

Chapter-1

Introduction

1.1 Membrane separation processes

A separation process is one, which converts a mixture or solution of two or more chemical substances into two or more distinct product streams. Many separation technologies are in existence like adsorption, filtration, distillation, desalination, flocculation and sedimentation, sublimation, crystallization, membrane separation processes and many more. In recent decades, membrane separation processes have gained high importance among the various available separation technologies. In membranes separation processes, membrane acts as a selective barrier by retaining a particular component or components from a mixture and allowing others to pass through it. These processes are being used in a variety of application because of their advantages of flexibility of application from a meso to nano size range of particles, simple mechanism, continuous operation and high selectivity. These processes require less amount of energy as compared to conventional thermal separation technologies. So membrane separation technology is economical as well as environment friendly. Membranes, the key part of these processes, are made of a large range of materials of different physiochemical properties which renders these processes suitable for very broad application area.

All membrane separation mechanisms are motivated from various natural activities of human body. Blood purification through the kidney is inspiration for electro dialysis technology. Skin works for selective passage of sweat from body analogous to reverse osmosis. Human liver works similar to microfiltration. A large range of membrane separation processes have been developed after getting understanding of different

variety of separation processes occurring in human body in recent decades and have emerged as most attractive technologies for pharmacological, food and various chemical processing industries. These are also very prominent in industrial effluent and wastewater treatment application. Today these technologies are not just limited to industries; these have now reached our house for purification of drinking water (Bassyouni et al., 2019).

1.2 Type of membrane separation processes

Membrane separation processes can be categorized on the basis of size of components removed, type of material used for membrane synthesis, separation mechanism and membrane configuration. However, a broader classification is done on the basis of driving force applied for the separation of components through the mixture or solution i.e. transmembrane pressure and concentration gradient (Wankat, 2006; Wintgens et al., 2005). A schematic representation of different kind of membrane separation processes on the basis of driving force is shown in figure 1.1.

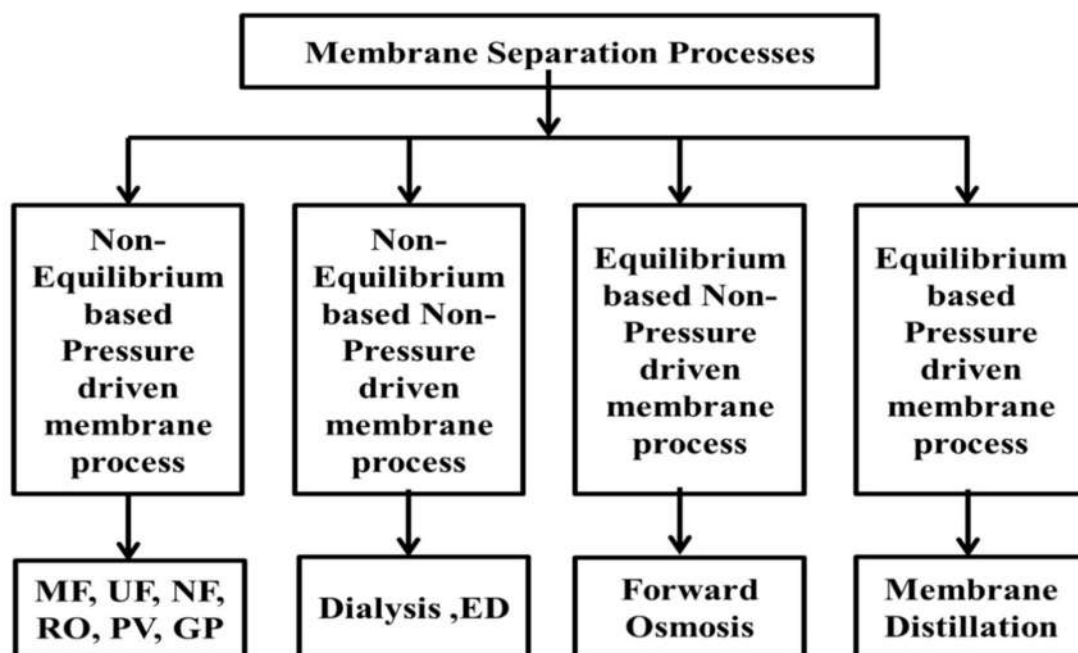


Figure 1.1: Classification of membrane separation processes

Non-equilibrium based Pressure driven membrane separation processes are very commonly used among all categories. Four main processes of this category are microfiltration (MF), ultrafiltration (UF), nano-filtration (NF) and reverse osmosis (RO). These are respectively classified on the basis of decreasing membrane pore size. Larger amount of driving force is required for lower passage of constituents through a lower pore size. Therefore microfiltration and ultrafiltration are also categorized as low-pressure membrane process while nano-filtration and reverse osmosis are categorized as high-pressure membrane process (Burton et al., 2014).

1.2.1 Microfiltration

Microfiltration and ultrafiltration processes require low-pressure difference for separation. Pressure range is below 2 bar for these processes. Separation in microfiltration takes place due to size exclusion and membranes have large pores in the range of 0.1-1.0 μm . This technology is commonly applicable for separation of suspended solids in wastewater, organic colloids and bacteria (del Pino et al., 1999). In water treatment plants, microfiltration membranes are used for removal of very fine suspended solids, protozoan cysts and coliform bacteria and up to 99% removal can be achieved by this technology (Rodriguez et al., 2009; Wilf, 2010). However, it is limited to virus disinfection (Wintgens et al., 2005).

1.2.2 Ultrafiltration

Ultrafiltration works on same mechanism of size exclusion but the pores are smaller in this process than microfiltration. It separates particles in the diameter range of 0.01-0.1 μm . In addition to suspended solids, organic matter, pathogens, colloids and viruses can be removed by this technology and biological oxygen demand; turbidity can be greatly reduced up to 95%. These processes are frequently used as pre-treatment for the reverse osmosis processes. Hydrodynamic conditions and physicochemical properties of

membrane materials are also responsible for the rejection achieved by these processes (Fane et al., 2011). However some studies have reported that UF membranes do not completely block bacterial permeation because of membrane deterioration due to biofouling (Warsinger et al., 2018; Wintgens et al., 2005). Ultrafiltration can also remove the soluble and colloidal forms of nitrogen, phosphorus and organic carbon and 10-85% rejection can be achieved depending on whether the contaminants are in soluble phase or particulate. However this technology has limitation in removing dissolved solids (Bartels et al., 2010).

1.2.3 Nanofiltration

Nanofiltration process works on high hydraulic pressure and used for separation of dissolved chemicals such as salts. It is quite similar to reverse osmosis and separates the same solutes as reverse osmosis, but its rejection efficiency is slight lower to reverse osmosis. It is used as low energy demanding processes as compared to reverse osmosis for some limited applications (Tchobanoglous et al., 2015). These processes were introduced in the recent 2-3 decades for purposely and selectively permeating some ionic solutes from feed to permeate. Nanofiltration has higher water permeability and requires low pressure as compared to reverse osmosis. Hence, it require less energy and in turn economical than reverse osmosis (Warsinger et al., 2018).

Solute rejection in this process involves different exclusion and transport mechanism than low-pressure membrane processes. Solute exclusion is done on the basis of dielectric, steric exclusion as well as adsorption to the membrane surface in some cases (Bolong et al., 2009; Bowen et al., 2002; Roy et al., 2017). Rejection rate of nanofiltration is reported 20-80% for monovalent ions and above 95% for divalent ions of the same charge (Bolong et al., 2009). In the case of uncharged solutes, rejection depends on molecular weight (Bellona et al., 2008). Therefore, nanofiltration permeate

sometimes contain molecules out of the size range of membrane pore (Van der Bruggen et al., 2008; Verliefde et al., 2008, 2009). In some new studies, some pre-treatment techniques like ozone pre-treatment and non-thermal crystallization are also suggested for improving the separation efficiency and reduction of membrane fouling (Aghdam et al., 2016; Park et al., 2017).

1.2.4 Reverse osmosis

In reverse osmosis process, high pressure is applied to pass the solvent through the membrane and most solutes are removed, mostly dissolved solids (Elimelech et al., 2011; Warsinger et al., 2018). The applied pressure is always higher than the osmotic pressure of feed to achieve desired separation by this process (Lee et al., 2010; Peñate et al., 2012). This process rejects mostly dissolved solids, organic molecules and viruses which are major contaminants in the wastewater. Microfiltration/Ultrafiltration are used for pre-treatment of feed before reverse osmosis to minimize the energy consumption as well as to improve membrane performance (Van Houtte et al., 2008). Reverse osmosis is commonly used in desalination of water and it can reject up to 99.5-99.8% of sodium chloride salt (Lee et al., 2011). Reverse osmosis provides complete rejection of pathogens due to sub-nanometer scale of RO membrane pores. Total organic compounds can be rejected up to 96% by RO and reduction in biological oxygen demand and chemical oxygen demand is reported 98% and 96% respectively (Rodriguez et al., 2009; Snyder et al., 2007; Tam et al., 2007).

Figure 1.2 shows different membrane separation process applicable for particular solutes on the basis of size and molecular weight cut-off (MWCO) and pore size range of different membrane processes (Warsinger et al., 2018).

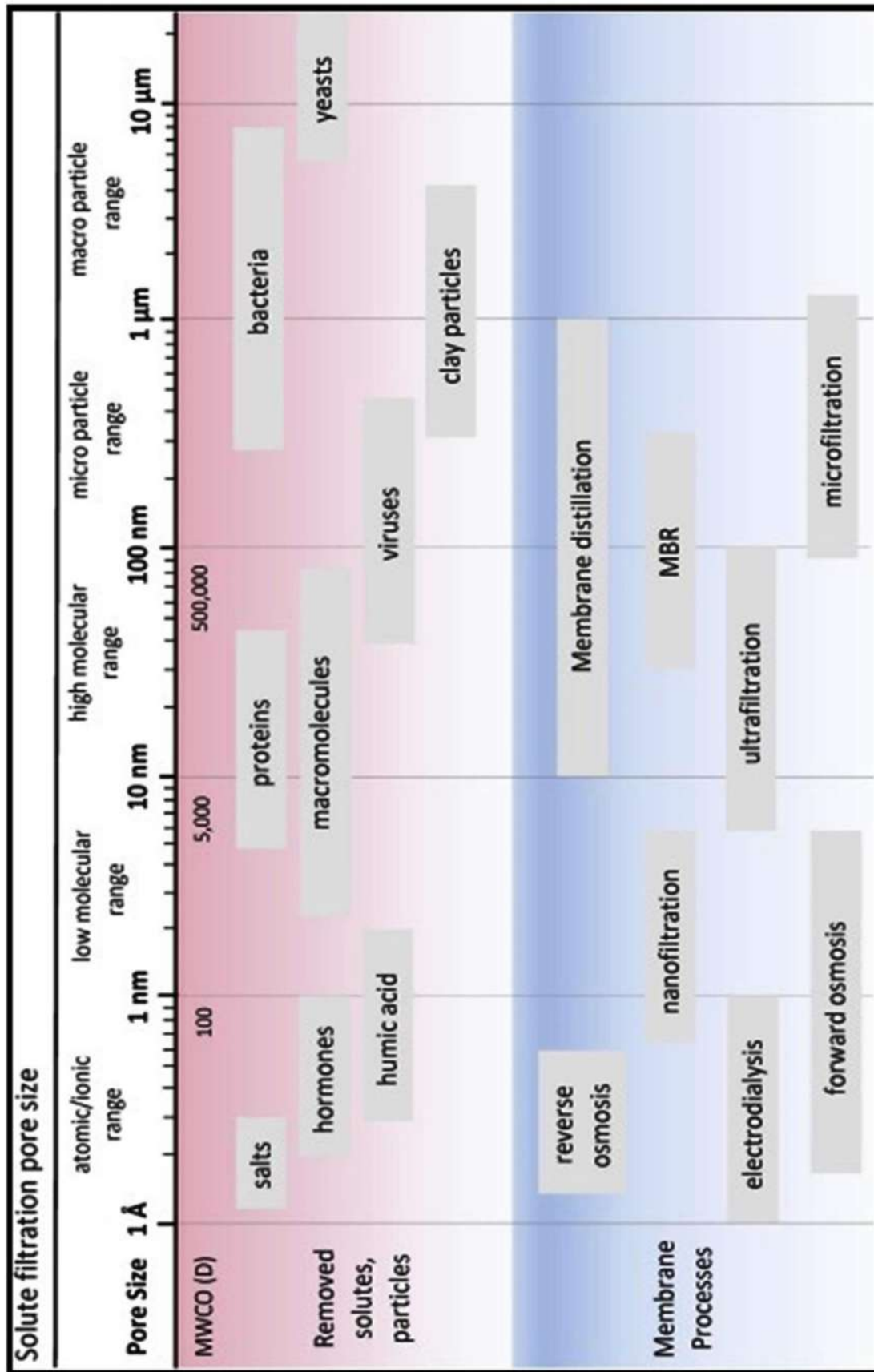


Figure 1.2: Membrane separation processes, pore sizes, molecular weight cut-off (MWCO) and examples of sizes of solutes and particles (Warsinger et al., 2018).

1.3 Membrane

Conventionally, membrane is defined as a selective barrier that separate two adjacent phases, allow transport of some ions, molecules, particle or components of feed and restricts the passage of various solutes in a selective manner. In other words, a membrane can be defined as a structure that has lateral dimensions much greater than its thickness, acts as a selective interphase to separate two phases, impedes the transport of variety of solutes and allows mass transfer through it under a certain driving force.

1.4 Factors affecting membrane performance

The performance of a membrane can be expressed in terms of separation efficiency, retention and permeability of membrane. Thus membrane structure, morphology, pore characteristics, Chemical resistance and mechanical properties of membrane material affect the membrane performance significantly. Some of the properties of the membranes that must be considered while selecting membranes for a particular application are described in the subsequent sections:

1.4.1 Pore size

The distance between two opposite walls of the pore is termed as pore size. Since pores in membrane structure are very irregular and do not carry a particular shape, the size of pore may not be uniform for entire pore structure. Pore structure is not uniform throughout the membrane. These can be slit-shaped between packed spheres or cylindrical voids. These pores can be blind pore, dead-end or through the membrane. Pore size is not same for whole membrane.

1.4.2 Permeability

The economic efficiency of a membrane is defined as fluid permeation through the membrane. Various factors such as porosity, pore size, tortuosity and membrane thickness affect the permeability of the liquid across the membrane. Since major resistance against fluid flow is due to the membrane, membrane is needed to be as thin as possible for maximum permeation across membrane. A support with higher pore size and good strength is provided on both sides of a thin membrane to provide sufficient strength to the membrane against the pressure created by feed side. Asymmetric structure of membrane pores supports the higher permeability.

1.4.3 Rejection

The rejection rate of a membrane is usually defined by testing the membrane performance on model solutes such as proteins, polyglycols or dextrans and expressed as molecular weight cut off.

The highest molecular weight, for which 90% particles are rejected by membrane is termed as molecular weight cut off. Numerous other factors such as temperature, pressure, cross flow fluid velocity, molecular shape of particles, membrane to particles interaction and fouling affects the rejection of membrane.

1.4.4 Mechanical properties

Mechanical properties such as tensile strength, elongation and modulus of elasticity of membrane are also very important parameters for consideration while selecting membrane material. Membranes should have enough strength to work under high pressure applied across the membrane for desired separation. Strength of membrane is depended on membrane material, porosity and synthesis procedure. Ceramic membranes have more advantage in strength than polymeric membranes. Therefore a

ceramic support is used with polymeric membrane for high-pressure application.

1.4.5 Chemical resistance

Membrane processes are applicable for separation of variety of solution/mixtures of different pH range. After filtration, membrane is back washed using corrosive chemicals. Chemical attack can affect the membrane structure and reduce strength, porosity, permeability, flux and overall performance. So it is very essential for a membrane to have strong chemical resistance to sustain in that environment.

1.5 Types of membranes

A wide diversity of membranes is being used for various industrial as well as domestic applications. Membranes are categorized on the basis of their pore structure, membrane cross-section, membrane material and shape. Membranes are either symmetric or asymmetric. These are also categorized as either porous or dense membranes based on cross-section. A large variety of materials are used for synthesis of membranes. These materials are either organic or inorganic in nature. So, membranes are also categorized on the basis of material as polymeric or ceramic membrane. Modular design of membrane is another criterion to categorize different membranes. Flat sheet membrane and spiral wound membrane are two types on the basis of membrane shape. Classification of membranes depending on different factors is briefly shown in figure 1.3.

However membranes may be categorized in numerous other ways. Still in general way these are identified as polymeric, ceramic or metallic membranes. As it is clear by the names that base material of polymeric membrane is polymer and inorganic ceramics for ceramic membranes.

Initially naturally found materials like cellulose, ethyl cellulose and cellulose acetate were used as base materials for preparation of membranes. These materials were easily available and economical also. But these materials have some limitations such as weak physiochemical properties like low chemical resistance, mechanical strength. To overcome these problems in recent years, researchers have focused on preparing membranes made of synthetic polymers which can sustain adverse environment and perform better for industrial and domestic applications (Hamid et al., 2011). Polymeric membranes have numerous advantages such as high selectivity for different solutes due to high range of physicochemical properties, easy pore-forming capacity, low cost and simple preparation methods. Apart from conventional uses these are now being used in some advanced applications like drug delivery development and whey protein fractionation (Bhattacharjee et al., 2006; Ng et al., 2013).

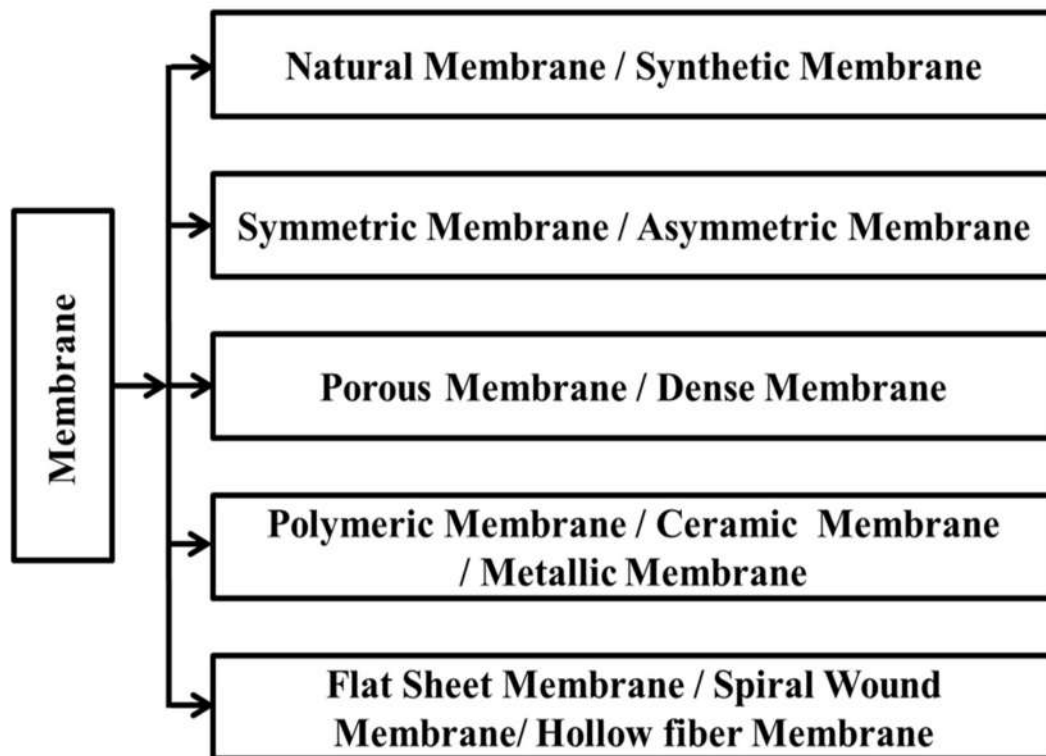


Figure 1.3: Classification of membranes

Polymeric membranes are abundantly used for majority of membrane processes because of a very large range of polymers of different properties are available for any particular application over last 2-3 decades and still presently, a lot of studies have been done by various researchers for synthesis of membranes with improved properties according to market demand, made of various polymers, such as cellulose acetate (Kim et al., 2019; Rajesha et al., 2019), polytetrafluoroethylene (Feng et al., 2018), polysulfone (Anadão et al., 2010; Kim et al., 2018b), polyacrylonitrile (Austria et al., 2019), polyethylene (Zuo et al., 2016), polyvinyl chloride (Behboudi et al., 2016; Farjami et al., 2019; Yong et al., 2019), polyethersulfone (Choudhury et al., 2019; Zhang et al., 2018) and polyvinylidene fluoride (Lee et al., 2019; Rosli et al., 2019). Polysulfone and polyethersulfone based polymeric membranes have attracted most interest for industrial and commercial applications because of their thermal stability and higher mechanical strength in comparison to other available polymers. However this material has a drawback of hydrophobicity which is a common reason of biofouling in membranes.

While polymeric membranes have been proved very suitable for variety of industrial applications, ceramic membranes are also in competition for commercial uses and have gained popularity in potable water reuse. Ceramic membranes are used in microfiltration/ultrafiltration processes as pre-treatment to decrease fouling in reverse osmosis membranes (Gray et al., 2015). Ceramic membranes are much more resistant to chemical attack, possess a good tolerance for wide pH range fluids, have very high mechanical strength and are thermally stable. Most important feature about ceramic membrane is that they have high resistance to chemical attack that can damage polymeric membranes (Mueller et al., 2010). Alumina is most common material for preparation of ceramic membranes and widely used for municipal water treatment (Lu et al., 2019). Other frequently used inorganic materials are zirconia oxide (Kujawa et

al., 2019), titanium oxide (Doke et al., 2014), zeolite (Luo et al., 2019) and silicon carbide (Li et al., 2019). These membranes are being used in various pore size ranges from microfiltration to nanofiltration for the treatment of secondary wastewater effluents (Farsi et al., 2015; Skluzacek et al., 2007). However ceramic membranes have disadvantage of high cost and lack the small pores size range which is required for pathogens removal and disinfection of potable water. So they are used as pre-treatment before reverse osmosis. Few researchers have studied the effects of hybrid membrane system by incorporating ceramic ultrafiltration membranes before polymeric reverse osmosis membranes and reported reduction in bio fouling (Kramer et al., 2015; Razmjou et al., 2012; Sayed et al., 2007). Another shortcoming of ceramic membranes is that the thickness of ceramic membranes is quite more than polymeric membranes. This thicker layer results in low flux across the membrane.

1.6 Filtration patterns

A target solvent/mixture, which needs to be separated, is fed from the feed side of the membrane. Membranes allow selective passage of fluid through it and exclude larger molecules. Fluid which pass through membrane is called permeates and particles which stay behind the membrane are known as retentate. Depending upon the direction of feed stream, there can be two types of membrane filtration process, dead-end filtration and cross-flow filtration or tangential flow filtration.

In dead-end filtration process, direction of feed is vertical to the membrane surface. In this type of filtration, retentate stay within the feed stream and creates a layer on membrane surface known as filter cake which reduces the filtration performance within some duration. This kind of filtration is a batch process and very suitable for low scale studies like lab experiments.

In cross-flow filtration process, feed travels tangentially across the membrane surface. This process works in a continuous mode and is used for large scale commercial-industrial applications. The main advantage of this process over dead-end filtration is that filter cake formed on membrane surface is continuously washed away in tangential direction during the filtration process. A schematic diagram is shown in figure 1.4 which depicts the working of both processes briefly.

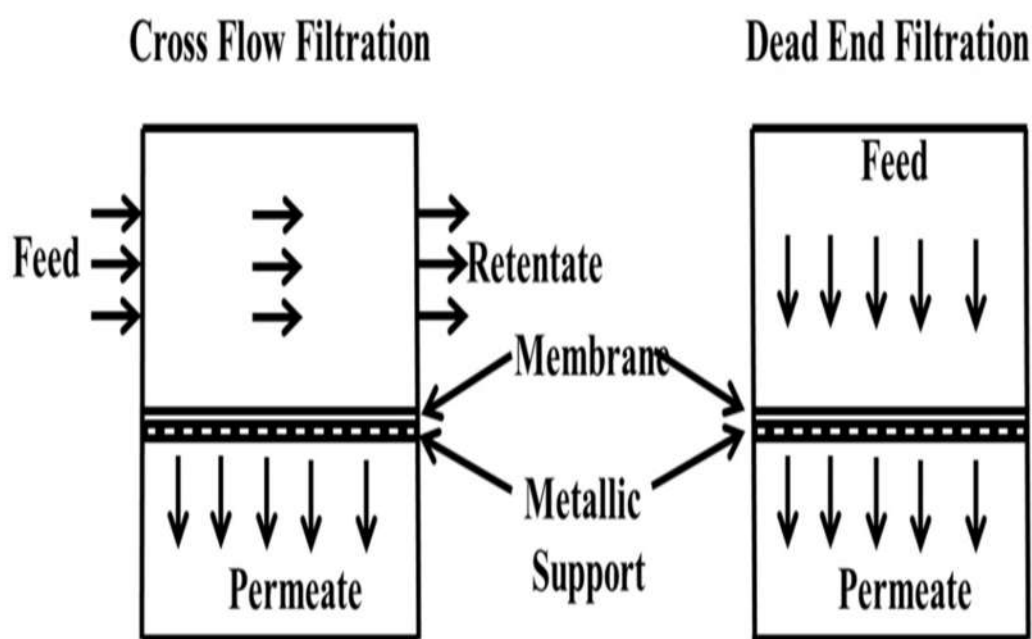


Figure 1.4: Schematic diagram of cross-flow filtration and dead-end filtration process

1.7 Synthesis of membranes

Various methods are available for synthesizing the membranes. These methods are selected depending on the membrane material and the application category (e.g. microfiltration to reverse osmosis). Phase inversion process and electrospinning are commonly used for preparation of membranes. Other methods are sintering, stretching, track etching and in-situ polymerization, dip coating, spray coating, layer-by-layer deposition and ion assisted deposition (Lalia et al., 2013b; Vrouwenvelder et al., 2009).

1.7.1 Phase inversion

Phase inversion is most common method among various available methods to synthesize membrane. This method is a de-mixing process which involves transformation of a homogenous polymer solution to the solid phase in a controlled environment. Phase inversion is also achieved in four different following ways: (Drioli et al., 2009; Mulder, 2012)

- ❖ Non-solvent induced phase separation (NIPS)/Immersion precipitation.
- ❖ Evaporation induced phase separation (EIPS)
- ❖ Thermally-induced phase separation
- ❖ Vapor induced phase separation (VIPS)

1.7.1.1 Non-solvent induced phase separation

This method involves three components viz. polymer, solvent and a non-solvent. A homogeneous polymer solution is prepared by dissolving polymer in the solvent and prepared solution is casted on a non-woven support. Then it is immersed in a non-solvent coagulation bath which is usually water. This results in penetration of solvent into non-solvent and penetration of non-solvent into the solution and this process continues till the equilibrium is attained. Finally two phases are evolved, one polymer-rich phase and other is liquid-rich phase. Polymer rich phase is membranes which possess asymmetric structure. Membrane is then dried and stored for further application. Membrane precipitates after immersing polymer solution to non-solvent. Therefore this method is also known as ‘immersion precipitation’ method. Factors that affect the structure and the pore size of the membrane prepared by this process are polymer concentration, solvent, non-solvent, type of additives and precipitation time (Baker, 2012). If polymer concentration is very high then the pore size and porosity decreases

and sponge-like structures are formed. While synthesizing membrane for ultrafiltration, polymer concentration should be in range of 12-20% and for reverse osmosis polymer concentration should be above 20% in casting solution (Baker, 2012). Solubility of polymer into solvent has also a significant effect on morphology of membrane. Higher solubility of polymer into solvent results in high porosity of membrane prepared. Sometimes few additives such as inorganic nanoparticles or high molecular weight organic materials such as polyvinyl pyrrolidone (PVP) or polyethylene glycol (PEG) are also added into the casting solution to improve morphology and physiochemical properties of the membrane (Chuang et al., 2000). Temperature of casting solution also affects the porosity of membrane. Researchers have done work on enhancement of rejection rate and water flux through membrane by optimizing these affecting factors while preparing membrane by immersion precipitation method (Mohammadi et al., 2009). A simple representation of immersion precipitation method is briefly shown in figure 1.5.

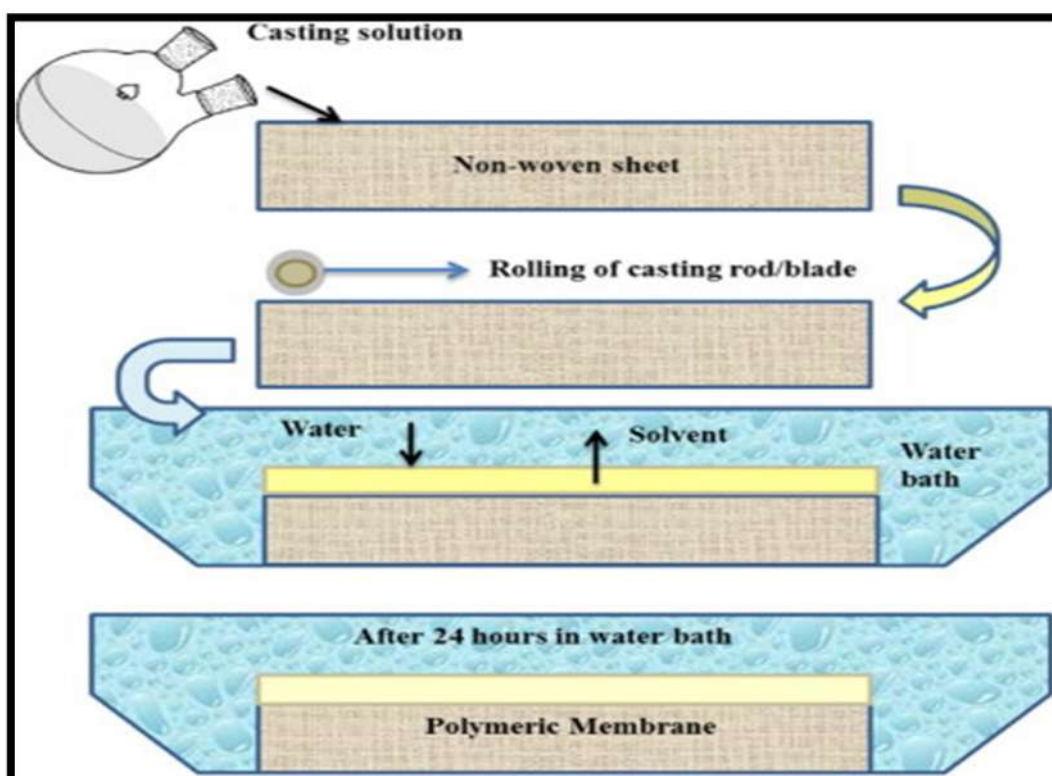


Figure 1.5: Membrane preparation by NIPS method (Jhaveri et al., 2016)

1.7.1.2 Evaporation induced phase separation

This process also involves three key components, polymer, solvent or mixture of solvent and non-solvent but non-solvent in this method is volatile in nature. This is simplest technique to prepare membrane by phase inversion method. After the preparation of homogenous polymer solution, it is casted on nonwoven support. Solvent evaporates into the environment and thin polymer film is prepared. This method is also known as solution casting method. Different boiling point solvents can be used in this method to control the morphology of the membrane. Effect of solvents of different boiling point on pore shape, size and surface morphology of membrane prepared by EIPS method has been reported by researchers (Nguyen et al., 2010; Zhao et al., 2013).

1.7.1.3 Thermally induced phase separation

In this method, polymer is dissolved in the solvent at high temperature and then resulting solution is casted on the non- woven support and allowed to dry. As the temperature decreases, solidification occurs and membrane is formed. This method has advantages of easy processing, high reproducibility, low defects and high porosity (Pinnau et al., 2000).

1.7.1.4 Vapor induced phase separation

In this method, after casting the polymer solution on support, it is placed in the environment that is saturated with non-solvent in vapor form. This enhances the evaporation of solvent and de-mixing process occurs. At equilibrium a thin film is formed.

1.7.2 Stretching

Stretching is the techniques usually employed for making microporous membranes for microfiltration and ultrafiltration. There is no solvent used in this method unlike phase inversion method. The polymer is heated to higher temperature beyond its melting point and then thin sheets are created through extrusion and later these are stretched to create porosity. This method is very suitable for making membranes from crystalline materials that possess amorphous area to provide porosity and crystalline are to provide strength to membrane structure. There are two variants of stretch known as cold stretching and hot stretching (Zhu et al., 1996).

Cold stretching results in creation of micropores while hot stretching supports to enhance porosity of membrane. However other properties of membrane material like melting point, tensile strength, crystallinity also affect the porous structure of the membrane. Researchers have examined the influence of various physical and chemical properties of membrane material on permeation and morphology of membranes fabricated through stretching method (Sadeghi et al., 2007, 2008; Sadeghi et al., 2009). The molecular weight of polymer is also a deciding factor for controlling membrane properties. Higher molecular weight supports the creation of well-distributed, uniform and better-connected pores. Effect of annealing before stretching on pores has also been reported in literature (Kim et al., 2008).

1.7.3 Track-etching

In membrane preparation by track-etching, a dense polymeric film is exposed to radiation which forms the linear tracks on the irradiated part of polymeric film. This method provides a very controlled pore size distribution across the membrane. Pore size and density are not dependent to each other and they can be in a controlled range or μm to few nm. Major factor which decide the porosity is time duration of radiation.

Membranes created by track-etching have low porosity and this method is used for the applications where very precise pore distribution is required (Apel, 2001; Kim et al., 2018a).

1.7.4 Electro-spinning

Electrospinning is a process of fabricating particles and fibers from a polymeric solution under high voltage as driving force. The size range of these fibers remains between micro to nano meter in diameter. This technique consists of a reservoir of polymeric solution which mounted with a blunt needle, connected with a pump and a high voltage power source and a collector. This technique is relatively new for fabrication of fibrous porous membranes. It provides formation of fibers with multiple morphological structures. Some common application of electrospinning is in the area of tissue engineering, food encapsulation, air and water filtration and others. The morphology of such created membranes depends on the electric voltage applied, solution flow rate, polymer molecular weight, viscosity of polymeric solution and the environment in which the membrane is being prepared (Lalia et al., 2013a; Prince et al., 2012). The fiber shape, size, surface morphology, pore size distribution, porosity and hydrophobicity can be controlled by optimizing these parameters. Adding some additive like sodium chloride salt can be very useful in controlling fiber diameter (Feng et al., 2008; Wang et al., 2019).

Based on available literature (Bassyouni et al., 2019; Liao et al., 2018), the advantages and disadvantages of membrane fabricating methods are summarized in table 1.1.

Table 1.1: Advantages and disadvantages of various membrane synthesis methods (Bassyouni et al., 2019)

Membrane Synthesis Methods	Advantages	Disadvantages/ Limitations
Phase Inversion	<ul style="list-style-type: none"> • Can be used for a wide variety of polymers • Can fabricate flat-sheet and tubular membranes • Simple to prepare and easy to scale up • Fast yield speed • Easy to optimize membrane thickness and pore size • High porosity of around 80% • Form small surface pores and large bulk pores naturally 	<ul style="list-style-type: none"> • The polymer must be soluble in a solvent or solvent mixtures
Track-etch Method	<ul style="list-style-type: none"> • Prepares symmetric membranes with mean pore sizes between 0.02 and 10 μm • Narrow pore size distribution • Cylindrical pores 	<ul style="list-style-type: none"> • Limited to suitable polymers • Low porosity 10% • High cost
Stretching	<ul style="list-style-type: none"> • Prepares symmetric membranes with mean pore sizes between 0.1 and 3 μm • Ladder like slits Porosity between 60% to 80% • Can use chemically stable materials such as PTFE, PE, polypropylene (PP) and ceramics 	<ul style="list-style-type: none"> • Needs high operational temperature

<p style="text-align: center;">Electro spinning</p>	<ul style="list-style-type: none"> • High level of versatility allow controls over nanofiber diameter, microstructure and arrangement • Vast material selection Easy to incorporate additives in nanofibers • Membranes with high porosity above 90% and high surface-to-volume ratio • One-step and straight process • Practicability in generating nanostructures, including core-sheath, Janus, tri-layer nanofibers 	<ul style="list-style-type: none"> • Hard to obtain nanofibers with diameters below 100 nm • Hard to obtain ENMs with maximum pore sizes smaller than 100 nm • Slow yield speed
<p style="text-align: center;">Template leaching</p>	<ul style="list-style-type: none"> • Prepare symmetric membrane with pore size between 0.5 and 10 μm • Extremely narrow pore size distribution • High flux 	<ul style="list-style-type: none"> • Hard to achieve nano pores • High cost • Difficult to scale up • Complex procedures
<p style="text-align: center;">Sintering</p>	<ul style="list-style-type: none"> • Prepare symmetric membranes with mean pore size between 0.1 and 10 μm • Suitable for chemically stable materials such as polytetrafluoroethylene (PTFE), polyethylene (PE), metals and ceramics • Solvents are not required 	<ul style="list-style-type: none"> • Requires particles with narrow size distribution • Hard to achieve pores below 100 nm • Low porosity: 10–20% • Needs high operational temperature

1.8 Membrane Fouling

Membrane separation process are gaining high importance in various industrial applications such as chemical, pharmaceutical and food industries as well as effluent treatment plants and water treatment due to their advantages of easy and simple mechanism, continuous operation, low energy requirement for separation, operational flexibility, a broad range of separation of solutes of different size from meso to nano range and high selectivity of membrane material for desired application (Baker, 2012; Lee et al., 2016; Strathman et al., 2006). Still, these separation processes have some limitations also. The major limitation is membrane fouling. Fouling is a phenomenon of deposition or adsorption of solute particles on the membrane surface as well as within the pores during the separation. This process not only decreases the membrane performance but also increases the resistance to the separation process. It results in lowering of permeation flux, separability of membrane, rejection rate, increase the energy requirement for separation and decrease the membrane life (Antony et al., 2012). Fouling is classified in different types on the basis of nature of solutes in feed solution to be filtered. When the fouling is caused by biological constituents such as microbial cells present in feed solution, then it is called biofouling (Drioli et al., 2010). In contrast if the foulant particles are of colloidal nature then fouling is known as colloidal fouling (Rana et al., 2010). During filtration, solute particles are rejected by the membrane and they start collecting on feed side. This result in a cake layer formation on the membrane surface of feed side and blocks the pores. This phenomenon of cake formation is known as concentration polarization. Inorganic fouling caused by salts is also termed as mineral scaling while organic fouling is caused by organic matter present in feed (Guo et al., 2012; Kochkodan et al., 2015).

For a membrane, total fouling is summation of reversible/temporary fouling and irreversible/permanent fouling. Decrease in membrane performance due to reversible fouling can be mechanically restored by regular back-washing or chemical cleaning of membrane. In general, cleaning frequency is once per day to per month depending upon the requirement and it is cleaned every 30 min for large scale applications (Peter-Varbanets et al., 2009). Polymeric membranes are less tolerant to chemicals than ceramic membranes (Porcelli et al., 2010). Some organic foulants have a tendency of attraction for hydrophobic surfaces and these are adsorbed on to the surface as well within the pore walls and causes irreversible or permanent fouling. Therefore, irreversible fouling can not be restored but it can be minimized by modifying the techniques used for the fabrication of membranes. However, partial performance of membrane can be restored by backwashing steps but it leads to operation shut down for maintenance (Madaeni et al., 2007; Wu et al., 2008). Major factors that are responsible for fouling are membrane material (physicochemical properties of membrane material); feed conditions (composition, pH, and concentration) and feed pre-treatment condition (Esfahani et al., 2019; Rana et al., 2010).

In general, the strong hydrophilicity of membrane surface is desirable to minimize the membrane fouling caused by the adsorption of soluble nature organic matters and microorganisms but hydrophilic polymers polyvinyl alcohol, polyacrylic acid, chitosan etc. lack the required mechanical properties, thermal stability and chemical resistance, which are urgently required to increase the lifespan of membrane during backwashing or air flushing for membrane regeneration once the fouling occurs. In contrast, polymers which have high thermal stability, good mechanical strength and high chemical resistance are hydrophobic in nature. Therefore, increase in the hydrophilicity and mechanical property for the membrane is of major concern for its potential practical

application in the desired industrial or municipal areas (Drioli et al., 2009; Fane et al., 1987; Le-Clech et al., 2006).

Typically following measures are adopted to mitigate membrane fouling:

- Feed Pre-treatment
- Optimization of operating conditions
- Membrane modification to enhance physical and chemical properties of membrane material

Membrane modification techniques are of two types, 2 dimensional and 3-dimensional modifications. 2-dimensional techniques are surface coating, surface bio-adhesion and surface grafting using surface modifiers either organic molecules or inorganic nanomaterials. 3-dimensional technique is physical blending of modifiers to base polymer with surface segregation (Zhang et al., 2016). Different types of modifiers, which are compatible with base polymer material for membrane, are blended with membrane matrix during membrane preparation to improve anti-fouling properties in surface segregation method. These modifiers are of different categories and used for enhancement of specific property of membrane to improve overall membrane performance. For example, pore-forming materials such as polyvinyl pyrrolidone, polyacrylic acid or polyethylene glycol are added to improve porosity of the membrane. These pore-forming agents are leached out from the solution during the phase inversion and create porous structure within membrane. Cross-linking agents such as tetra ethoxy silane, urea or glutaraldehyde are used for internal cross-linking of polymer material present in casting solution and improves their strength and insolubility. Inorganic nanoparticles such as alumina, titania, zirconia or silica for the enhancement of hydrophilicity, chemical resistance and mechanical strength.

Various researchers have used the above techniques to prepare porous polymeric mix matrix membranes by modification of hydrophobic polymers like polyvinyl chloride, polyvinylidene fluoride, polyethersulfone and polysulfone using many different nanomaterials to investigate their effect on antifouling properties and performance of the membrane. Thus prepared composite polymeric membranes have shown improved performance as compared to pure polymer membranes. Incorporation of these nanomaterials increases pore structure, higher hydrophilicity, surface morphology, strength which in turn results in better performance and antifouling nature of membrane (Huang et al., 2012; Jafarzadeh et al., 2015; Maximous et al., 2009; Saleh et al., 2012; Shokri et al., 2016; Wu et al., 2015; Zhang et al., 2011).