoscale car built of oligo(phenylene ethynylene) with alkynyl axles and four spherical C60 fullerene (buckyball) wheels. In response to increases in temperature, the nanocar moved about on a gold surface as a result of the buckyball wheels turning, as in a conventional car	Tour et al.	2006
Lithium-ion battery built with a common type of virus that is nonharmful to humans at the Massachusetts Institute of Technology (MIT). The batteries have the same energy capacity and power performance as state-of-the-art rechargeable batteries being considered to power plug-in hybrid cars.	Belcher et al.	2007
Creating DNA-like robotic nanoscale assembly devices	Seeman	2009–2010
First carbon nanotube computer developed by Stanford University researchers		2013

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