Chapter 2. Literature survey

This chapter presents significant literature on various methods used for UF membrane preparation, factors affecting membrane performance and stability. Fouling, concentration polarization, compaction, interactions of solutes with membrane material, etc. are discussed with this respect. The literature on effects of membrane preparation parameters and chemical modification of membrane (leading to the variation in membrane performance in terms of flux, rejection and pore morphology) will be discussed in Chapters 3 and 4, respectively. The literature on solvent/thermal resistant membranes and poly(benzimidazole) (PBI) as a membrane material is discussed in Chapter 5.

2.1. UF membrane preparation

There are various methods known for the synthesis of porous membranes. The significant methods are sintering, stretching, track-etching, phase inversion, sol-gel process, vapor deposition and solution coating [Agoudjil (2007), Awasthi (2006), Apel (2001), Machado (1999), Mulder (1998), Zeman (1996)]. Sintering is a technique that allows porous membrane preparation using organic as well as inorganic materials. The obtained pore size is in the range of 0.1 to 10 μm. Only microfiltration membranes can be conveniently prepared by this method. In stretching method, partially crystalline polymeric materials such as poly(tetrafluoroethylene), poly(propylene), poly(ethylene), etc. are used [Bottino (2005), Mulder (1998)]. The pore size of these membranes is in the range of 0.1 to 3 μm, which also falls in the microfiltration range.

The track-etching and phase inversion methods are used mainly for UF membrane preparation. In track-etching technique, choice of the polymer depends mainly on its thermal and chemical resistance as the polymer film is subjected to high energy (0.3 - 1MeV/particle) radiation, usually applied perpendicular to the surface of the film [Zeman (1996)]. Poly(carbonate), poly(imide), poly(ethylene terephthalate) are mainly used for the preparation of track-eched membranes [Awasthi (2006), Apel (2001), Mulder (1998), Yamazaki (1996), Vilenskij (1994)]. Such membranes show pore size in the range of 0.02

to 10 μm. The parallel cylindrically shaped pores of uniform dimension can be obtained by this technique. Because of this simple and directly measurable pore geometry, track etched fibers have been used extensively in the basic research dealing with the solvent and solute convective and diffusive transport through membranes [Zeman (1996)]. These membranes have found specific applications in analytical chemistry, microbiology, medical diagnostic cytology [Matteson (1987)]. In electronics, polyimide is well known polymer and its track etched membranes are used to foresee ultraprecise separation under extreme temperature or chemical conditions. The main drawback of these membranes are the limited high energy particle penetration depth, low porosity (~ 10%) and polymer used should be thermally stable [Zeman (1996)]. Most commercially used UF membranes are obtained by phase inversion method [Mulder (1998)]. This is a versatile technique allowing almost all kinds of morphologies to be obtained and is described in more details in the following section.

2.1.1. Phase inversion method

In phase inversion process, polymer solution prepared using appropriate solvent is transformed in a controlled manner from a liquid to a solid state through gelation and precipitation. Phase inversion membranes can be prepared from a wide variety of polymers. The only requirement is that the polymer must be soluble in a solvent or a solvent mixture. The process of solidification is very often initiated by the transition from one liquid state (solution) into two liquids (liquid-liquid demixing). At a certain stage during demixing, one of the liquid phases (the higher polymer concentration phase) solidifies so that a solid matrix is formed. By controlling the initial stage of phase transition, the membrane morphology can be controlled. Membranes made by phase inversion usually have a very thin, selective top layer and a much thicker porous support [Boom (1993)]. The concept of the phase inversion covers a range of different techniques such as, nonsolvent (typically water) induced phase separation or immersion precipitation, vapour induced phase separation, solvent evaporation induced phase separation and thermally induced phase separation; which are elaborated in following sections.

2.1.1.1. Immersion precipitation

Immersion casting is probably the most widespread technology for manufacturing UF membranes [Zeman (1996)]. In this technique, a polymer solution is cast on a suitable support and immersed in a coagulation bath containing a nonsolvent. The immersion induces an exchange of solvent and nonsolvent between the coagulation bath and the polymer solution [Reuvers (1987)] by diffusion and convection. The membrane structure is formed as a result of combined effects of mass transfer and phase separation [Mulder (1998)]. The membrane is characterized by a flimsy top layer, commonly recognized as the selective layer that serves as control function during separation processes, and underneath a porous solid matrix. The flimsy skin layer provides a major resistance to the permeation of solute through the asymmetric membrane, whereas the porous solid matrix acts exclusively as mechanical support [Feng (2006)].

The pore size and its distribution of a membrane is mainly controlled by the kinetic effects. This means, it depends upon the immersion of polymer solution into a coagulation bath, where mass transfer mainly determines the asymmetric structure of the membrane [Kang (1991)]. The mass transfer is normally expressed by the exchange rate of solvent/nonsolvent at the interface between the polymer solution and the gelation medium. This exchange rate depends upon the nonsolvent tolerance of the polymer solution, solvent viscosity, etc. [Kang (1991)]. Two different structures such as finger-like and sponge-like could be obtained, depending on the rate of precipitation. Low precipitation rates produce membranes mainly with sponge-like structures [Strathmann (1975)].

2.1.1.2. Vapour induced phase separation

A cast film, consisting of a polymer and a solvent is placed in a vapor atmosphere where the vapor phase consists of a nonsolvent saturated with the same solvent. The high solvent concentration in the vapor phase prevents evaporation of the solvent from the cast film. The pore formation occurs because of the penetration (diffusion) of the nonsolvent into the cast film [Strathmann (1975)]. The extent and rate of nonsolevnt (water) transfer can be controlled by adjusting the velocity, relative humidity and temperature of the air as well as the exposure time [Khare (2005)]. The mechanism of pore formation in

poly(etherimide) (PEI) films exposed to humid air was studied [Menut (2003)], Caquineau (2003)]. The film cross-sections showed an asymmetric morphology, with large cells close to the film/air interface, and a decreasing cell size away from this interface.

2.1.1.3. Solvent evaporation induced phase separation

In this case of phase inversion method, the polymer is dissolved in a mixture of solvent and nonsolvent (the mixture acts as a solvent for polymer). Since the solvent is more volatile than nonsolvent, the composition shifts during evaporation to a higher nonsolvent and polymer content. Because of this, polymer precipitation takes place and a skinned membrane is formed [Mulder (1998)].

2.1.1.4. Thermally induced phase separation

The thermally induced phase separation process (TIPS) is based on the phenomenon that the solvent quality decreases when the temperature is decreased. Thus, upon removal of the thermal energy by cooling or quenching a polymer-diluent solution, phase separation occurs [Matsuyama (2000)]. After the phase separation, the diluent is removed, typically by solvent extraction and the extractant is evaporated to yield a microporous structure. A controlled evaporation of the solvent allows the formation of skinned membrane. Typically, the TIPS process has been used to produce isotropic structures; that is, the pore size does not vary with direction in the membrane. A few studies have reported on the formation of anisotropic and asymmetric membranes by the TIPS process [Matsuyama (1998, 1999, 2000) Caneba (1985), Lloyd (1988)]. TIPS cast membrane can be extruded in a variety of forms and shapes, including tubes and hollow fibers [Zeman (1996)]. Commercially available poly(tetrafluoroethylene) (PTFE) membrane and poly(propylene) (PP) membrane, usually produced using stretching or thermal method [Chlubek (1992), Casttro (1981)].

2.2. Factors affecting membrane performance and stability

The membrane performance depends mainly upon porosity, surface properties and operating parameters. Flux and selectivity are the major membrane properties, which are

governed by various preparation parameters like choice of solvent nonsolvent system, nature of polymer and its concentration in the dope solution, temperature of coagulation bath, composition of polymer solution, use of additives and evaporation rate. Effects of these parameters are discussed in more details in Chapter 3 (Section 3.1). The membrane performance is affected by the properties of the solution to be treated such as pH, ionic strength, viscosity and concentration. The operational parameters like temperature and pressure also severely affects the membrane performance and its stability. The pH and ionic strength of the solution affects the conformation and shape of the solute molecule which, in turn, affects the rejection. Increase in temperature results in higher flux due to lowering of solution viscosity and increasing diffusivity [Cheyan (1996)]. This phenomenon can be useful to enhance the separation of proteins. High ionic strength can shield the ionic interactions. The solute membrane interaction leads to physical adsorption of solutes on the membrane surface and the pore walls. The hydrophobic membranes foul rapidly during macromolecular solute separation. In such cases, membrane surface chemistry plays an important role to enhance performance of UF membrane [Reddy (2008), Hilal (2005)]. The operation of membrane at higher pressure leads to the compression across the thickness, known as compaction, which leads to decline in the flux. The effects of some of these parameters on membrane stability are discussed below.

2.2.1. Concentration polarization

Concentration polarization is a phenomenon in which, the solute rejected by the membrane builds up at its surface. It is more pronounced at higher pressure and lower velocities. The concentration at the surface can be determined by the balance between solute brought to the membrane surface by convective flow of the solvent and that, which back-diffuses to the bulk. The result of concentration polarization shows higher feed side concentration resulting in reduced flux as well as reduced apparent rejection [Kulkarni (1992)]. Concentration polarization leads to smaller incremental increase in flux as pressure is increased until a gel layer is formed, at which point the flux shows no further increase with pressure. The flux at this point is called as the "limiting flux". Concentration polarization is dependent on operating parameters such as pressure,

temperature, feed concentration, and velocity; but is not a function of time [Kulkarni (1992)]. One of the ways to control this phenomenon is by manipulating operational parameters such as increasing shear at the membrane surface or by the use of turbulence inducers. Increased shear is obtained by pumping the feed at higher flow rates or by using thin flow channels above the membrane surface [Winzeler (1993)].

2.2.2. Membrane fouling

Fouling phenomenon is observed due to solute accumulation at the membrane-solution interface and solute adsorption onto membrane pores [Mulder (1998), Fane (1987)]. In fouling, the solute may be deposited within the membrane pores as a consequence of factors such as pore geometry/tortuosity or solute/pore wall interactions. Due to this, the pores may be effectively reduced in diameter or completely blocked. This leads to the reduction in flux through the membrane, while the rejection of solute may be either constant or may increase. Fouling is dependent mainly on physical and chemical parameters such as feed concentration, temperature, pH, ionic strength and specific interactions (hydrogen bonding, dipole-dipole interactions) [Mulder (1998)]. The rate and the extent of fouling depend on the strength of the membrane-solute interactions, together with the hydrodynamic forces acting on the macrosolutes and the chemical nature of the membrane [Zeman (1996), Cheryan (1986)]. Therefore, surface chemistry, solute-solute and solute-membrane interactions are key parameters in fouling. It is known to be a time dependent phenomena [Kulkarni (1992)]. The type of separation problem and the type of membrane used in these processes determine the extent of fouling. Roughly, three types of foulant can be distinguished, organic precipitates (macromolecules, biological substances, etc.), inorganic precipitates (metal hydroxides, calcium salts, etc.) and particulates.

Fouling due to biological substances results in the formation of biofilms on membrane surfaces. Once bacteria get attached to the membrane surface, they start to multiply and produce extracellular polymetric substances (EPS) to form a viscous, slimy hydrated gel. EPS typically consists of heteropolysaccharides and have high negative charge density. This gel structure protects bacterial cells from hydraulic shearing and from chemical attacks of biocides such as chlorine [Liu (2008)]. The most important

identified foulants found in surface water filtration is natural organic matters (NOM). Surface water (lake, river) typically contains higher NOM than ground water. For source water high in NOM, organic fouling is believed to be the most significant factor contributed to flux decline [Mallevialle (1989), Lahoussine-Turcaud (1990), Lee (2008)]. The labile nature and complex structure of biological foulant such as proteins have been characterized via monitoring decline in the flux and observation of rejection changes [Chan (2004)]. Inorganic fouling or scaling is caused by the accumulation of inorganic precipitates such as metal hydroxides, and "scales" on membrane surface or within pore structure. Precipitates are formed when the concentration of chemical species exceeds their saturation concentrations.

Membrane fouling is generally irreversible by physical means, though its effect can be reduced by various techniques. It can be reduced by optimizing membrane surface chemistry and solution environment. Increasing the hydrophilicity of the membrane surface can reduce fouling and improve biocompatibility for the membranes [Reddy (2008), Zhu (2007), Pieracci (2002), Zeman (1986)]. Internal fouling which includes solute adsorption on the pore walls can be reduced by back flushing the membranes and membrane cleaning. Membrane cleaning can be done by following four methods.

2.2.2.1. Hydraulic cleaning

This can be done by backflushing the membrane by periodically reversing the flow direction or by using pulsatile flow. Liang et al. (2008) compared four kinds of hydraulic cleaning methods for algae-fouled UF membrane. These methods were forward flushing, backwashing, forward flushing followed by backwashing and backwashing followed by forward flushing for removal of algae from water. Backwashing followed by forward flushing was more effective, which showed 80% flux recovery within 20 min. time duration. Breslau et al. (1975) obtained 90% flux recovery after a city water ultrafiltration when the membrane was backflushed with 1% chlorine solution. Urbain et al. (1996) obtained only 8% flux recovery by backwashing twice an hour, coupled with chlorination once in a day. Shon et al. (2007) achieved 14.8% net productivity of membrane during waste water treatment by following periodic relaxation step and/or a periodic increased cross flow rate at a decreased pressure protocol.

2.2.2.2. Chemical cleaning

It is the most important method to reduce the fouling with a number of chemicals being used separately or in combination. The concentration of the chemicals and the cleaning time are important parameters. The use of an inappropriate cleaning agent could adversely affect performance of the membrane [Weis (2003)]. The selected materials should be chemically stable, safe, cheap and washable with water. They must also be able to dissolve most of the precipitated materials on the surface without damaging the surface [Lindau (1994), Kim (1993)]. Chemicals commonly used for cleaning UF membranes in water industry fall into five categories, caustic, oxidants/disinfectants, acids, chelating agents and surfactants [Liu (2008)]. Caustic is typically used to clean membranes fouled by organic and microbial foulants. The function of caustic is two-fold: (1) hydrolysis and (2) solubilization. There are a number of organic materials including polysaccharides and proteins can be hydrolyzed by caustic. A very important function of caustic is to increase negative charges of humic substances. Therefore, they are easier to be removed from membranes [Liu (2008)].

Another type of chemical cleaning agents is oxidants, which include chlorine and hydrogen peroxide. The oxidation of organic polymers generates more oxygen containing functional groups such as ketone, aldehyde and carboxylic acids. Existence of these functional groups generally increases hydrophilicity of their parent compounds [Liu (2008)].

Acids are also used primarily for removing scales and metal dioxides from fouling layers. When membrane is fouled by iron oxides, citric acid is very effective because it not only dissolves iron oxides precipitates, but also forms complex with iron. The removal of divalent cations by either acids or chelating reagent such as EDTA can also improve the cleaning of membranes fouled by organic foulants [Hong (1997)].

Surfactants are compounds that have both hydrophilic and hydrophobic structures. They can form micelles with fat, oil and proteins in water and help to clean the membranes fouled by these materials [Hilal (2005)]. Some surfactants may also interfere hydrophobic interactions between bacteria and membranes [Rosenberg (1990, Ridgway (1985, 1988), Paul (1984)]. In addition, surfactants can disrupt functions of bacteria cell walls. Therefore, surfactants affect fouling dominated by the formation of biofilms.

2.2.2.3. Mechanical cleaning

Some foulants can be effectively removed from the membrane surface by mechanical means. Effects of operating parameters such as turbulence promoters, increased flow rates, mixers, backflushing, pulsing, backflushing, high shear, pulsatile and reversal flow, vortex generation, gas sparging, force fields, ozonation, etc. are reviewed by Hilal et al. (2005). Transmembrane pressure pulsing is variation of backflushing [Redkar (1995), Rodgers (1993)]. Backflushing can be applied to hollow fiber and flat sheet membrane with appropriate feed channel spacers [Zeman (1996)], while tubular membranes can be cleaned by using oversized sponge balls to physically wipe away the foulant layer [Mulder (1998)]. The use of pulsed electric fields for physical cleaning to release filter cakes is also a demonstrated technique [Sarkar (2008), Oussedik (2000), Robinson (1993)].

2.2.2.4. Electrical cleaning

By applying an electric field across a membrane at certain time intervals, charged particles or molecules would migrate in the direction of electric field. A drawback of this method is the requirement to use electric conducting membranes and a special module arrangement with electrodes. A tubular geometry filter leads to the most effective use of electrical power to prevent fouling [Wakeman (1987)]. It was reported that in situ intermittent electrolytic membrane cleaning (IIEMC) or intermittent electric field pulses could effectively clean pores as well as remove filtration cakes [Bowen (1989)]. As reported by Zumbusch et al. (1998), an alternating electric field diminished the membrane fouling and increased the specific filtrate flux. Tarazaga et al. (2006) investigated that the electric field is potentially good cleaning strategy to decrease the fouling during ultrafiltration of bovine plasma.

2.2.2.5. Different techniques of foulant analysis

Qualitative information on foulant morphology of different proteins can be provided by different techniques such as scanning electron microscope (SEM) imaging [Schossig-Tiedemann (2001), Bache (1998), Lee (1975), Glover (1974)], energy dispersive X-ray spectroscopy (EDX) [Bansal (1991)], protein stripping, transmission

electron miscroscopy (TEM) [Ratner (1996), Sheldon (1991)], matrix-assisted laser desorption ionisation mass spectrometry (MALDI-MS) [Chan (2002)], radio labeling [Matthiasson (1983)], electron microscopy for chemical analysis (ESCA or XPS) [Ratner (1996)], attenuated total reflection-Fourier transform infrared spectroscopy (FTIR-ATR) [Campbell (1999), Ratner (1996)], UV spectrophotometry [Reisterer (1993)], electron paramagnetic resonance spectroscopy (EPRS), small angle neutron scattering (SANS), ellipsometry [Chan (2004)], confocal microscopy [Reichert (2002)], atomic force microscopy (AFM) [Chan (2004), Ducker (1991)], etc.

2.2.3. Membrane compaction

Membrane compaction is the mechanical deformation of a membrane matrix which occurs in pressure-driven membrane operations such as reverse osmosis, ultrafiltration, nanofiltration, microfiltration, etc. [Mulder (1998)]. During these processes, the porous structure densifies and as a result, the flux decline occurs. After relaxation (effected by reducing the pressure), the flux generally does not return to its original value since the deformation process is often irreversible. In ultrafiltration, compaction may occur as well, and the extent depends on the pressure employed and membrane morphology. The compaction provided a dominant contribution to the observed flux decline below 400 kPa during ultrafiltration of cottage cheese whey [Tarnawski (1986)]. There are various methods to determine compaction pressure of the membrane. Persson et al. (1995) studied the compaction phenonmenon statically as well as hydrostatically. In static method, the membranes were precompressed in a hydraulic press either in wet or dry condition. In another method, the membrane were compressed hydrostatically in the membrane module by increasing pressure step wise and the pure water flux was measured as a function of time. Arthanareeswaran et al. (2004) and Vidya et al. (2008) studied membrane compaction by compressing membrane at 414 kPa pressure for certain duration and water flux was measured with an interval of an hour. Bohonak et al. (2005) observed compaction of hydrophilized poly(vinylidene fluoride) (PVDF) membrane with the skin-side down, which resulted in a 10-20% reduction in permeability.

2.2.4. Interaction of solute with membrane material

Membrane fouling is a complicated phenomenon which severely affects the membrane flux and selectivity. It occurs mainly due to the interactions between fouling materials and membrane or between fouling materials themselves. It is known that if the membrane is hydrophilic and charged with the same type of charge as the molecules in solution, it is less apt to be fouled [Brink (1990), Gekas (1990), Golander (1988)]. High charge densities keep the molecules away from each other and from the membrane and also retention is usually increased. If proper charge conditions are not naturally fulfilled, membranes can be modified with hydrophilic, charged polymers or the solution conditions can be changed to a pH; which increases the absolute charges of the membrane material or of the molecules in the solution [Nystrom (1991), Kim (1988)]. It has been recognized that electrostatic interactions and hydrophobic/hydrophilic interactions between membranes and fouling materials have a significant bearing on membrane fouling.

2.2.4.1. Electrostatic interactions

Surface charge of membrane is the result of ionization of particular functional groups existed on the membrane surface (e.g., carboxyl and amine). Because ionization of a functional group depends on pH, surface charge of a particular membrane is also pH-dependent. In pH range of typical natural waters, most membranes appear to have a neutral to negative net surface charge. On the other hand, colloids, particles and dissolved organic matters typically carry negative charges at the pH of natural water. Therefore, there is a tendency of electrostatic repulsion between membranes and these constituents. Conditions other than pH may also affect the interactions between fouling materials and membranes. For example, high ion strength of a solution can compress "double electric layer" of colloids, which could reduce their repulsion to negatively charged membranes [Liu (2008)]. Another example is divalent cations, which can act as "salt bridge" between a negatively charged membrane and other negatively charged species in the fluid by charge neutralization. The electrostatic interaction between the charged membrane surface and charged NOM acids can increase the NOM rejection [Cho (2000)].

2.2.4.2. Hydrophobic interactions

The hydrophobic fraction of NOM has been specifically identified as the primary membrane foulant [Combe (1999), Yuan (1999), Nilson (1996)] in water filtration since it possessed higher aromaticity (hydrophobicity characteristic) and greater adsorptive character. Schafer et al. (2001) observed that humic acid exhibited higher flux decline and caused greater irreversible fouling than that for the hydrophilic fraction (reversible fouling). This was mostly occurred through adsorption fouling due to hydrophobic interactions. Hydrophobic interaction can be described as "like attracts likes". That is, there is a natural tendency of attraction between membranes and solutes with similar chemical structures. Hydrophobic attraction results from the Van der Waals force between molecules. Hydrophobic/hydrophilic interactions are functions of structure similarities between membranes and fouling materials, the types and density of functional groups on both membrane surfaces and fouling materials and solubility of molecules of fouling materials [Liu (2008)].