Chapter 1. Introduction

Membrane based filtration is becoming more and more significant in industrial separation processes. It has emerged as a separation technology that is competitive in many ways with the conventional separation techniques, such as distillation, adsorption, absorption, extraction, etc. The key component in all the membrane based separation processes is the membrane. It can be described as a thin barrier between two bulk phases that permits transport of some components, but retain others. The driving force that is necessary for the transport to occur could be a transmembrane pressure gradient (ΔP), concentration gradient (ΔC) or activity gradient (ΔA), electrical potential gradient (ΔE) or temperature gradient (ΔT). The pressure driven membrane processes can be classified based on the membrane porosity as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). MF is designed to retain particles in the range of 0.1 - 5 μm (suspended particles, yeast, bacteria, etc.) and operating pressure is typically < 2 bar; while UF retains only macromolecules or particles larger than about 10 - 200 Å with operating pressure of 1 - 10 bar. NF membranes have < 2 nm pore size, which retains divalent ions and usually the operating pressure is 5 - 20 bar. RO is essentially considered to be a dewatering technique, which retains salts and sugars with operating pressure as high as 80 bar [Mulder (1998), Petersen (1993), Cheryan (1986), Lonsdale (1982)]. Membranes can also be classified based on symmetric or asymmetric nature of porosity all over the membrane depth. In porous symmetric membranes, pores can either form long channels or the membrane can have a porous sponge-type structure. A symmetric membrane can also be non-porous (e.g. homogeneous film, liquid membranes). Nevertheless, in these cases, a structural gradient is absent in the membrane cross section.

Most UF membranes have an asymmetric structure; which consist of a toplayer or skin supported by a porous sublayer. UF process is defined as a pressure driven membrane separation process in which low molecular weight components are separated from those with high molecular weight. UF is principally used in the separation of macromolecules having molecular weight in the range of 300 to 5,00,000 Da. Both, polymers and inorganic materials are used for the preparation of membranes. Polymeric UF membranes are very often prepared by the immersion precipitation process. Membranes can be prepared in two configurations, flat and tubular. The flat sheet membranes are used in a plate-and-frame or spiral wound systems; whereas tubular membranes are used in hollow fiber, capillary and tubular systems. UF membrane performance is generally characterized by molecular weight cut-off (MWCO) and by pore size distribution. However, cut-off values are only approximate, since the same molecules can have different radii depending on solution properties such as pH and ionic strength. Osmotic pressure effects in UF membranes are small. This is primarily to overcome viscous resistance of liquid permeation through the porous network of the membrane. The separation mechanism of UF membranes is conceived as a sieving action, where an increase in applied pressure increases the flux rate. Although, the membrane - solute interactions hold a considerable role for the separation of solutes.

UF membrane materials

Membrane technology became commercially attractive with the development of asymmetric cellulose acetate RO-membranes by Loeb and Sourirajan in 1962 [Loeb (1962)]. Michaels and his coworkers (1971) produced UF membranes from cellulose acetate (CA). CA is a derivative of the natural polymer, cellulose. The major traditional source of cellulose is wood pulp. CA is hydrophilic, which is very important in minimizing fouling of the membrane. Nevertheless, the chemical stability of this class of materials is low; it has very poor resistance to chlorine as it oxidizes CA which weakens the membrane and opening up the pores. It is highly biodegradable and has a relatively narrow range of pH-tolerance [Cheryan (1986)]. Furthermore, CA membranes cannot be used at temperatures above ~ 30 °C and the membrane performance changes with time due to polymer creep. Therefore, other polymers were introduced as membrane materials. Polymers those are used very successfully include poly(sulfone) (PSF) and poly(ethersulfone) (PES). UF membranes prepared from these materials show a wide range of pH and temperature resistance and are fairly resistant to chlorine. This means that sterilization and cleaning in applications such as dairy and pharmaceuticals can be carried out by hypochlorite solutions, which is a standard procedure in these industries.

On the other hand, irreversible membrane fouling by adsorption of feed components at the membrane surface, e.g. proteins, may cause a very severe flux decline. In addition, PSF and PES membranes are not very resistant to hydrocarbon media. Therefore, a number of other polymers have been investigated as UF membrane material, such as hydrophilic polymers or polymer blends to prevent irreversible protein fouling. These include chemically stable polymers such as regenerated cellulose, poly(acrylonitrile), poly(vinylchloride), poly(imide), poly(vinylidenefluoride), etc. [Mulder (1998), Cheryan (1986)].

Poly(acrylonitrile) (PAN) is one of the popular membrane materials for water treatment [Nouzaki (2002)]. It has thermal stability upto 130 °C (Zhao (2004) and has stability towards many organic solvents [Wang (2006), Jung (2005), Jung (2004), Yang (2003), Scharnagl (2001)]. Due to the highly hydrophilic properties of PAN than other membrane materials such as poly(sulfone), poly(ethersulfone), poly(ethylene) and poly(propylene), it has been known as low fouling membrane material for aqueous filtration and has already been commercialized. Compared to other polymer materials, PAN has also good resistance against chlorine and cleaning agents such as sodium hypochlorite [Jung (2004)].

1.1. Applications of UF membrane processes

UF membrane was initially developed primarily for the treatment of wastewaters and sewage to remove particulate and macromolecular materials [Cheryan (1998)]. Its applicability is now widened considerably to include diverse fields such as chemical processing, food processing, biotechnology, water treatment, etc.

1.1.1. Water treatment

There are mainly two types of water qualities of interest to membrane technologists: process water for the manufacturing industries and potable (drinking) water for human consumption. The use of UF membrane for cleaning potable water is potentially the largest single application of the UF membrane technology. Conventional water treatment systems typically employ a wide range of physical, chemical and biological processes to produce water with desired purity [Zeman (1996)]. UF membranes are beneficial in removing pathogenic species (viruses and bacteria) that may constitute a health hazard [Arnal (2004), Ciardelli (2001), Cheryan (1998)]. Natural organic matter (NOM) is a complex matrix of organic compounds present in natural surface water sources. UF has proved to be a valuable and effective technique in terms of removal efficiency, process complexity and cost [Aoustin (2001)]. UF serves as an alternative pretreatment to further treatment steps, such as softening, removal of micropollutants (pesticides) and nitrate removal [Bruggen (2003)]. One particular group of contaminants that is present in drinking water is humic acid. UF showed potential towards the removal of humic acid and other organic matter [Lowe (2008)].

Applications of UF membrane technology for process water treatment are demonstrated in various industries like semiconductor and electronics for washing integrated-circuit chips and other devices. Pharmaceuticals [Zeman (1996), Marcus (1988)] and biotechnology industries [Lutz (2006)] need pure water for tissue culture media, bacteriological media, buffer solutions, rinsing of equipments, etc. Polymer industry needs water for polymerization, washing, etc.

1.1.2. Wastewater treatment

Almost every manufacturing industry (e.g. automobiles, food, steel, textiles, animal handling and processing, etc.) and service establishments (hotels, transportations, etc.) generates large quantities of wastewater daily. The need for stringent pollution control provides treatment opportunities for membrane technology in all aspects of pollution control. Membrane processes are proven effective from end of pipe treatment to the prevention and reduction of the waste.

There are two approaches to the wastewater treatment depending on (i) if the permeate is to be reused or (ii) if the permeate is to be disposed off and the objective is to reduce the volume of solids or reduce pollution hazards of wastewater. Some of the typical examples aiming these are given below.

1.1.2.1. Oily wastewater

Industries such as steel, aluminum, food, textile, leather, petrochemical and metal finishing reports high levels of oil and grease in their effluents [Cheryan, M. (1998a)].

Oil and grease in wastewater can exist in several forms: free, dispersed or emulsified [Rhee (1987)]. UF method produces a water phase that is usually clean enough to be discharged to a sewer with no post-treatment and an oil phase that can be incinerated, if concentrated enough [Cheryan (1998)].

1.1.2.2. Textile industry

In the textile industry, and in particular the textile finishing sector, the availability of high quality water is a key factor in many processes such us washing, bleaching, printing and coating of textile products [Fersi (2005)]. The textile industry uses synthetic warp sizing agents such as poly(vinyl alcohol) (PVA) [Porter (1998)], polyacrylate and carboxymethyl cellulose (CMC) in cotton blends, in place of starch and natural gums [Cheryan (1998)]. After weaving, the size agents must be washed out, which requires large volume of wash water. The sizing agents are, however, expensive and nonbiodegradable; thus they pose challenging waste treatment and/or recovery problems. The UF membrane process is used to recover the PVA and CMC from the wastewater of textile industry. Dyes can also be effectively recovered by UF membrane from wastewater [Capar (2006), Ciardelli (2001), Alves (2000), Zeman (1996), Eykamp (1995), Kulkarni (1992), Cheryan (1986)].

1.1.2.3. Pulp and paper industry

The pulp and paper industry produces enormous amounts of highly polluted water and discharges effluents which produce high inorganic and organic pollution loadings [Liu (2004)]. Effluents are at extremes of pH, highly colored and non-biodegradable for the most part. It is quite difficult to meet stringent environmental regulations by conventional treatment techniques such as coagulation and activated sludge processes. However, UF can be used to concentrate and recycle some of the effluents prior to discharge. Some applications include color removal from kraft mill bleaching effluents, concentration of dilute spent sulfite liquor, metal removal, recovery of lignin from kraft black liquor and recovery of paper coating from waste water [Mänttäri (2007), Liu (2004), Tavares (2002), Zeman (1996), Eykamp (1995), Kulkarni (1992), Cheryan

(1986)]. Membranes are used to recycle of paper, news print, cardboard and the purified water can be reused in the paper manufacturing process [Pizzichini (2005)].

1.1.2.4. Tanning and leather industry

Leather industry has been always considered one of the most polluting industries. Organic pollutants (proteic and lipidic components) come from skins or they are introduced during the working cycle (for example tannins). Inorganic pollutants are a residual of the used chemicals that are not completely fixed by skins owing to the low efficiency of the operations [Cassano (2001)]. UF can be used to recover sulfides from spent dehairing baths, recover and desalt vegetable tannin baths and recycle or at least remove chromium from spent chrome tannin [Zeman (1996), Eykamp (1995), Kulkarni (1992), Cheryan (1986)].

1.1.3. Dairy industry

Application of UF membrane technology is well established in the dairy industry [Zeman (1996), Eykamp (1995), Kulkarni (1992)]. UF of skim milk is widely used in the world in order to control the protein content before the cheese making process [Rabiller-Baudry (2008)]. Cheese manufacturing can be defined as a fractionation process whereby protein (casein) and fat are concentrated in the curd, while lactose, soluble proteins, minerals and other minor components are lost in the whey. UF provides an extremely attractive technique for whey processing, which is the byproduct in cheese making [Daufin (2001), Zeman (1996)]. On the large scale separation of milk into well-defined fractions application of UF lead to more optimal use of milk components (milk fat, casein, serum proteins) [Brans (2004)]. It is reported that lactose and soluble salts pass through UF membranes, while protein, fat and some of the insoluble or bound salts are retained. UF has been used to compensate for the poor taste and to maximize the concentration of desirable protein and calcium. Poly(ethersulfone) based UF membranes are most popular in the dairy industry, even though they foul more than cellulose membranes. Poly(ethersulfone) (PES), and poly(sulfone) (PSF) have the advantage that higher temperature can be used [Cheryan (1986)].

1.1.4. Biotechnology

UF plays an important role to separate or recover microorganisms, concentrate protein, exchange buffer system, clarify suspensions for cell harvesting, enzymes and sterilize liquids to remove bacteria [Charcosset (2006)]. UF membranes are very well suited to the processing of biological molecules since they operate at relatively low temperatures, pressures and involve no phase changes or chemical additives; which minimizes the extent of denaturation, deactivation of highly labile biological products [Zeman (1996)]. UF membranes are widely used for the recovery of biological products in steps such as cell broth clarification, cell harvesting, concentration or diafiltration of protein solution prior to separation and final concentration [Pieracci (2002)]. Flaschel (1983) and Babbaric (1980) showed that UF membranes are used to recover enzymes from plant and microbial sources. In biotechnological applications, pure water is required for tissue culture media, bacteriological media, etc. The UF membranes can be used for getting pure water for these purposes.

Membrane bioreactors (MBRs) is one of the fast growing application of UF membranes, which can be broadly defined as systems integrating biological degradation of waste products with membrane filtration. MBRs have been introduced over 30 years ago [Yang (2006)]. Until now, their main industrial applications have been for wastewater treatment (e.g., industrial, domestic and municipal). They are alternative approaches to classical methods of immobilizing biocatalysts such as enzymes, microorganisms and antibodies, which are suspended in solution and compartmentalized by a membrane in a reaction vessel or immobilized within the membrane matrix itself. Membrane bioreactors have been used for the production of aminoacids, antibiotics, anti-inflammatories, anticancer drugs, vitamins, optically pure enantiomers and isomers, etc. [Charcosset (2006)]. Advantages of the MBR include good control on biological activity, high quality effluent that is free of bacteria and pathogens, smaller plant size, and higher organic loading rates [Cicek (2003)]. Chemical and biological conversions using enzymes and microorganisms as catalysts are commonly used in the production of organic chemicals, food products, pharmaceuticals, hormones, vitamins and other biological products. Protein hydrolysis, carbohydrate hydrolysis has been studied using membrane bioreactor [Cheryan (1996)].

1.1.5. Food and beverages

UF membranes can be used for clarification of fruit juices. Conventional clarification requires several unit operations such as centrifugation, treatment with pectinases and rotary vacuum filtration with diatomaceous earth. UF processes have been developed for apple, grape, pineapple, pear, canberry, mosambi and kiwi fruit juices [Cassano (2007), Rai (2007), Cassano (2004), Cheryan (1998), Blanck (1986), Garrison (1986), Paulson (1985)]. UF membranes are also successfully used in honey processing and for clarifying lime juice at the point of production [Cheryan (1986)].

In alcohol industries, UF can be used either before the fermentation (i.e. for clarifying the "must") or after the fermentation (for treating the finished wine). They are used for the treatment of wine to remove off pigments and to reduce browning caused by oxidation of polyphenols. UF system can also be used to remove precipitated potassium tartrate from freshly made wine, removal of yeast from beer in the fermentation vessel and for removal of haze proteins [Cheryan (1986)].

1.1.6. Animal products

Hybrid system with UF membranes is demonstrated to treat waste water from meat industry before being discharged into receiving water [Bohdziewicz (2006)]. Animals provide some of the most desirable-high-quality protein known to man. These proteins can be recovered from the plasma and red blood cells from red meat by UF. Gelatine is obtained from skin, hides and bones of animal as a by product and is separated by UF membrane technique [Cheryan (1986)].

1.1.7. Applications of UF in non-aqueous systems

There are enormous potential applications of UF in non-aqueous systems. UF membranes are developed for organic (nonaqueous) applications such as recovery of solvent from petrochemical and food industries [Edwards (2002), Kulkarni (1986)]. Poly(imide) based UF membranes may be used on many of the organic solutions that were previously difficult to treat [Iwama (1982)]. Some of the examples are discussed below.

1.1.7.1. Paint solvent recovery

Recovery of electrocoat paint is an important application of UF membrane [Breslau (1980)]. During the paint manufacturing and in automated painting baths, it is necessary to frequently change the type and colour of the paint. For this purpose, the just applied paint has to be removed from the mixing vessels and filling lines by means of rinsing with paint solvents. The solvents, contaminated with resins and pigments are usually disposed off by incineration [Smallwood (1993)]. When applying an UF process, paint solvents can be recovered from the waste stream and can be reused for rinsing or as fresh paint solvents.

1.1.7.2. Recovery of dewaxing aids during oil dewaxing processes

Crude waxy hydrocarbon oils are usually dewaxed by using mixtures of aliphatic ketones (acetone, methyl ethyl ketone), aromatic hydrocarbons (toluene, xylene) and halogenated hydrocarbons (chloroform, dichloroethane). Cellulose acetate and regenerated cellulose membranes were demonstrated to recover solvent from the dewaxed oil [Wernick (1987), Hafez (1985)]. The dewaxing aids, i.e., poly(alkylacrylates), poly(ethyleneoxides), poly(vinylpyrrolidone), etc., remain in the solvent-free wax. Recovery of these components by conventional separation techniques is very difficult and costly. However, these can be recovered by UF of the wax at 70-100 °C through a poly(ethersulfone) or poly(imide) membrane, while the purified wax can be used for other purposes. During the Exxon-DILCHILL process, the waxy oil is chilled to 3 °C or less [LaFrenière (1989)]. Cold dewaxing solvent is added in small amounts to this mixture, so that small crystallites are formed. These crystallites are then removed by UF [LaFrenière (1989) Thompson (1985), Anderson (1990)].

1.1.7.3. Heavy oil upgrading or deasphalting

A vacuum distillation step is one of the typical processes during crude oil refinery. Products from this step are middle boiling distillates and heavy vacuum residual oil (HVR). The HVR oil is unsuitable for conventional cracking methods, since it contains several sulfur and metal containing compounds as well as polar components, that foul and deactivate the cracker catalysts. The general deasphalting step is performed in a flasher-stripper combination [Gerhartz (1988)]; however, upgrading can be done more energy-efficiently by UF of a mixture of HVR with toluene, chloroform, hexane or heptane through various UF membranes [Osterhuber (1989), Funk (1986), Kulkarni (1986)].

1.1.7.4. Treatment of used lubricating oil

Used lubricating oil contains several degraded components such as polymers, dispersion agents, and antioxydants, as well as contaminants like asphaltenes, lead, and combustion by-products. After removal of these degraded components and contaminants, the regenerated oil can be reused as fuel. UF of a mixture of the used oil with solvent (hexane) through poly(acrylonitrile) membranes showed very promising results, and most of the contaminants were removed from the oil [Desfives (1978)].

1.1.7.5. Edible oil processing

In the edible oil industry, oil is extracted from its raw material (e.g., oilseeds, fruit pulps, animal remains or fish) with solvents such as hexane, ethanol, or isopropanol. After extraction, the mixture of 70-75% solvent with extracted oil (the miscella) is usually separated by distillation. However, UF or reverse osmosis process was said be very effective and much more energy efficient [Köseoglu, S. (1990a)]. Various 'tight' commercial UF membranes were tested for this separation [Köseoglu, S. (1990b)]. UF membranes were also used for degumming of vegetable oils [Ochoa (2001)].

1.2. Advantages of UF membrane

UF membrane has several advantages over conventional separation processes. These include i) acceptable product quality, ii) energy consumption is generally lower thus low processing cost, iii) separation can be carried out continuously and under mild conditions and iv) modular configuration is possible. These advantages are elaborated as follows.

1.2.1. Acceptable product quality

The separation can be carried out continuously and under milder conditions. No additional chemicals are required and thus product purity is maintained. During processing, changes in the temperature, pH and ionic strength of the product can be minimized. This is important while processing biomolecules like proteins and enzymes, which are sensitive to the changes in solution environment. Hence, the purity of the product with membrane processes is usually better than that those obtained from conventional processes.

UF membranes are beneficial in removing microorganisms from drinking water without using additional chemicals; while conventional water treatment include several steps such as coagulation, flocculation, sedimentation, filtration and disinfection, usually with chlorine [Cheryan (1986)].

Antibiotic recovery involves three main processing steps: initial clarification of the fermentation broth, a primary isolation step and the final purification. The main advantage of membrane systems is in the initial recovery of antibiotics with high yield [Zeman (1996)].

1.2.2. Low energy consumption

Energy consumption is generally low in UF process as they operate at relatively lower pressures (1-10 bar) and ambient temperatures with no phase change. It can be combined with the other separation processes (hybrid processing) and separation can be carried out continuously.

Sugar processing is one of the most energy-intensive processes in the food and chemical industries. In processing of raw sugar juice, UF membrane is an alternative method to chemical purification process [Hinkova (2002)].

Crude vegetable oils contain various minor substances such as phospholipids, free fatty acids, waxes and coloring pigments. These substances may affect the quality of the oil and are removed form the crude oil by several steps of refining which consume large amount of energy. Membrane techniques are reducing the energy costs and are able to take place in the vegetable oil industry [Koris (2006), De Moura (2005), Koris (2002)]. In conventional degumming (phospholipids separation) processes, several operation steps should be repeated, in order to overcome severe oil losses and waste-water contamination. In this area, UF membranes find process advantages [Kim, I. (2002a)].

The conventional method to remove dye from waste water requires several chemical or physical methods [Mozia (2005), Petrov (2003)] such as ozonation, bleaching, hydrogen peroxide/UV, electrochemical techniques. These were found to be inadequate because most textile dyes have complex aromatic molecular structures that resist degradation. They are stable to light, oxidizing agents and aerobic digestion. The application of membrane filtration processes not only enables high removal efficiencies, but also allows reuse of water and some of the valuable waste constituents [Fersi (2005)].

1.2.3. Continuous separation under mild conditions

Conventional methods of producing clear single strength fruit juices involve several batch operations that are labor and time consuming. Membrane technology replaces the holding, filtration and decantation steps [Cheryan (1996)].

Extractive UF is a separation technique that combines an extraction step with a membrane filtration step. This combination offers the advantages of the high selectivity of the reactive extraction and the high permeation rates and energy efficiency of the UF step, which leads to a relatively inexpensive separation technique [Watters (1989)]. This technique has been satisfactorily applied to the recovery of organic compounds, such as valeric acid [Rodr′iguez (1996), Rubio (2000)], phenol, acetic acid and oxalic acid [Scott (1992)] from aqueous waste streams in which the solute is in a very low concentration.

1.2.4. Modular configuration

Application of membranes on technical scale requires large membrane area. The smallest unit into which the membrane area is packed is called a module. A number of module designs are possible and are based on two types of membrane configuration i) flat and ii) tubular. The choice of module configuration, as well as arrangement of the modules in a system, is based solely on economic considerations. The module maximize membrane packing densities (ratio of membrane area to device volume); minimizes manufacturing costs, permit easy access for cleaning and/or membrane replacement, operational lifetime and incorporate modularity of design for easy scale-up, staging or cascading.

1.3. Rationale for the work

Majority of the UF membrane applications are confined to water solutions. These are associated with issues like fouling, porosity (control on pore size versus density), long term stability without significant loss in performance, etc. In UF membranes, fouling (decline in flux due to adsorption, gel layer formation) is a severe issue and can be controlled, at least to some extent by manipulating membrane surface chemistry. Thus, making a membrane that would have simultaneously high flux, rejection and antifouling characteristics is challenging. Such issues can be better addressed by proper selection of membrane material, optimization of membrane surface chemistry, morphology and preparation parameters. Though several polymers are demonstrated in the literature as UF membrane materials, the membranes demonstrated may not possess optimum properties in terms of their combined flux and rejection criteria. Membrane preparation conditions such as use of appropriate solvent and additives can still be optimized to improve the properties with desired membrane material. Polyacrylonitrile (PAN) is one of such polymers, which has a large potential owing to its inherent characteristics such as better hydrophilicity and organic solvent stability than the common UF membrane materials like poly(sulfone) (PSF) and poly(ethersulfone) (PES). Surface chemistry of PAN based membrane can be better tuned by modification of its nitrile functionality by hydrolysis.

Pharmaceutical and other chemical industries need various solvents, wide pH conditions and temperatures during their separation processes. Membranes prepared using polymers that can withstand such stringent conditions is a challenge. There are certain polymers that can withstand extreme pH conditions and solvent environments such as poly(imide), poly(*p*-phenylene-terephthalamide), poly(urea), etc. Preparation of UF membranes using such polymers though is a challenge, is certainly worth addressing in view of new developing separation applications that need to meet economic criteria. Poly(benzimidazole) is widely known as proton exchange membrane (PEM) material, which is used under stringent thermo-oxidative environments. The issue of UF membranes based on PBI is weakly addressed in the literature. It could be worth employing excellent thermal, chemical and mechanical stability of PBI for UF membrane preparation, especially for non aqueous applications involving stringent chemical/pH environments.

1.4. Scope of the work

PAN has a large potential to explore further as a UF membrane material. This polymer has better hydrophilicity and its nitrile functionality can be easily hydrolyzed in a controlled manner. These properties can be employed effectively in better tuning the membrane properties and thus performance. A controlled hydrolysis can offer increased hydrophilicity and render negative charge on the membrane surface. Optimization of UF membrane preparation by varying PAN concentration, solvent, additive in dope solution and support material can lead to membrane with better control on membrane porosity. The effect of porous fabric used for supported membrane preparation is weakly addressed in the literature and can play a significant role in governing PAN membrane porosity. It is known that inorganic additives complexes with the polymer. Use of low molecular weight polycarboxylic acids, which can form complex with basic solvent than the polymer could lead to a better controlled demixing during the phase inversion process and thus was thought to be investigated. PAN as a membrane material can also have better solvent stability and thus was decided as a material for further investigation.

The issue of membrane stability towards extreme solvents and pH can be better addressed by using poly(benzimidazole) (PBI) as a membrane material having excellent thermo-chemical stability. ABPBI, a member of PBI family is obtained from single monomer which is relatively cheaper. This polymer has even better solvent stability than PBI based on isophthalic acid (used as PEM material). Its solubility is known only in methane sulfonic acid, sulfuric acid, formic acid, trifluoroacetic acid, phosphoric, poly(phosphoric acid) and is insoluble in common organic solvents. Thus, it was thought that ABPBI is worth investigating as UF membrane material.

1.5. Aims and objectives

The aim of this thesis was (1) to optimize PAN based UF membrane preparation by varying casting parameters and post-preparation hydrolysis of membrane surface while aiming at membrane characteristics for drinking water purification; and (2) to explore applicability of ABPBI for membrane preparation by phase inversion. These aims were thought to be met by defining following objectives.

(1) Optimization of preparation parameters for PAN based UF membranes

Systematic variation in parameters such as PAN concentration, solvent, additive in dope solution and porous support material was planned for the preparation of supported membranes.

Controlled hydrolysis of PAN based membrane by using different bases and optimizing base treatment protocol by varying treatment time, concentration and temperature; while anticipating increased hydrophilicity and thus improved water flux. It was also thought to prepare a PAN based membrane with possible low MWCO and further reduction in pore size while aiming at arsenic (As-V) rejection. This was thought to be investigated by following strategies like (i) post-annealing and post-hydrolysis of PAN membrane having lowest possible MWCO and (ii) grafting of styrene sulfonic acid (SSA) on membrane surface. Thus formed membranes would exhibit negative charge on the surface and render arsenic rejection capabilities by Donnan exclusion principle.

(2) ABPBI based membrane

To investigate ABPBI based membrane preparation by phase inversion while varying membrane preparation parameters such as support material, nonsolvent and ABPBI concentration. Investigation of membrane stability towards various organic solvents, autoclave condition, concentrated acid and base were planned. The effect of glycerol treatment was assessed to avoid pore collapse after drying the membrane.

1.6. Organization of the thesis

This thesis presents optimization of poly(acrylonitrile) (PAN) and poly(benzimidazole) (PBI) based UF membrane preparation and is organized into following six chapters.

Chapter 1: Introduction

This chapter begins with applications of UF membranes. Need for the investigations in UF membrane are described. The scope of the work is defined, followed by the objectives of the work. At the end of this chapter, organization of the thesis and terminologies are presented.

Chapter 2: Literature survey

This chapter briefly reviews various methods for ultrafiltration membrane preparation. Factors affecting membrane performance and stability viz., concentration polarization, fouling, compaction, interactions of solutes with membrane material, etc. are briefly addressed.

Chapter 3: PAN based UF membranes: Optimization of preparation parameters

This chapter begins with introduction, which reviews various membrane preparation parameters and their effects on membrane performance. Experimental section describes the preparation of PAN based membranes by optimizing some of the crucial parameters such as polymer concentration, solvent and additive in the dope solution and support material. Potential of some of the membrane was examined for water disinfection by bacteria (*E. coli*) rejection analysis.

Chapter 4: Surface modification of PAN based UF membranes

Introduction of this chapter reviews literature on hydrolysis aspects of PAN and its membranes, preparation of PAN based membranes with low porosity, presence of arsenic in drinking water and its removal methods. In experimental section, membrane preparation and surface modification, annealing methodology, techniques used to characterize membrane and surface morphology are described. Results obtained with hydrolysis and application of this methodology for the removal of arsenic (As-V) is discussed.

Chapter 5: ABPBI based UF membranes

This chapter begins with literature survey on solvent resistant membranes. Few available reports on PBI as a membrane material for nanofiltration (NF) and UF applications are discussed. Experimental section describes synthesis and characterization of ABPBI, its membrane preparations and characterization methods used. Effects of various parameters viz., polymer concentration, solvents and non solvents used, porous support and casting parameters (air dry time, gelation temperature) on membrane performance are discussed. The stability of ABPBI membrane towards organic solvents, concentrated acid and base was evaluated. The effect of glycerol impregnation into pores was studied in order to prevent pore collapse.

Chapter 6: Conclusions

This chapter summarizes the results obtained and conclusions of this work.