“Investigations in ultrafiltration membranes based on polyacrylonitrile and AB-polybenzimidazole”

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Research Guide

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Dedicated to my parents

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Certificate of Guide

Certified that the work incorporated in the thesis entitled **“Investigations in ultrafiltration membranes based on polyacrylonitrile and AB-polybenzimidazole”** submitted by Harshada Ramesh Lohokare was carried out under my supervision. Such material as has been obtained from other sources has been duly acknowledged in this thesis.

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Declaration by the Candidate

I declare that the thesis entitled **"Investigations in ultrafiltration membranes based on polyacrylonitrile and AB-polybenzimidazole"** is my own work conducted under the supervision of Dr. U. K. Kharul, at Polymer Science and Engineering Division, National Chemical Laboratory, Pune. I further declare that to the best of my knowledge, this thesis does not contain any part of work, which has been submitted for the award of any degree either of this University or any other University without proper citation.

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Terminologies

Compaction: Compression of membrane structure due to a pressure difference across its thickness, causing a decrease in membrane permeability.

Concentration polarization: Development of a concentration gradient of the retained components across the boundary layer near the membrane surface.

Cross flow: Mode of operation where the feed flows parallel to the membrane, while the permeate has a transverse flow direction.

Dead end: Mode of operation where the whole feed is forced to pass through the membrane.

Fouling: Phenomenon in which the membrane adsorbs or interacts in some manner with solutes in the feed stream, resulting in a decrease in membrane performance.

Flux: Volume or mass of permeate or of any component in the permeate, passing through the membrane per unit area and unit time.

$$J_w = \frac{P}{(\Delta p - \Delta \pi) l}$$

where, P is permeability coefficient, Δp is the hydrostatic pressure difference, $\Delta \pi$ is the osmotic pressure difference between feed and permeate phases and l is the membrane thickness.

Housing: The vessel in which a membrane element is placed with ports and fittings to direct the feed, retentate and permeate streams through the membrane element.

Mass transfer coefficient: A measure of the solute's mobility due to forced or natural convection in the system. It is defined as the ratio of the diffusive solute flux at the membrane surface $(-D\, \partial C/\partial y)_w$, to the overall concentration driving force for diffusion (C_w - C_b).

$$k = \frac{-\left(D \frac{\partial C}{\partial y}\right)_w}{C_w - C_b}$$

where, D is binary solute diffusion coefficient, C is local solute concentration, y is fluid velocity in transmembrane direction, C_w and C_b are the solute concentrations at the membrane surface and in the bulk solution, respectively.

Module: It refers to the membrane and its housing.

Molecular weight cut off (MWCO): The smallest molecular weight species for which the membrane has > 90 % rejection.

Permeability: The flux of a component through the membrane per unit driving force.

$$K = \frac{J_w}{\Delta P}$$

where, K is permeability, J_w is flux ($\mathrm{l.m.^{-2}h.^{-1}}$) and ΔP is transmembrane pressure

Permeate: The portion of the feed passing through the membrane.

Retentate: Portion of the feed not passing through the membrane.

Rejection: A measure of how well a membrane retains or allows passage of a solute.

$$\%\,\mathrm{R} = \left[1 - \left(\frac{C_p}{C_f}\right)\right] \times 100$$

where, C_p is concentration of the permeate, while C_f is the feed concentration.

Spacers: A mesh like material used in flat sheet modules (e.g. plate, spirals, pleated sheet) to separate successive layers of membranes. Spacers control the feed channel dimensions in these modules.

Trasmembrane pressure: The driving force for flux. In cross flow systems, it is measured as the average of the inlet and outlet pressures, minus permeate backpressure.

List of Abbreviations

AFM	:	Atomic force microscopy
BSA	:	Bovine serum albumin
DMF	:	*N*,*N*-dimethyl formamide
DMAc	:	*N*,*N*-dimethyl acetamide
DMSO	:	*N*,*N*-dimethyl sulfoxide
EDAX	:	Energy dispersive analysis of X-rays
ESCA	:	Electron spectroscopy for chemical analysis
FTIR-ATR	:	Fourier transform infrared-attenuated total reflectance
MSA	:	Methane sulfonic acid
MWCO	:	Molecular weight cut off
NF	:	Nanofiltration
PAN	:	Poly(acrylonitrile)
PSD	:	Pore size distribution
PSF	:	Poly(sulfone)
PES	:	Poly(ethersulfone)
PEG	:	Poly(ethyleneglycol)
PI	:	Poly(imide)
PVA	:	Poly(vinylalcohol)
PVP	:	Poly(vinylpyrrolidone)
RO	:	Reverse osmosis
SEM	:	Scanning electron microscopy
SSA	:	Styrene sulfonic acid
TMP	:	Transmembrane pressure
TGA	:	Thermogravimetric analysis
UF	:	Ultrafiltration
WAXD	:	Wide angle X-ray diffraction analysis

List of Symbols

A : Membrane area (cm^2)

ωA : Work of adhesion (mN.m.$^{-1}$)

γ_w : Surface tension (dyne.cm.$^{-1}$)

σ_p : Geometric standard deviation

P : Transmembrane pressure (bar)

R : Rejection (%)

J_w : Water flux (l.m.$^{-2}$h.$^{-1}$)

L : Pore length (μm)

R_m : Membrane resistance (Pa.m.$^{-1}$s.$^{-1}$)

ρ_p : Density (g.cm.$^{-3}$)

d_s : PEG diameter (nm)

a : Stoke's radius (nm)

M : Molecular weight of PEG (Da)

θ : Polymer-water contact angle (°)

η : Viscosity of water (poise)

σ : Interfacial tension (dyne.cm.$^{-1}$)

r_p : Pore radius (cm)

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. Rational 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.

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)].

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

3.1. Introduction

Applications of UF membranes in various areas like water treatment, pharmaceutical, chemical, dairy and food, paper, textile industry, etc. are rapidly growing, stressing the need for surge on new membranes with improved properties. The membrane performance in terms of flux, solute rejection, fouling characteristics, stability under operating conditions, etc. becomes crucial for large scale applications. The membrane porosity (size and density) plays a crucial role in depicting many of these properties.

3.1.1. Parameters affecting membrane preparation and performance

There are various factors affecting membrane performance. Some of them, viz., concentration polarization, fouling, compaction, interactions of solute with membrane material, etc. are already discussed in Section 2.2. This section focuses on the membrane performance depicted by the membrane preparation parameters resulting in variation in the membrane porosity. It is well known that the membrane porosity can be manipulated by systematically varying membrane preparation parameters like composition of the dope solution (polymer concentration, nature of solvent and additives in the dope solution), evaporation time, nonsolvent used, composition of coagulation bath and its temperature, etc. Flat sheet supported phase inversion membranes are usually prepared by coating a uniform layer of a polymer solution onto the porous support, followed by gelation and precipitation. The effect of preparative parameters on the structure, porosity and UF membrane performance are documented [Munari (1990)]. Some of these parameters affecting membrane performance are discussed below.

3.1.1.1. Polymer concentration in the dope solution

Increasing polymer concentration in the casting solution leads to increased viscosity [Nouzaki (2002), Ismail (2002), Munari (1983)] and lower membrane porosity

[Mulder (1998)]. It is reported that increase in polymer concentration leads to decrease in pore size as well as flux of the membrane [Congjie et al. (1987)]. As observed by Ahmad et al. (2005), average pure water permeability (PWPs) decreased with increasing polymer concentration from 18 to 22 wt. %, while PEG rejection was increased for integrally skinned poly(sulfone) (PSF) based UF membrane. Paul et al. (1992) and Nouzaki et al. (2002) observed lowering in flux with increasing PAN concentration in the casting solution. The effect of PAN molecular weight (MW) on membrane performance was studied by Nouzaki et al. (2002). It was observed that the flux of the membrane prepared from low molecular weight PAN (70 kDa) was almost double than the one prepared from high molecular weight PAN (400 kDa); while the rejection of dextran was almost same. This was attributed to the low concentration and high viscosity of the casting solution prepared using PAN (400kDa) and thus the prepared membrane could not form a fine skin layer. Mosqueda-Jimenez et al. (2004) studied effects of concentration of polymer in the dope solution and solvent evaporation time on the performance of resulting flat sheet poly(ethersulfone) (PES) membranes. It was observed that the mean pore size and MWCO of membranes decreased either by increasing the PES concentration in the casting solution or by increasing the solvent evaporation time. However, effect of the PES concentration was more important than that of evaporation time.

Bessie`res et al. (1996) noticed that the mean surface roughness (R_a) of the membrane increased with an increase in MWCO for the sulfonated polysulfone UF membranes. Singh et al. (1998) also observed the similar increase in R_a with increasing MWCO of the poly(ethersulfone) (PES) membranes. Authors explained this relationship in terms of the aggregation of the polymeric nodules that were less tightly packed when membranes were cast from the solutions having lower concentration of the polymer. It is reported that in order to induce chain entanglement and therefore reduce the formation of the macrovoid in the skin layer, a higher polymer concentration is required [Ahmad (2005)]. In case of the asymmetric porous membrane preparation based on poly(vinylidene fluoride-*co*-hexafluoro propylene), the membrane cast from the lower polymer concentration in the dope (9.1 wt. %) showed clear finger-like pores [Feng (2006)]. With increase in the polymer concentration (16.7 and 26.5 wt. %), finger-like pores are gradually suppressed and slimmed. Munari et al. (1983) also observed the decrease in finger-like cavities when the concentration of polymer (and thus viscosity of the solution) was increased. SEM images showed that the lower polymer concentration was more effective for the preparation of membranes with larger pores. The membrane prepared using high polymer concentration showed improved mechanical properties and decrease in pore size [Feng (2006)].

3.1.1.2. Solvent used in the dope solution

The solvent used for the preparation of dope solution is an important component affecting membrane properties. It dissolves the polymer and works together with additives to form a homogeneous casting solution of certain viscosity. The status and degree of extension of polymer molecules and their aggregates in the casting solution differ according to the different varieties and quantities of solvents. It is said that the physico-chemical properties and quantities of these solvents clearly exert a strong influence on the pore size of the membrane formed [Giajun (1985)]. A membrane with either finger-like or sponge-like structure can be obtained for ternary solutions (polymer + solvent + cosolvent) by selecting the cosolvent, concentration of the polymer and the evaporation period before the phase inversion. By the addition of volatile cosolvent in the dope solution, the flux of the membrane decreased and rejection increased [Munari (1983)].

Wang et al. (1993) studied the precipitation values (PVs) of several organic nonsolvents for different polymer “poly(sulfone) and poly(ethersulfone)” and solvent (*N*-methyl-2-pyrrolidinone and *N*,*N*-dimethylacetamide) systems at different temperatures (10 to 80 °C) by the direct titration method. The effect of organic nonsolvents were compared with those of water in the same systems and observed that with DMAc as the solvent, the PVs were about one half than those of obtained with NMP as the solvent. Rana et al. (2006) observed that the poly(ethersulfone) membrane casted from NMP as a solvent showed higher porosity as compared to the membrane prepared with DMAc as the solvent.

3.1.1.3. Role of additive

Additives in the dope solution can cause different effects such as they may change the viscosity of the casting solution, shift the position of the binodal, cause specific interactions (between polymer and additive, solvent and additive, coagulant and additive), change the diffusion rate of the non-solvent into the casting solution, change the diffusion rate of the solvent into the coagulation bath, influence the solidification process of the membrane (influence on Tg, crystallization, toplayer formation, etc.) [Beerlage (1994)]. The additive used may be water [Wang, D. (2000a), Wang, D. (2000b)], non-solvent [Laninovic (2005), Khayet (2002)], inorganic salts [Lee (2002), Kim (1996), Bottino (1988), Kraus (1979)], low molecular weight organics [Feng (2006), Chuang (2000), Han (1999), Petrov (1996)], surfactants [T-sai (2000)], polymer [Chou (2007), Shivkumar (2006), Jung (2004), Machado (1999), Torrestiana-Sanchez (1999), Xu (1999), Kim (1998)], mineral fillers [Bottino (2001), Aerts (2000a), Aerts (2000b)] or mixtures of them [Wang (2000b), Torrestiana-Sanchez (1999)].

Upon addition of low molecular weight components to the casting solution, the membrane formation process is altered by a combination of the effects mentioned above. Additive is, in general, selected to work as a nonsolvent against the polymer; the addition is designed to have the solution composition move close to the miscibility region [Han (1999)]. Subsequently, the thermodynamic equilibria for the system reveal that precipitation of a cast solution into film can be accelerated by the nonsolvent additive. It is also called a "swelling agent" [King (1972)], which may be due to the permeability increase observed in the gas separation or reverse osmosis membranes prepared with the nonsolvent additive. Kim et al. (1996) observed electroviscous behavior after the addition of $ZnCl_2$ to the PSF solution. Addition of 3 wt. % $ZnC1_2$ to PSF induced a red shift in a IR peak at 1152 cm^{-1}, which was assigned to the symmetric vibrational stretching of sulfonyl group, because of $ZnC1_2$ interacted with PSF chains. The PSF/NMP solution with $ZnC1_2$ required less water for the precipitation point than the saltless solution did. It was also observed that the addition of $ZnC1_2$ increased the rejection rate and lowered the molecular weight cut-off (MWCO) of the PSF membrane. Wang, Z. et al. (2006a) used water and water-PEG (PEG_{400} or PEG_{200}) or water-glycerin mixture as nonsolvent additives. It was found that the nonsolvent used could induce the gelation of dope solution before immersion, thus suppressed the formation of macrovoids effectively.

Polymer additives are widely used for the structure control of membranes. These include poly(vinylpyrroidone) (PVP), poly(ethylene glycol) (PEG), etc.; used during the fabrication of ultrafiltration and microfiltration membranes [Kim (1998)]. Effects of PVP addition of different molecular weight on morphology of the poly(etherimide) hollow fiber membrane was investigated by Xu et al. (1999). It was observed that when the higher molecular weight of PVP was added, bigger pores were made [Xu (1999)]. Wang et al. (1999) also found similar results that the decrease in the concentration of PVP results in lower water flux and higher rejection. Boom et al. (1992) studied the role of poly(vinyl pyrrolidone) (PVP) additive in poly(ethersulfone) membrane. It was found that the addition of PVP to the ternary system suppresses the formation of macrovoids in the sub-layer, while the ultraflltratlon type top layer consists of a closely packed layer of nodules. The porosity and average pore radius of poly(vinylidene fluoride-*co*-hexafluoro propylene) membrane increased with the addition of PEG_{400} [Feng (2006)]. It was observed that the finger-like pore size increasingly expands along the direction of additive molecular weight.

It is generally accepted that the macrovoid formation is suppressed as the organic acids are used. This is because acids form the acid-base complex with basic polar solvents such as NMP, DMF, DMAc [Han (1999), Kesting (1989)]. The membrane with a more uniform porous structure is obtained from the polymer solution that contains acid-base complexes [Laninovic (2005)]. The precipitation rate of the cast solution film was enhanced with the addition of nonsolvent (propionic acid, PA) in the casting solution. When the cast film was solidified by the immersion precipitation, the addition of PA resulted in the increase of membrane permeability. The use of dicarboxylic acids as additives, especially maleic acid, has been documented for cellulose acetate reverse osmosis membrane preparation in several reports of the Office of Saline Water [Beerlage (1994)]. The phase separation experiments using cellulose acetate with dioxane, methanol, water and maleic acid were performed by Bokhorst et al. (1981). It was found that with an increase in maleic acid concentration, the solution requires more nonsolvent to demix, i.e., the binodal has been shifted to the polymer/nonsolvent axis.

3.1.1.4. Evaporation time

Evaporation time is one of the most important parameters in the membrane formation [Ahmad (2005), Scharnagl (2001), Munari (1983)]. A decrease in pure water flux and an increase in solute rejection for poly(ethersulfone) membranes as evaporation time increased was noted [Hwang (1996)]. It was further stated that the solute rejection of PES membranes was, however, more likely dependent upon the solvent evaporation from the casting solution/air interface, rather than the change of thermodynamic quality of the casting solution. Sabde et al. (1997) observed the densification of the polymer network with the loss of the solvent during evaporation and leaching in the gelling bath. It was reported that the skin layer of the asymmetric membrane became defect free by introduction of the solvent evaporation step [Ismail (2002)]. Increase in solvent evaporation time decreased the mean pore size of poly(ethersulfone) membrane [Mosqueda-Jimenez (2004)]. This effect was more significant at lower PES concentrations. Feng et al. (2006) observed that with an increase in solvent evaporation time, the pore size and porosity of the membrane decreased. The trend is related to the evaporation of solvent, which increases the solvent concentration gradient and casting solution viscosity at the interface between the solution and the precipitating bath.

3.1.1.5. Coagulation bath composition

The addition of solvent to the coagulation bath is a parameter which strongly influences the type of membrane structure formed. This addition results in a delayed onset of liquid-liquid demixing, which tends to produce nonporous membranes with thick and dense top layers [Mulder (1998)]. Many authors [Frushour (1985), Ziabicki (1976), Craig (1962)] have studied the influence of the coagulation bath conditions on the structure of poly(acrylonitrile) (PAN) hollow fibers. They reported that a denser and finer structure resulted from the slow coagulation condition, low temperature, a high solvent concentration in the coagulation bath and high polymer concentration in the spinning dope. They showed that the denser and finer structure improved the mechanical properties such as tensile strength and modulus. It is important to characterize the skin layer of the asymmetric membrane because the structure and property of the skin layer determines the membrane performance [Strathmann (1971)]. Wang, D. et al. (1998a) discussed the effect of precipitating bath conditions on the membrane structure, but their attention apparently focused on relationship between precipitating bath composition and surfactant additive. Authors proposed that the high miscibility induces formation of macrovoids, while the poor would suppress it. By the choice of different nonsolvent (coagulant), the polymeric membrane can be changed from asymmetric to symmetric. Usually, water as the nonsolvent (coagulant) is the most common choice in preparing asymmetric membranes.

Adding solvent into the water is a common method to suppress the formation of macrovoids [Albrecht (2001), Cheng (1996)]. It was reported that increasing the amount of DMAC in the coagulation bath could delay the demixing during phase inversion, increase the stability of the polymer ternary system which results into the reduction of pore specific volume of sub-layer and the pore size in the skin layers [Chun (2000)].

Different kinds of coagulants such as water, aqueous solution of sodium chloride (NaCl) and aqueous solution of sodium carbonate (Na_2CO_3) were used to preapare PAN based UF membranes [Yang (2003)]. A decrease in permeability and retention properties was observed when the coagulation bath was aqueous solution of NaCl. It was also said that Na_2CO_3 in the coagulation bath reacts with $CaCl_2$ in the casting solution and produces precipitate of $CaCO_3$. The increase in pure water flux was observed when the concentration of Na_2CO_3 was high enough. Feng et al. (2006) reported that the increase of *n*-butyric acid concentration in the precipitating bath prolonged demixing time, i.e. induced liquid/liquid delayed demixing or postponed solidification time. The formation of large cavities in the sublayer was inhibited due to this addition.

3.1.1.6. Coagulation bath temperature

An increase in gelling bath temperature usually offers more productive membranes, but at the same time rejection decreases. Sabde et al. (1997) studied that increase in the gelation bath temperature improved water permeation rate due to a faster rate of gelation, wherein water diffuses into the nascent film at a faster rate creating more open channels. Productivity of the membrane was found to be almost double with every 15 °C rise in the temperature of gelling bath. Change of coagulation temperature also showed impact on exchange rate of solvent and nonsolvent [Feng (2006)]. Increase on the coagulation temperature within a lower range (< 40 °C) enhanced mobility of macromolecule chains, consequently promoting disentanglement process, which was favorable to the growth of the top layer pores [Feng (2006)]. It was observed that the flux of poly(ethersulfone) membranes was higher when temperature of gelation bath was 4 °C than the membrane made at the ambient temperature [Rana (2006)]. Retention of Dextran T250 and tensile strength of membrane increased while the temperature of the precipitation bath decreased [Scharnagl (2001)].

3.1.1.7. Support material

Most of the UF membranes used for large scale applications are prepared using porous support fabric. The properties of such supports, e.g. material of construction, porosity, surface properties, etc. could affect properties of the UF membrane. During the membrane preparation, the coating of dope solution on such fabric would involve certain aspects such as intrusion depth by the solution, compatibility of coating solution with the support, etc., which could be crucial in dictating the resulting membrane porosity. The material of support may play a role while deciding the applicability of membranes prepared using these supports. This issue is weakly addressed in the literature. The effect of certain preparative parameters on the structure, porosity and UF membrane performance was studied by Munari et al. (1990). Membranes with support and without support showed different performance, and the earlier type exhibited additional pores due to stretches. Daisley et al. (2006) reported that use of polypropylene support showed no adverse affects with NaOH, minor affect with 10 wt. % phenol and minor to moderate affect with HCl.

Above literature reports indicate that the membrane performance is highly dependant upon membrane preparation parameters, viz., polymer concentration, solvent, additive in the dope solution, coagulation bath composition and its temperature and support material. Effect of these parameters is widely reported with poly(sulfone) or poly(ethersulfone) as the UF-membrane materials. A systematic optimization of these parameters leads to a membrane with improved performance in terms of flux and rejection. Some of such investigations for PAN as a material though are reported in the literature, a thorough investigation interlinking effects of these parameters for a PAN of same properties (origin, molecular wt., etc.) are not documented. Present study focused on analyzing membrane properties, while aiming at certain MWCO that would reject pathogenic species. The objective of this work was to prepare a membrane with improved flux with ≥ 90% BSA rejection. The BSA rejection was set as the criteria based on our previous study which showed that the membrane with BSA rejection of > 90% exhibit excellent capability of virus rejection (5-log) from the drinking water [Vaidya (2004)].

3.2. Experimental

Polyacrylonitrile (PAN) was received from IPCL, Vadodara (MW 75000 $g.mol^{-1}$). The nonwoven polyester fabrics, Viledon - H3160 and H1006 were procured from Frudenberg (Germany); Hollytex - 3329, 3324 and 3265 from Ahlstrom (USA); while woven PES-111 was procured from Frank Industrial Corporation (Baroda, India). The properties of these materials as supplied are given in Table 3.1. Citric acid (CA), maleic acid (MA), tartaric acid (TA), poly(acrylic acid) (mol. wt.: 2000), *N,N*-dimethyl formamide (DMF), *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethyl acetamide (DMAc), *N,N*-dimethyl sulfoxide (DMSO), and potassium iodide (KI) (all AR grade) were procured from Merck-India, hydrochloric acid (HCl), barium chloride ($BaCl_2$, AR grade) and iodine (I_2, AR grade) from SD Fine Chemicals, zinc chloride ($ZnCl_2$, GR grade) from Loba Chemie, while isobutanol was obtained from Qualigens Fine Chemicals. Bovine serum albumin (BSA, faction-V), lysozyme, ovalbumin (grade-V) and potassium bromide (KBr) were obtained from Sigma Chemicals, (USA); while trypsin (from bovine pancrease) and pepsin were obtained from SRL Chemicals (India). The DMF was dried using 4A- molecular sieves, while $ZnCl_2$ was purified by melt process. All other chemicals were used as received. The feed spacer (LWS netting, 020″ thick, 16 strands per inch, 50″ width) was procured from Nalle Plastics Inc. (USA), while permeate spacer (Tricot Tt 20Ea, 40″ width) was from Hornwood Inc. (USA). The polyurethane glue (Grade UR – 3501- part A and B) was procured from ASC export (USA). Organic acids were vacuum dried at 60 °C for 24 hours, while $ZnCl_2$ was fused at 400 °C. KBr was dried in vacuum oven at 80 °C for 24 hours before FT-IR analysis. The Milli-Q water with 18.3 mΩ.cm resistivity was used for all solution preparation, flux and rejection analysis.

3.2.1. Determination of porosity of support material

Porosity of the support used was determined using the Eq. 3.1 [Wang (1998b)].

$$\text{Bulk porosity}\,(\%) = \frac{V_m - V_p}{V_m} \times 100 = \frac{D \times A - \left(W_m / \rho_p \right)}{D \times A} \times 100 \tag{3.1}$$

where, V_m is the volume of the sample (equals to D × A) and V_p is the volume occupied by the polymer (equals to W_m/ρ_p), A is the coupon area having thickness D and mass W_m of the support material, ρ_p is the density of the polyester (material of construction for fabric).

3.2.2. Water holding capacity of support and membrane

The support and membrane samples of 5 × 5 cm size were immersed in water for 24 hours and weighed. These samples were kept in vacuum oven at 60 °C for 24 hours and again weighed. The water holding capacity was calculated by following Equation [Tamura (1981)].

$$\%\ \text{Water content} = \frac{\text{Wet sample weight - Dry sample weight}}{\text{Wet sample weight}} \times 100 \tag{3.2}$$

3.2.3 Membrane Preparation

Flat sheet PAN based UF membranes were prepared using H1006, H3160, 3324, 3329, 3265 and PES-111 as the porous support. The properties of these support materials are given in Table 3.1. A dope solution containing desired amount of PAN powder and 4 wt. % of additive ($ZnCl_2$, MA, CA, TA and PAA_{2k}) in a desired solvent (DMF, DMAc, DMSO, NMP) was prepared while stirring for 48 hours under dry conditions. The viscosity of the dope solution was measured using Brookfield viscometer (Model DV-I) at 10 rpm. The formed dope solution was degassed and then centrifuged at ~ 2700 rpm for 3 hours. The membrane was casted on a moving nonwoven support fabric using pilot scale continuous membrane casting facility at 20 °C gelation temperature and 40 °C curing temperature. The photograph of the casting machine used for membrane preparation is shown in Figure 3.1. The formed membrane had an average thickness of ~ 250 μm and was stored with aq. formalin solution (0.5%) at 4 ºC until further use. These membranes were designated as PAN_x, where, the subscript 'x' denotes the polymer concentration used in the dope solution.

Table 3.1 Support material properties.

Support fabric	**Weight ($g.m^{-2}$)**	**Thickness (mm)**	**Air permeability**	**Tensile strength**	**Elongation (%)**	**Water holding capacity (wt. %)***	**Bulk porosity of support (%)***
H3160	60	0.07	30 ($dm^3.s^{-1}.m^{-2}$) (at 2 mbar)	210 N/50 mm	22	23.08	41.77
H1006	75	0.11	70 ($dm^3.s^{-1}.m^{-2}$) (at 2 mbar)	125 N/50 mm	15	38.58	53.68
3329	96.5	0.13	5.1 cfm	CD 28 $lbs.in^{-1}$ MD 55 $lbs.in^{-1}$	CD 72	24.15	49.57
3324	99.9	0.13	9 cfm	CD 28 $lbs.in^{-1}$ MD 60 $lbs.in^{-1}$	CD 80	29.12	47.79
3265	81.2	0.13	20 cfm	CD 21 $lbs.yd^{-2}$ MD 65 $lbs.in^{-1}$	CD 70	28.26	57.56
PES-111	112.6	0.18*	8-10 cfm	NA	NA	28.05	56.13

*: The data generated as given in Section 3.3.4, NA: Not available

Figure 3.1 Continuous membrane casting machine.

3.2.4. Flux and rejection analysis

3.2.4.1. Flux analysis

Water flux of membranes was measured using either Amicon type cell in a dead end mode (11 cm^2 active area) and/or rectangular cell (191 cm^2 active area) in a cross flow mode at 1 bar pressure. The photograph of the dead end and cross flow cell assembly is shown in Figure 3.2 and 3.3b, respectively. Initially, 100 ml of deionized (DI) water was allowed to permeate through the membrane in order to remove the formalin and then the water flux was measured.

Figure 3.2 Dead end cell assembly

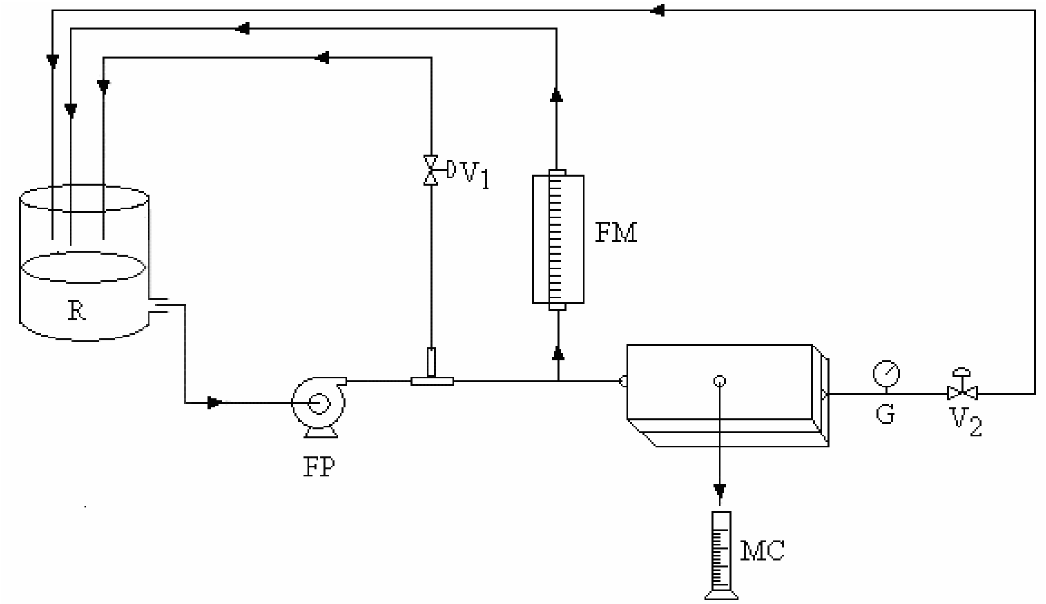


Figure 3.3a Schematic of cross flow setup; R: reservoir, V_1 and V_2: control valves, G: pressure gauge, FP: feed pump, FM: flow meter, MC: measuring cylinder.

Figure 3.3b Cross flow cell assembly.

3.2.4.2. Protein rejection

The rejection analysis of proteins with different molecular weight (0.1% concentration in the feed) was performed at pH 7.5 using McIlvaine buffer (0.1M citric acid and 0.2M disodium hydrogen orthophosphate) in dead end mode. For 100 ml buffer solution, 92.25 ml 0.2M Na_2HPO_4 and 7.75 ml citric acid was mixed. The protein concentration in the feed and permeate was analyzed at 280 and 260 nm wavelength [Jayaraman (1981)] by the double beam UV spectrophotometer (Chemito, Spectrascan UV 2700) using Equation 3.3.

$$\text{Protein concentration} = (1.55 \times A_{280}) - (0.76 \times A_{260}) \tag{3.3}$$

The percent rejection (%R) was calculated by using Equation 3.4.

$$\% \mathrm{R} = \left[1 - \left(\frac{C_p}{C_f}\right)\right] \times 100 \tag{3.4}$$

where, C_p is concentration of the permeate, while C_f is the feed concentration.

3.2.4.3. Bacteria rejection analysis

Escherichia coli (E. coli) NCIM 2067 was used as the test organism for the microbiological evaluations. Bacteria were grown overnight on nutrient agar at 37 °C. For flat sheet membrane analysis, the concentration of *E.coli* culture used in feed was ~ 10^6 CFU/ml. The feed, permeate and retentate samples from permeation experiments using flat sheet and spiral modules were collected in sterile sampling bottles and the count of bacteria was tested by using multiple tube fermentation test (MPN/100 ml water sample) as described in Standard methods of water and wastewater analysis [Greenberg (1992)].

3.2.5. Analysis of bubble point and pore size distribution

3.2.5.1. Bubble point analysis

The maximum pore size of the membrane was determined by the bubble point method using water (σ - 76 dyne.cm^{-1}) or isopropyl alcohol (σ - 21.78 dyne.cm^{-1}) and air. The continuous flow of air was measured through the prewetted membranes. The pore size was calculated using Cantor's Equation 3.5 [Mulder (1998), Capannelli (1983)].

$$r_{P_i} = \frac{2\sigma\cos\theta}{P_i} \tag{3.5}$$

3.2.5.2. Pore size distribution analysis

Membrane porosity was determined by the liquid-liquid displacement technique using water saturated isobutanol/water as the solvent pair (surface tension, σ = 1.7 dyne.cm^{-1}). The pore size and pore density were calculated using Cantor's Equation 3.5 and Hagen-Poiseuille's Equation 3.6 [Capannelli (1983)].

$$n_i = \left(J_i - \frac{J_{i-1}\, p_i}{P_{i-1}}\right)\frac{8\eta\ell}{\pi\, P_i\, r_{p_i}^4} \tag{3.6}$$

where, r_{pi} is the radius of the pore, θ is the polymer-water contact angle, n_i is the number of pores per unit area, η is the viscosity of water, *l* is pore length that is assumed to be equal to the membrane skin layer thickness of 1 μm and J_i corresponds to the flux measured at the ith increment where the applied pressure is P_i.

3.2.6. Compaction pressure of membranes

The schematic diagram of cross flow set up used for the determination of membrane compaction pressure is shown in Figure 3.3a. The membrane was mounted in the cross flow UF cell. The DI water at 0.6 lit.min^{-1} was fed to the cell with an incremental rise in pressure. Membranes were allowed to equilibrate with the pressure at 30 minute before the flux was recorded at a particular pressure. In all the cases, though a steady flux was obtained after ~ 2.5 hours, the flux at the 4th hour was recorded as the flux at that applied pressure. At least three coupons were analyzed for each membrane and the data averaged.

3.2.7. Membrane resistance

To determine the membrane resistance (R_m), pure water flux (J_w) was measured using dead end set up at various transmembrane pressures (ΔP) before compaction pressure. The membrane resistance (R_m) was determined as the inverse of slope of the graph of transmembrane pressure vs water flux using Equation 3.7 [Kesting (1971)].

$$R_m = \frac{\Delta P}{J_w} \tag{3.7}$$

3.2.8. SEM analysis

The membrane cross sections were investigated by Scanning Electron Microscopy (SEM), Leica, Stereoscan, 440. The membrane specimen were dried by sequential solvent exchange (dipped in IPA for 24 hour then in hexane for 24 hours), fractured at liquid nitrogen temperature and then dried in vacuum oven at 40 °C for 24 hours. These samples were coated with gold by sputtering. The gold layer of ~ 30 nm was deposited on the samples.

3.2.9. FT-IR analysis

FT-IR spectra were recorded on Perkin Elmer 16 PC FT-IR. The KBr pelletes containing organic acid (CA, MA. TA) and $ZnCl_2$ powder (~ 16 mg in 85 mg KBr) were prepared using KBr presser. The spectra were recorded after drying these pelletes in vacuum oven at 60 °C for 24 hours to remove adsorbed moisture during its preparation. The additive concentration used in the dope solution was 4% (w/w), thus the FT-IR analysis was done with the same composition of additive and solvent. For recording the spectrum, a small drop of solution was placed and spread evenly in between KBr pellets (single crystal). These spectra of pure DMF and pure acids were compared with the additive solution prepared in DMF.

3.2.10. Spiral preparation and analysis

3.2.10.1. Double leaf spiral module preparation

Spiral modules were constructed using flat sheet PAN_{16} membranes prepared using DMF as a solvent, $ZnCl_2$ or citric acid (CA) as an additive and Viledon H1006 as a porous support. The flat sheet membrane was prepared by following same procedure as described in Section 3.2.3. The feed spacer used was 30″ in length and 14″ in width, while permeate spacers with 31″ and 36″ in length and 14″ in width. The permeate spacer with 31″ piece was stitched to 36″ piece by leaving initial 5″ space to match one end of both the spacer with each other. The flat sheet membrane was cut into two pieces of 58″ length. The defects (pinholes/fish eyes if any) were marked/encircled with the marker and to that area, the PU glue was applied on the permeate side of the membrane. The membrane pieces were folded in such a way that feed side faces each other. One piece of the membrane was folded at 29 - 29″ and other piece at 28 - 30″ mark. The feed spacer was inserted into each membrane leaf. The permeate spacer was glued on the permeate tube at the edges. The permeate tube with the length of 14″, OD of 22 mm and ID of 16 mm was used. This tube was perforated after the 5th inch from beginning of the tube and at a distance of 1½″. The membrane leaves along with permeate space were glued at three edges. The PU glue (thoroughly mixed 70 g of part A and 35 g of part B was used). Initially, the glue was applied to the edges (1″ inside) of permeate spacer and wound upto 6″ by using winder assembly (Figure 3.4) and then gluing continued till end of the permeate spacer. The membrane leaves along with feed spacer were inserted in the permeate spacer and wound till 6″ remained. Then the glue was applied to the horizontal side of the permeate spacer and the backside of the membrane. The winding was continued till the end. The cellophane tape was wound all over the length of the spiral. These spirals were kept for 24 hours to cure the glue. The edges were cut so that the feed channels open up clearly. One side of the permeate tube was plugged. The schematic of spiral is shown in Figure 3.5.

The formed spiral was fitted into a tubular PVC casing with the end pieces which provides feed, reject and permeate streams to the resulting module. The PVC pipe with ID 56 mm, OD 63 mm and pressure withstand capacity of 7 bar was used to prepare casing. The end pieces were used to seal permeate and feed side against each other with the help of 'O' rings. The anti telescoping device (ATD) was used at both ends to prevent distortion of the spiral during operation. The side connector of the centre plugged end was used as the retentate side, the centered connector of the second cap acts as permeate while side connector acts as feed. At the reject side, the throttling valve was used in order to control the pressure.

Figure 3.4 Spiral winder assembly.

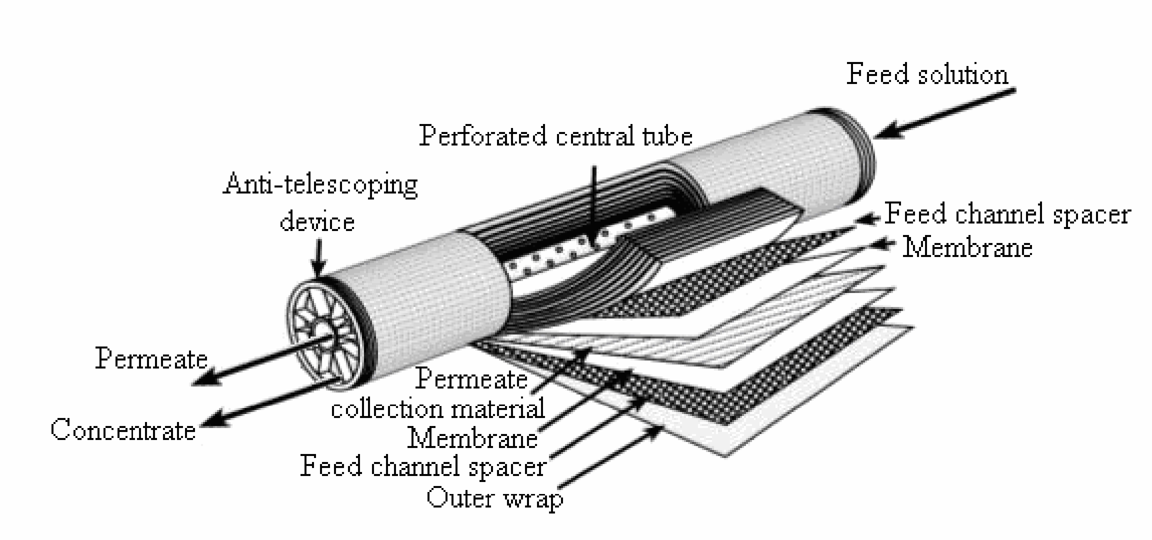


Figure 3.5 Spiral wound module.

3.2.10.2. Water flux analysis of spiral modules

Water flux of the spiral wound modules (using DI water) was measured in dead end mode at 1 bar transmembrane pressure. The spiral module was mounted vertically, where the feed and permeate side was at the bottom. The module was initially washed by passing ~ 1 lit. of water through permeate side before recording the flux.

3.2.10.3. Bubble point analysis of spiral modules

The water/air bubble point of spiral wound module was measured using the assembly as given in Section 3.2.5.1.

3.2.10.4. BSA rejection analysis of spiral modules

The rejection analysis of spiral wound modules was done by using BSA (0.1% w/v concentration in feed) in cross flow mode. The pressure used for modules prepared with membranes based on $ZnCl_2$ as an additive was 1 bar, while the same for CA based spirals was 0.3 bar. The procedure for BSA analysis is similar to as described in Section 3.2.4.2.

3.2.10.5. Bacteria rejection analysis of spiral modules

The bacteria *(E. coli)* rejection analysis of spiral wound modules was performed using 1100 CFU/ml and 100 CFU/ml feed concentration in cross flow mode at 0.7 pressure with 0.3 lit. min.$^{-1}$ retentate flow rate. The detail analysis protocol is given in Section 3.2.4.3.

3.3. Results and discussion

3.3.1. Effect of polymer concentration in dope solution

DMF was used as the solvent and $ZnCl_2$ as an additive for investigating effect of variation of the PAN concentration in the dope solution. Membranes were prepared with 15, 17, 18.5, 20, 20.5, 21.5, 23, 25% (w/w) concentration of PAN in the dope solution under identical casting conditions of 20 °C gelation temperature, 8 second air dry time, 40 °C curing bath temperature and Viledon H1006 as the porous support. As expected, increased PAN concentration in the dope solution led to an increase in dope solution viscosity and decrease in water flux (J_w), as shown in Figure 3.6. Up to 20% PAN concentration in the dope, decrease in J_w was sharper, after which, increase in concentration showed comparatively smaller effect on J_w.

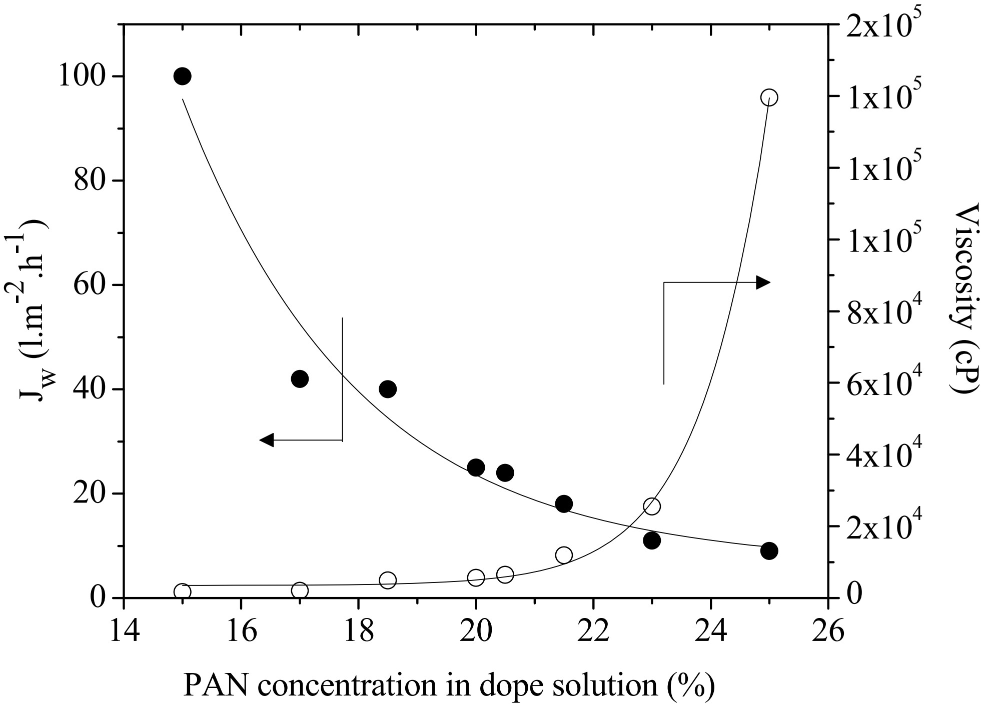
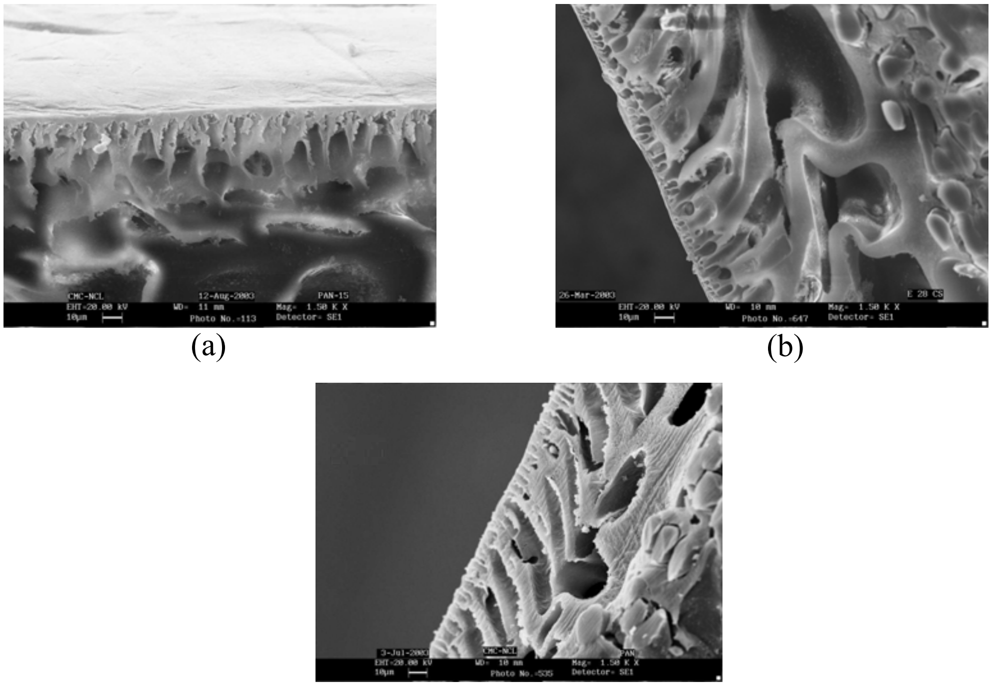


Figure 3.6 Effect of PAN concentration on water flux (•) and dope solution viscosity (o).

The largest pore size as analyzed by bubble point measurement (IPA/air pair, Table 3.2) showed that till the dope solution concentration of 20.5%, size of the largest pore decreased continuously with the increase in concentration. Beyond 20.5% concentration, the pore size was again found to be increased. This increase in pore size and decrease in water flux beyond 20.5% concentration was a result of decrease in pore density. Figure 3.7 shows SEM images of (a) PAN_{15}, (b) PAN_{17} and (c) PAN_{20} membranes with same magnification (1.5 k). It could be seen that PAN_{17} and PAN_{20} membranes exhibited denser skin layer as compared to PAN_{15} membrane. Similar observations were noted by Ahmad et al. (2005). It is stated that an asymmetric membrane with a thin and porous skin layer and open cell sublayer was prepared by a polymer solution with a lower concentration. It is evident from the SEM that the macrovoids were suppressed as the polymer concentration in the dope increased.



(a) (b)

(c)

Figure 3.7 SEM images of cross section of (a) PAN_{15}, (b) PAN_{17} and (c) PAN_{20} membranes prepared using $ZnCl_2$ as an additive.

The protein rejection of these membranes also supported the findings of the bubble point analysis (Table 3.2). The water/air bubble point of PAN_{15} membrane was 2.7 bar and for membranes prepared with higher dope solution concentration it was > 4 bar. For the detection of larger pores at lower pressure low surface tension liquid (IPA) was used. PAN_{15} showed 2.7 bar bubble point determined by using water/air pair, which was reduced to 1.4 bar by using IPA/air pair. Upto $PAN_{20.5}$ the membrane showed good control on porosity and above this concentration, the membrane showed macrovoid formation. The rejection of pepsin (protein with lowest molecular weight among investigated) for $PAN_{20.5}$ membrane was highest than for all other membranes. This is in agreement with the lowest pore size of this membrane as observed by bubble point measurement. Protein rejection analysis also reveals that PAN_{15} and PAN_{17} membranes exhibited MWCO of ~ 68 kDa, while all other membranes have MWCO between 43 and 33 kDa. This indicated that merely increasing polymer concentration in the dope solution does not necessarily lead to lowering of the pore size.

Table 3.2 Rejection and bubble point analysis of membranes prepared while varying PAN concentration in the dope solution ($ZnCl_2$ as an additive and H1006 as the support).

PAN concentration (%)	R_{pepsin} (%)	$R_{ovalbumin}$ (%)	R_{BSA} (%)	Bubble point (bar) IPA/air	Pore size (cm)
15	59	64	98	1.4	3.14×10^{-5}
17	57	82	96	2.1	2.09×10^{-5}
18.5	66	93	95	2.5	1.75×10^{-5}
20	57	93	95	4.5	9.76×10^{-6}
20.5	78	94	97	6.9	6.37×10^{-6}
21.5	67	95	-	5.4	8.14×10^{-6}
23	71	93	-	3	1.46×10^{-5}
25	63	96	-	3.8	1.15×10^{-5}

3.3.2. Effect of organic additives on PAN_{13} and PAN_{15} membrane

Use of additives in the casting solution is one of the efficient ways to control pore formation in the membrane. Various types of additives are demonstrated in the literature including inorganic salts [Lee (2002), Kim (1996)], low molecular weight organics [Feng (2006), Chuang (2000)], polymer [Chou (2007), Jung (2004)], etc. There are different mechanisms through which such additives can affect the resulting membrane porosity via changing solvent capacity, precipitation kinetics and thermodynamic properties associated with membrane formation. Solvents commonly used for UF membrane preparation are DMF, DMAc and NMP, which are basic in nature. The –COOH group of the organic acid is anticipated to have strong H-bonding interactions with these solvents [Jung (2004)]. It was thought to use common organic acids (having two or more –COOH functionality) as an additive in the dope solution and to analyze their effect on pore formation and thus water flux and BSA rejection performance. PAN_{13} and PAN_{15} membranes were prepared while using DMF as a solvent and 3265 and H1006 as a support material. The capability of organic acids as an additive in the dope solution towards flux enhancement vis-à-vis $ZnCl_2$ as an additive was investigated. The membranes prepared with $ZnCl_2$ as an additive was assumed as the base case since membranes prepared with this additive were shown to have excellent combination of flux and rejection performance [Vaidya (2004), Shinde (1999)]. Organic acids having two or more –COOH functionality and those are water soluble were chosen as additive in the dope solution.

Membranes casted with various additives and 15% PAN concentration in the dope solution showed higher viscosity for CA as compared to MA, TA, PAA_{2k} and $ZnCl_2$ as an additive (Table 3.3). The membranes prepared with organic acid additive showed higher water flux than membranes casted with $ZnC1_2$ as an additive without a large change in BSA rejection (Table 3.3). In present case, CA and TA as an additive offered in general higher flux and thus act as the better pore former during the immersion precipitation. On the basis of these results, the reduction of PAN concentration in the dope solution was studied in presence of these additives. Table 3.4 shows that even after the PAN concentration was reduced to 13%, CA or TA works as a better additive, since membranes based on them showed higher water flux and acceptable BSA rejection.

In general, the membranes casted on 3265 support showed higher water flux and wider BSA rejection than membranes casted on the H1006 support. This difference could be attributed to the porosity of these support fabric as given in Table 3.1, more open structure of 3265 support offered less resistance to the penetration of polymer solution into the pores of support during casting. In present case, CA and TA as an additive offered in general higher flux without sacrificing BSA rejection for both 13 and 15% PAN concentration in the dope solution.

Table 3.3 Variation in membrane properties prepared using different additives and PAN_{15} concentration in the dope solution.

Additive used	Dope solution viscosity (cP at 10 rpm)	3265 as support material		1006 as support material	
		J_w ($l.m^{-2}.h^{-1}$)	R_{BSA} (%)	J_w ($l.m^{-2}.h^{-1}$)	R_{BSA} (%)
None	1015	881	42-82	333	90-94
$ZnCl_2$	1270	*	*	84	97
MA	825	426	91	180	100
CA	1442	432	96	152	100
TA	988	441	95	172	93
PAA_{2K}	1336	380	94	210	94

*: Membranes not prepared

Table 3.4 Variation in membrane properties prepared using different additives and PAN_{13} concentration in the dope solution (support used: 3265).

Additive used	Dope solution viscosity (cP at 10 rpm)	J_w ($l.m^{-2}.h^{-1}$)	R_{BSA} (%)
None	305	1026	76-80
$ZnCl_2$	472	460	89
MA	295	533	86
CA	645	661	92
TA	491	1030	93
PAA_{2K}	310	612	95

3.3.2.1. Interactions between additive and solvent

The complex formation between additive and solvent was studied by FT-IR analysis. The characteristic IR bands for the neat DMF arise from >C=O stretching (1676 cm^{-1}) [Jacob (2000)], O–C–N stretching (1400 cm^{-1}), and O–C–N bending (620 cm^{-1}) vibrations [Waghorne (1982)]. FT-IR spectra of neat DMF and solutions of additive in DMF are shown in Figure 3.8. The changes in these frequencies are given in Table 3.5.

The >C=O stretching frequency in neat DMF was observed at 1670 cm^{-1}. After addition of organic acids (MA, CA, TA) and $ZnCl_2$ in DMF, this frequency was increased as given in Table 3.5. The increase in >C=O frequency for CA and TA additive was high as compared to the $ZnCl_2$ additive. This increase in frequency indicates strong interactions between these additives with DMF than that of solvent and $ZnCl_2$. Jacob et al. (2000) and Wang et al. (1996) reported strong interactions between inorganic salt and DMF, leading to the increase in >C=O frequency. The O–C–N stretching frequency which appeared at 1392 cm^{-1} in neat DMF remained almost unchanged after the addition of organic acids as well as $ZnCl_2$ in DMF. The O–C–N bending frequency in neat DMF was also remained almost unchanged in case of organic acids as an additive. The broad peak at 3200 - 3500 cm^{-1} is a characteristic peak of –OH group in acids [Silverstein (2002)]. FT-IR spectra of dried organic acid powders were recorded and the shift of –OH peak was observed after dissolving these acids into DMF. In present case, a strong blue shift was observed in –OH peak as given in Table 3.5. This blue shift in frequency suggests strong interactions between –OH of the acid with basic solvent DMF leading to considerable increase in the –OH frequency. In case of $ZnCl_2$ in DMF, the peak appeared at 3558 cm^{-1} which is attributable to the presence of moisture.

Table 3.5 Change in FT-IR frequencies of additives after complexation with solvent.

	>C=O frequency (cm^{-1})	**O–C–N stretching frequency (cm^{-1})**	**–OH frequency (cm^{-1})**
Pure DMF	1670	1392	-
MA	-	-	3385
CA	-	-	3460
TA	-	-	3325
MA in DMF	1695 (+25)	1393 (+1)	3551 (+166)
CA in DMF	1693 (+23)	1393 (+1)	3551 (+91)
TA in DMF	1672 (+2)	1393 (+1)	3499 (+173)
$ZnCl_2$ in DMF	1686 (+15)	1391 (-1)	-

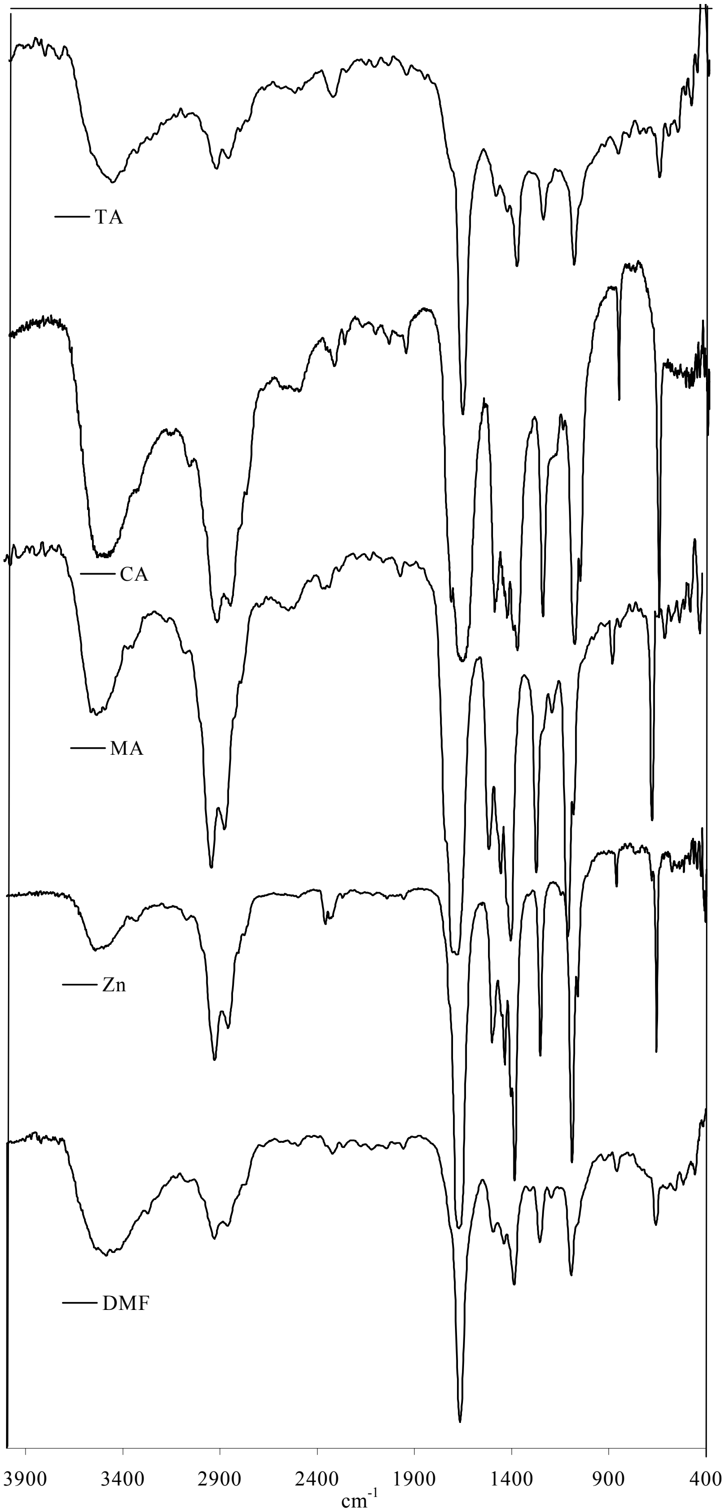


Figure 3.8 FT-IR analysis of organic acid additives (MA, CA, TA) and $ZnCl_2$ solution in DMF.

3.3.2.2. Spiral analysis

The spiral wound module prepared using PAN_{16} membranes prepared with $ZnCl_2$ and CA as an additive showed water flow rate of 21.2 and 37.4 lit. hr.$^{-1}$, respectively. The higher flow rate for the spiral prepared with membrane based on CA additive was attributable to the high flux of these membranes as observed with flat sheets (discussed in Section 3.3.2). Though the bubble point of these spirals was lower, they possessed satisfactory BSA rejection of > 90%. The spiral module prepared with the membrane using CA additive showed less variation in flow rate, bubble point and BSA rejection analysis. In view of these observations, it was thought to analyze both type of modules for bacteria rejection analysis.

Table 3.6 Analysis of spiral wound module.

PAN_{16} Membrane prepared with additive	**Flow rate (lit.hr^{-1})**		**Bubble point**		**BSA rejection (%)**		**No. of spirals analyzed**
	Average	**Variation (%)**	**Average**	**Variation (%)**	**Average**	**Variation (%)**	
$ZnCl_2$	21.2	20	3.2	21.6	86	1.4	12
CA	37.4	13.4	0.8	12.6	92	0.5	7

3.3.2.3. Bacteria rejection analysis of flat sheet and spiral module

Prior to bacteria rejection analysis on spiral level, it was thought to analyze flat sheet membranes prepared with $ZnCl_2$ and CA additives. The analysis was carried out in a stirred cell assembly. The disinfection of the assembly, requisite glassware as well as DI water was done by autoclaving at 15 psi pressure and 121 °C for 20 min. For the flat sheet analysis, the concentration of bacteria chosen was higher. The main emphasis here was to evaluate log reduction value (LRV, as calculated by Equation 3.8 below [Cheryan (1998)] for both the types of membranes.

$$\mathrm{LRV} = \log_{10}\begin{pmatrix}\text{Concentration of} \\ \text{cells in the feed}\end{pmatrix} - \log_{10}\begin{pmatrix}\text{Concentration of} \\ \text{cells in the permeate}\end{pmatrix} \qquad (3.8)$$

E. Coli solution with the concentration of 10^6 CFU/ml was charged to the membrane and the permeate was collected at 0.5 bar feed pressure. The pressure was kept low in order to avoid pressure effects on bacteria survival. Experiment repeated thrice with fresh membrane samples. The analysis of the permeate samples for the presence of bacteria in it was done as described in Section 3.2.4.3. It was found that no bacteria was present in any of the permeate sample, accounting to the LRV of 6. Since this value is sufficient for the membrane to be used for drinking water application, it was decided to analyze spiral modules also based on these membranes. For spiral analysis, the assembly and the spiral module was initially disinfected by hypochlorite solution (10 ppm) and then with disinfected water to wash off hypochlorite. The bacteria analysis of the spiral modules (prepared using membranes with $ZnCl_2$ and CA additive) was done in cross flow mode at 0.7 bar feed pressure and 1100 and 100 CFU/ml feed concentration. Lower concentration of bacteria solution was used for spiral analysis. As the large volume was required for cross flow system and handling bacteria solution with higher concentration could be difficult. Secondly, in actual practice (epidemic situations, in worst case), the highest bacteria count expected could be much lower than the concentration used for flat sheet analysis. The permeate sample was collected in autoclaved bottle and the analysis was done as described in Section 3.2.4.3. Two modules of each type (membrane with $ZnCl_2$ or CA as additive) were analyzed. Both these types of modules did not show any bacteria in the permeate. Thus these types of membrane modules can be implemented for purification of drinking water, provided further work on the membrane fouling and clean-up protocol is developed, which is a separate study.

3.3.3. Effect of solvent used for dope solution preparation

The effect of solvent (DMF, DMAc, DMSO and NMP) on membranes prepared using different polymer concentration (15, 18.5, 20.5 and 23%) in the dope solution while using $ZnCl_2$ as an additive and Viledon H1006 as a porous support material was investigated. Figure 3.9 shows the water flux of these membranes. It could be seen that the difference in J_w for different solvents decreased as PAN concentration increased and became insignificant at the concentration of 23%. The membrane prepared by using DMF and DMAc as a solvent exhibited similar fluxes at all PAN concentration and were lower as compared to membrane casted using DMSO and NMP as the solvent (Figure 3.9).

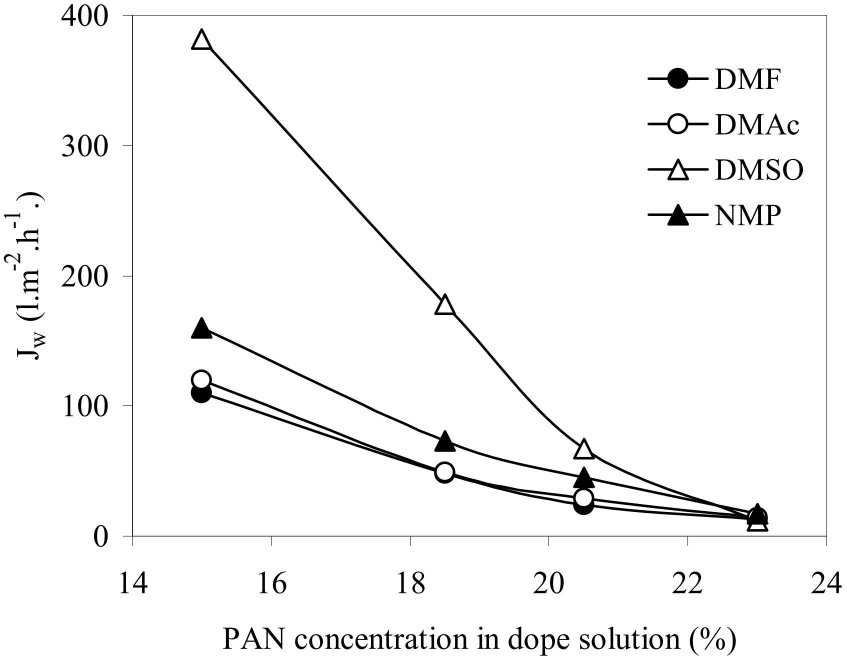


Figure 3.9 Water flux analysis of PAN membrane prepared using different solvents in dope solution.

The diminishing effect of solvent at higher PAN concentration was also reflected in the rejection analysis. The protein rejection (Figure 3.10) shows that except for PAN_{15}, which exhibited MWCO of 68 kDa for all the solvent cases, all other membranes ($PAN_{18.5}$, $PAN_{20.5}$ and PAN_{23}) exhibited MWCO of < 43 kDa. Membranes prepared by using DMSO as a solvent offered higher flux but the rejection performance for different proteins was lower as compared to other membranes prepared using solvents, for all polymer concentrations (Figure 3.10). This clearly indicated that DMSO casted membrane has poor control on porosity. It is reported that the difference in membrane performance by changing solvent for the casting solution was due to the affinity between the solvent and water (nonsolvent) [Rana (2006)]. In present case, NMP as a solvent offered higher flux as well as appreciable rejection for all membranes prepared by varying polymer concentration and acted as a better solvent. This is also observed by

Rana et al. (2006) in case of poly(ethersulfone) membrane. It was concluded that the solvent/water affinity or density or both may be the reason for the higher water content of the membranes cast from NMP solvent which shows higher permeation rate.

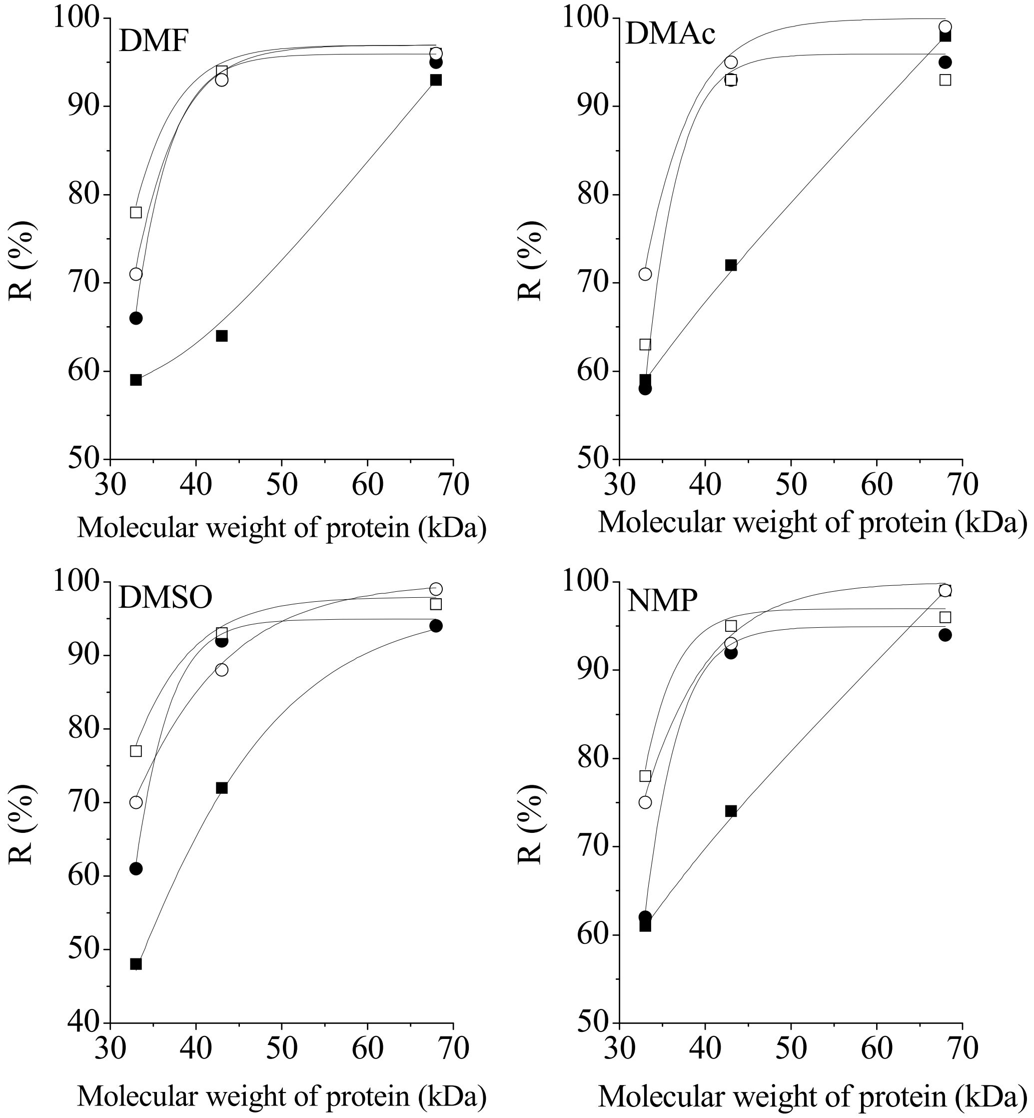


Figure 3.10 Rejection analysis of PAN membrane prepared by varying solvent and polymer concentration in dope solution; PAN_{15} (■), $PAN_{18.5}$ (●), $PAN_{20.5}$ (□), PAN_{23} (○).

3.3.4. Effect of support materials

One of the objectives of the present work was to assess the applicability of various support materials. Membranes were casted on these supports by keeping all parameters viz., dope solution composition (17% polymer concentration, $ZnCl_2$ as the additive and DMF as a solvent), casting conditions including air dry time, gelation and curing time, temperature of respective bath the same. Variation in properties of membranes so prepared thus can be considered to be resulting from the variation in support material used of different origin. The physical properties of support materials used are given in Table 3.1. The thickness for H3160 support was lowest, while for PES-111 it was the highest among the series used, as also reflected by their GSM value. The water holding capacity of all these polyester based supports did not match with the support porosity, probably due to the different processing during their manufacture. The membrane prepared using these supports had a total thickness of 250 ± 25 μm. The macroscopic observation of the membranes prepared using these supports indicate that except for M-3265 and M-111, other membranes did not exhibit noticeable defects. The penetration of the dope solution on the other side of the membrane observed only for M-3265 and M-111, which was more intense for the later case. Intermittent patches showing penetration of dope solution through the pores and the presence of pinholes in these cases indicated that the porosity of this support is higher for the used dope solution viscosity. Though this problem could have been solved by varying membrane casting parameters, was not attempted since the objective was to make the membranes with identical conditions. The membrane samples for further analysis were selected from these membranes such that they contained no defects. SEM analysis (Figure 3.11) of the membrane cross section shows that all these membranes exhibited structure having well defined skin layer on the top as common to UF membranes.

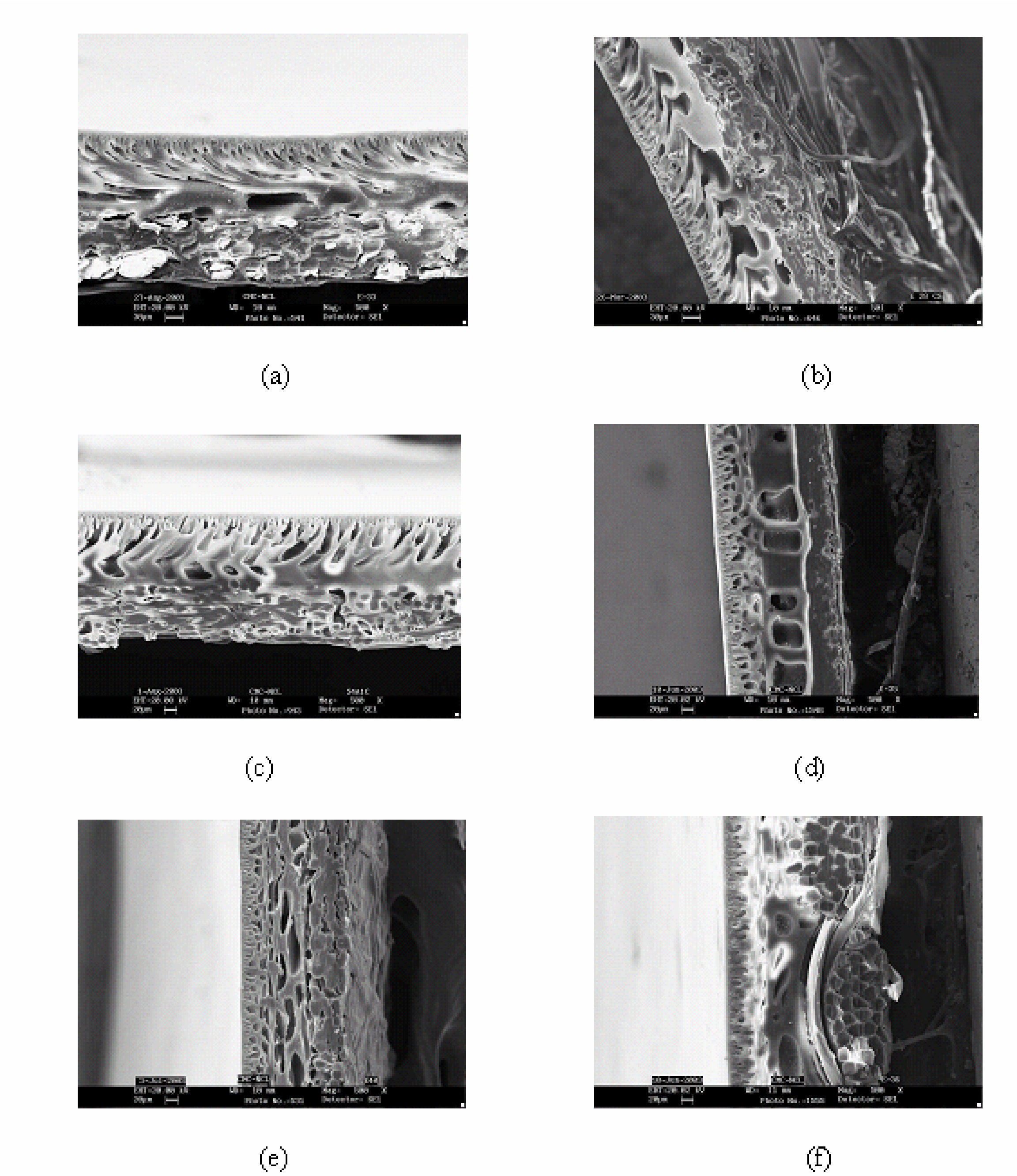


Figure 3.11 Scanning electron micrographs of cross sections of membranes casted on different supports; (a) M-3160, (b) M-1006, (c) M-3329, (d) M-3324, (e) M-3265, (f) M-PES -111.

Table 3.7 Properties of membranes casted on various supports.

Membrane identification	Support used	Physical observation of membrane		Bulk porosity of membrane (%)	Water flux, J_w ($l.m^{-2}.h^{-1}$) at 1 bar				$R_{ovalbumin}$ (%)
					Dead end mode		Cross flow mode		
		Penetration through support	Presence of pinholes		Average ($l.m^{-2}.h^{-1}$)	Variation (%)	Average ($l.m^{-2}.h^{-1}$)	Variation (%)	
M-3160	H 3160	Negligible	No	60.49	36	34	51	-	85
M-1006	H 1006	Negligible	No	61.24	42	26	44	11	82
M-3329	3329	No penetration	No	57.01	70	29	77	7	80
M-3324	3324	No penetration	No	60.42	81	16	76	7	85
M-3265	3265	Very less	Yes	55.4	119	27	152	30	74
M-111	PES-111	Intermittent patches	Yes	57.86	196	29	213	31	53

Water flux (J_w) by dead end mode was lower and exhibited higher variation for different samples than that for cross flow mode, as anticipated (Table 3.7). The J_w for membranes M-3160 and M-1006 was lower, followed by flux for M-3329 and M-3324. The flux for M-3265 and M-111 was on higher side. Though the percent variation in flux looks on higher side for dead end mode, it was lesser for cross flow mode (except for M-3265 and M-111) due to larger membrane area used in cross flow case (17.4 times). The higher variation even in cross flow mode for M-3265 and M-111 could be attributed to the larger pore size variations in these cases. This is evident from the pore size distribution curves (Figure 3.12a and b), which shows that M-3265 and M-111 membranes exhibited wider pore size distribution than other cases. This is further supported by rejection analysis. All the membranes showed > 90% rejection for BSA (Figure 3.13), indicating their MWCO to be less than 68 kDa. An ovalbumin rejection was > 80%, except for M-3265 (74%) and for M-111 (49%).

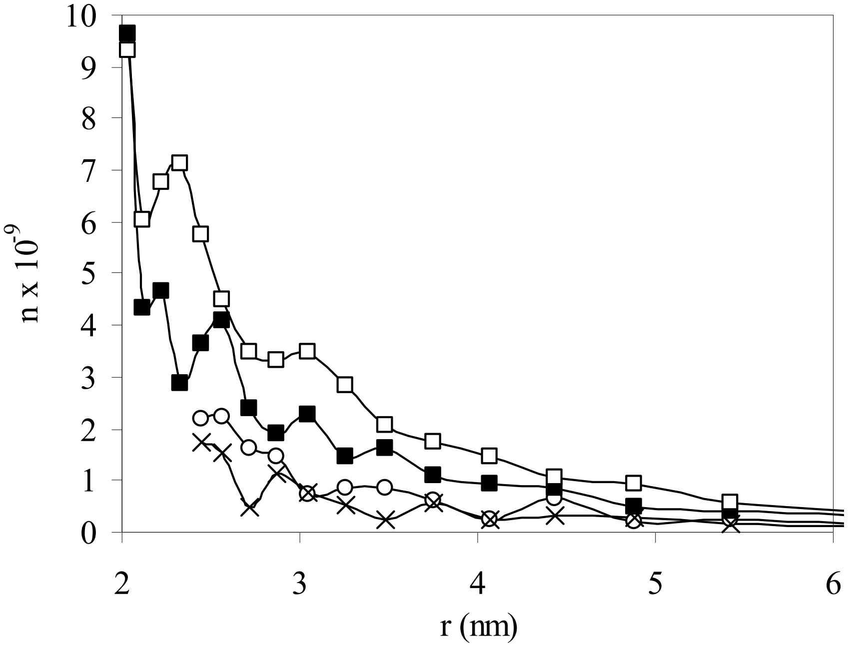


Figure 3.12a Pore size distribution of membranes; –×–: M-3160, –o–: M-1006, –■–: M-3329, –□–: M-3324.

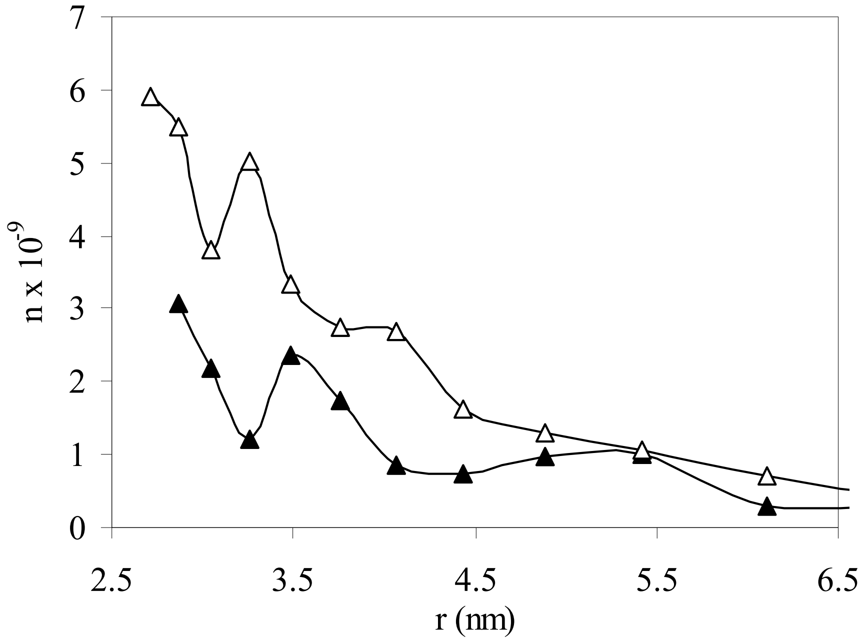


Figure 3.12b Pore size distribution of membranes; –Δ–: M-3265, –▲–: M-111.

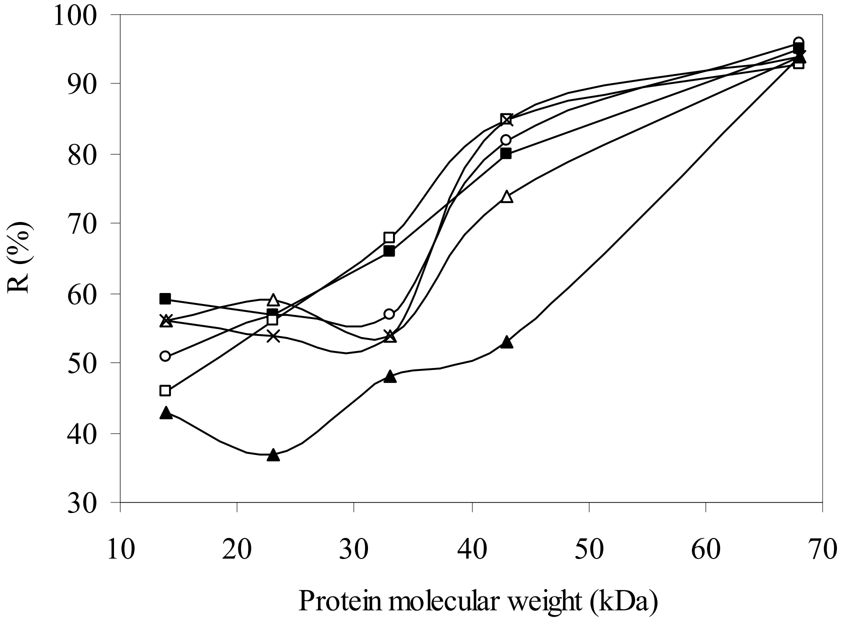


Figure 3.13 Rejection analysis of membranes using proteins of different molecular weight; –×–: M-3160, –o–: M-1006, –■–: M-3329, –□–: M-3324, –Δ–: M-3265, –▲–: M-111.

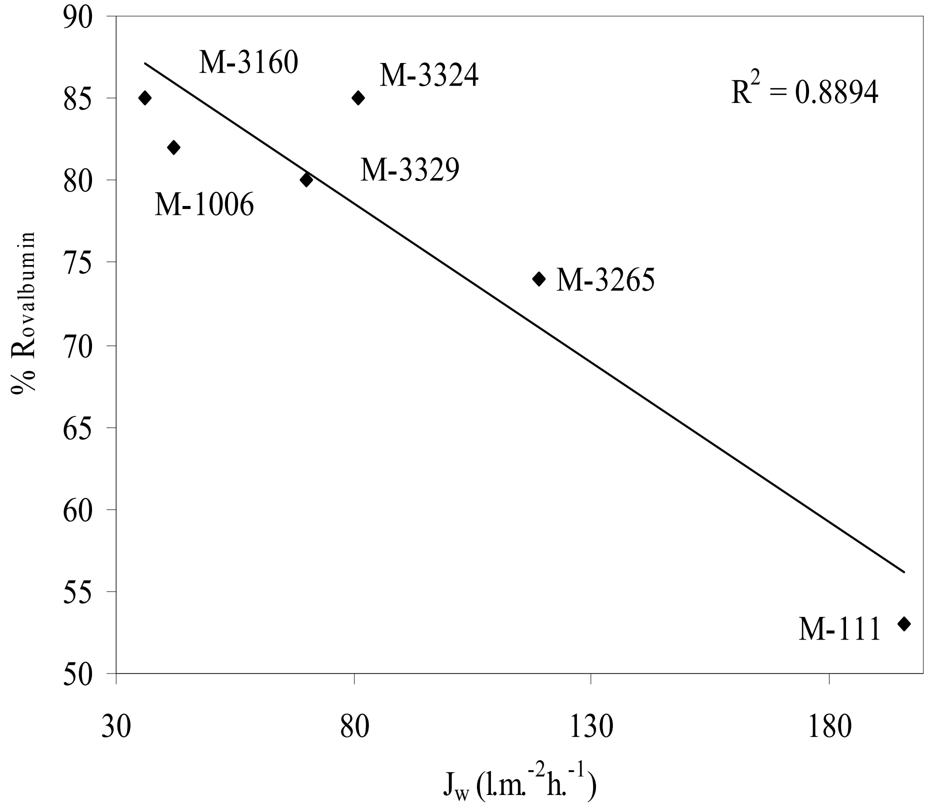


Figure 3.14 Relationship of water flux and ovalbumin rejection for various membranes.

Figure 3.13 shows that rejection of other proteins (pepsin, trypsin and lysozyme) was > 40% for most of the cases at pH of 7.5. A good correlation ($R^2 = 0.89$) was seen between water flux and ovalbumin rejection (Figure 3.14). This showed that though the casting parameters for all these membranes were same, pore size of the membranes casted on different supports are different. The pore size distribution as calculated using Equation 3.6 and plotted in Figures 3.12a and b. Membranes M-3329 and M-3324 showed more number of pores near to smaller pore size of ~ 2 nm. Membranes M-3160 and M-1006 showed their lowest pore size of 2.5 nm. Their pore density and surface porosity was also lower than other membranes. Thus they exhibited lower water flux. In other words, the backing H1006 and H3160 produced tighter membranes. This was also supported by the membrane resistance as given in Table 3.8. Membranes M-3160 and M-1006 exhibited the highest resistance in series. A graph for variation in water flux and ovalbumin rejection with support porosity showed that if PES-111 is neglected, there is increase in permeation and decrease in rejection as support porosity increases (Figure 3.15). Though no correlation was found between membrane bulk porosity (obtained from wet and dry weights) and support porosity, membrane surface porosity increased with the support porosity (Figure 3.16). This observation though looks attractive, other membrane characterization also need to be considered while selecting appropriate backing.

Table 3.8 Membrane properties determined by pore size distribution and compaction analysis.

Membrane	**Pore density (n x 10^{10})**	**Surface porosity (%)**	**Compaction pressure (bar)**	**R_m $Pa.m^{-1}.s^{-1}$**
M-3160	0.7	0.30	4	1.54×10^{10}
M-1006	1.3	0.45	5	1.35×10^{10}
M-3329	7.9	1.55	4	7.54×10^{9}
M-3324	6.8	1.77	5	4.73×10^{9}
M-3265	2.1	1.01	4	4.75×10^{9}
M-111	4.2	1.96	2	2.47×10^{9}

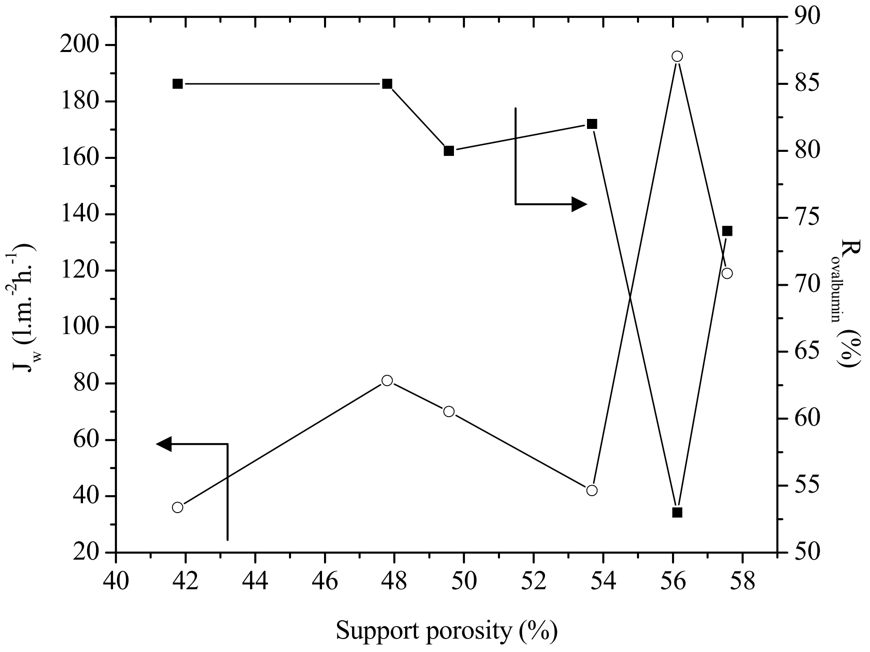


Figure 3.15 Variation in water flux (J_w) and ovalbumin rejection ($R_{ovalbumin}$) with support porosity.

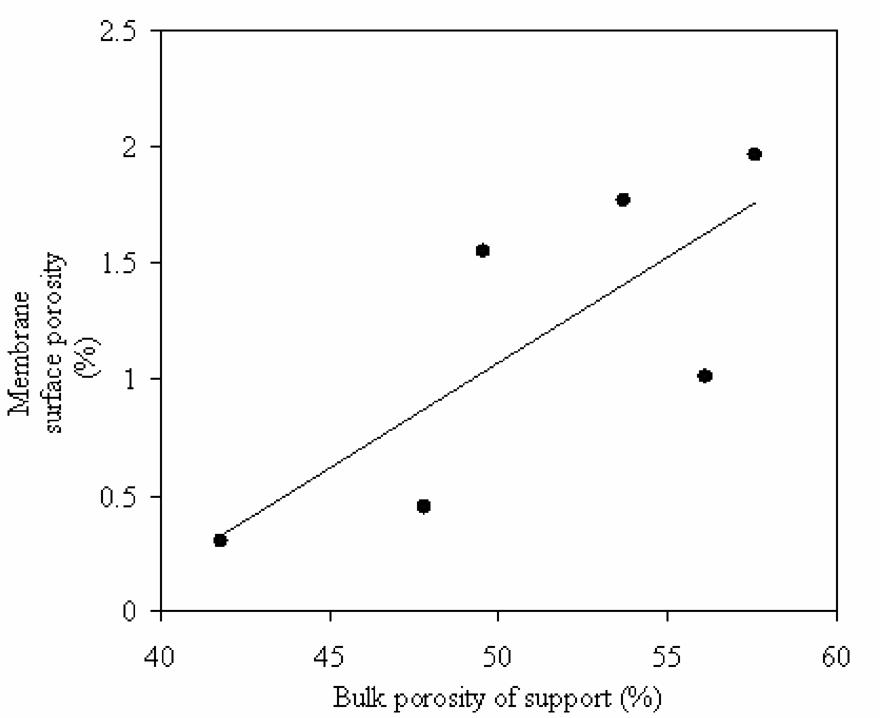


Figure 3.16 Variation of membrane surface porosity with bulk porosity of the support material.

3.3.4.1. Membrane compaction

The membrane compaction of these membranes was studied by compressing these membranes hydrostatically in cross flow mode using setup as shown in Figure 3.3a/b. Though there are various methods of studying membrane compaction, [Bohonak (2005), Arthanareeswaran (2004), Persson (1995)], we chose to do the compaction hydrostatically since this method is nearer to real case situations. Initially, the time required to obtain a constant flux at certain pressure was determined. For all the membranes and pressures studied, the flux became constant after ~ 2.5-3 hours. The steady water flux after four hours of applying particular pressure is plotted in Figure 3.17. It can be seen that the compaction pressure for PES-111 was lowest. The compaction pressure for other membranes was ≥ 4 bar. This distinctly conveys that membranes prepared using woven support PES-111 got compacted more easily, and not only that, flux declined after compaction pressure. Though M-3265 exhibited flux nearer to this membrane, its compaction pressure was closer to the membranes casted using non-woven supports. The support used for making M-3265 and M-111 have higher porosity than other supports as reflected from their porosity and air permeability. Though M-3265 have higher porosity, its compaction pressure was almost double than that of M-111. The flux of M-3160 and that of M-1006 remained almost similar at all pressures. Though the flux of M-3329 and M-3324 were identical at 1 bar, the difference increased at higher pressure. On this basis and also, M-3324 has good rejection performance, appreciable pore density, surface porosity and lesser membrane resistance, the support 3324 appears to be better choice than any of the supports investigated.

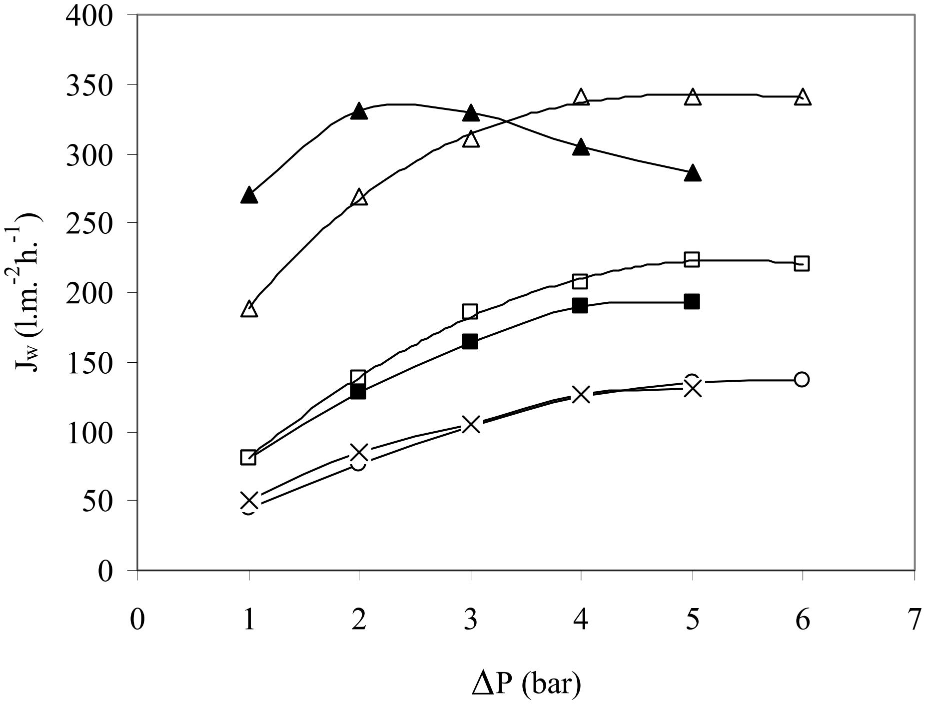


Figure 3.17 Variation of average water flux (J_w) with transmembrane pressure (ΔP) for membranes prepared with different backing; –×–: M-3160, –o–: M-1006, –■–: M-3329, –□–: M-3324, –Δ–: M-3265, –▲–: M-111.

3.4. Conclusions

At high polymer concentration, viscosity of the dope solution increased and flux decreased as expected. At higher PAN concentration (> 20%), the resultant membrane showed macrovoid formation due to increase in dope solution viscosity, which could be leading to delayed demixing. Among the solvents studied, NMP offered membranes with better combination of flux and rejection at studied dope solution concentrations (15, 18.5, 20.5 and 23%). Water flux offered by membranes prepared with acid as an additive was upto 2.5 times higher than membranes prepared with $ZnCl_2$ as an additive, while offering similar BSA rejection performance. FT-IR analysis showed that the citric acid and tartaric acid form stronger interactions with the solvent used (DMF) as compared to $ZnCl_2$. The formation of macro voids was also suppressed by the use of organic acid as an additive for the membranes investigated (PAN_{13} and PAN_{15}) as revealed by flux and rejection analysis. In case of PAN_{15}, 3265-support offered membranes with higher water flux and acceptable rejection than the membranes prepared using H1006-support with similar set of casting conditions. Spiral modules were prepared using membrane based on $ZnCl_2$ and citric acid (CA) as an additive. Both type of spirals showed excellent BSA rejection and no passage of bacteria (*E. Coli*). Spirals based on membranes prepared with CA additive exhibited higher flux and smaller variation in properties than those based on $ZnCl_2$ based membrane.

Effect of various support materials for the preparation of supported membrane was investigated by keeping membrane preparation conditions similar. The membrane characterization established the suitability of these types supports. Though two broad types, woven and non-woven supports were investigated, the membrane casted on earlier one exhibited higher water flux but showed poorer rejection and compaction behavior. This membrane also contained defects generated during its formation. Among the membranes prepared using non-woven supports, though M-3265 showed highest water flux, this membrane contained some defects. The membrane prepared with M-3324 had intermediate water flux but exhibited excellent membrane forming capacity, high rejection and good resistance to compaction than membranes prepared with other nonwoven supports.

Chapter 4: Surface modification of PAN based UF membranes

4.1. Introduction

Polyacrylonitrile (PAN) is widely used as the UF membrane material and has certain advantages over other conventional polymers like poly(sulfone), poly(ethersulfone), etc. PAN has more hydrophilicity, good solvent stability and is cheaper than other polymers. The use of PAN based UF membranes for drinking water purification is one of the potential applications. The desired characteristics of the membrane for this application are high water flux, ability to reject pathogenic species (viruses, bacteria, etc.) and low fouling. The membrane with these combined properties can be obtained by modifying its surface. In case of PAN, chemical modification can be done easily to alter its properties. The membrane after surface modification has amide and carboxyl functionality on the surface, which would help to offer resistance to fouling as well as improvement in flux due to increase in its hydrophilicity. Though increased hydrophilicity using hydrolysis is reported in the literature, most of the treatments led to the reduction in porosity and hydraulic permeability due to pore swelling [Kim, I. (2002a), Oh (2001), Bryjak (1998), Yang (1997)]. To improve water flux, optimization of some of the treatment parameters such as type of base and its concentration, treatment temperature and time, post-treatment, etc. plays an important role. The objective of the present study was to systematically investigate the variation in water flux and BSA rejection, caused by surface modification of the PAN membrane using organic (ethanolamine/triethylamine) and inorganic bases (NaOH/KOH) while varying treatment conditions (time and temperature). The effect of modification method (dead end versus cross flow) was also assessed.

4.1.1. PAN membrane hydrolysis by bases

The modification of PAN with various types of bases is documented in the literature. Its modification using primary amines showed that the affinity to water increased with increasing the amine concentration [Chiang (1990)]. Moreover, the modified polymer became water-soluble when a large amount of amine had reacted with PAN. The pervaporation membranes based on ethanolamine modified polyacrylonitrile [Hu (1991)] for water-ethanol separation showed that both, the separation factor and permeate flux for water increased as the ethanolamine component in the membrane increased. The hydrolysis of PAN microporous membrane by aqueous NaOH solution converted nitrile groups of PAN into poly(acrylic acid) and the pore diameter of the microporous membrane became larger with increasing hydrolysis time as verified by SEM micrographs [Wang (2000)]. On the other hand, it is reported that NaOH-induced hydrolysis of nitrile groups on the PAN membrane surface resulted in decreasing pore diameter and the modified membranes were less prone for protein deposition [Bryjak (1998)]. Another study reported partial hydrolysis with NaOH, wherein, the nitrile groups of the PAN membrane were mainly changed to carboxyl groups, which improved membrane hydrophilicity and resulted in a negative surface charge [Godjevargova, T. (1992a)]. The hydrolysis of polyacrylonitrile hollow fiber membranes by circulating NaOH solution of varying concentration at different temperatures produced a thin PAA layer, swelling of which reduced the hydraulic permeability between pH 5 and 6 [Yang (1997)]. It was also said that the number of carboxylic groups increased with increasing time, temperature and concentration of NaOH solution. The hydrolysis of PAN membrane by varying concentration of NaOH solution concentration and time by keeping the temperature constant was studied [Oh (2001)]. At lower NaOH concentration, morphological changes were negligible and the hydrophilicity change was dominant; while at higher NaOH concentration, morphological changes became evident with increased hydrophilicity [Oh (2001)].

Effects of hydrolysis of annealed membrane were studied by Kim, I. et al. (2002a) using different concentrations of NaOH and CH_3ONa. With an increasing treatment period of 1M NaOH or CH_3ONa, the rejection rate of PEG_{600} was decreased, whereas the permeability was considerably increased. However, when 2M NaOH or CH_3ONa was used, after 2 hour treatment period the rejection rate of PEG_{600} was increased, whereas the permeability was decreased. This was due to the change of surface morphology.

4.1.2. Manipulation of membrane porosity

PAN membrane showed significant changes in flux at different pH [Oak (1997)] due to pore swelling [Kim, I. (2002a), Oh (2001), Bryjak (1998), Yang (1997)], caused by the reduction in porosity. After modification, these membranes showed a decrease in hydraulic permeability and increase in rejection performance [Yang (1997)].

Annealing of membranes in hot water (80 °C) led to the reduction in pore size and the water flux also decreased [Jung (2005)]. The effect of annealing while varying temperature and surface hydrolysis on the membrane performance was studied [Kim, I. (2002a)]. These membranes showed small pore size and reduced MWCO. Kim, I. et al. (2002b) investigated the effect of 1,4- dioxane as a cosolvent on polyetherimide (PEI) UF membrane. Its low miscibility with water resulted in reducing membrane pore size. It is known that the surface hydrolysis led to increase in hydrophilicity of the membrane, reduction in porosity and hydraulic permeability due to pore swelling [Kim, I. (2002a), Oh (2001), Bryjak (1998), Yang (1997)].

4.1.2.1. Manipulation of surface properties of PAN membranes

The negatively charged PAN based membranes can be prepared by surface hydrolysis using bases or grafting by using vinyl monomers. A number of methods have been published on the surface modification or grafting of membranes to impart antifouling properties [Ulbricht (1996), Mukherjee (1996), Ulbricht (1995), Yamagishi (1995)]. It involves the use of UV or plasma to generate surface radicals and the initial reaction is in the gas phase. Ulbricht et al. (1995) applied plasma technique to modify PAN ultrafiltration membranes. PAN membrane surface was treated with low temperature helium or helium/water plasma followed by exposure to air. The results indicated that hydrophilicity for the membrane surface was significantly increased with only minor changes in permeability [Ulbricht (1995)]. Initiation by an oxidation-reduction system (redox system) is an effective method capable of inducing grafting even at relatively low temperatures [Jimbo (1998)]. The grafting of diethylaminoethyl methacrylate, dimethylaminoethyl methacrylate and 2-acrylamido-2-methylpropanesulfonic acid onto acrylonitrile copolymer (PAN) membranes was achieved using hydrogen peroxide ($FeSO_4$-H_2O_2) redox initiator [Godjevargova (1994, 1995)]. Using ceric ammonium nitrate (Ce^{4+}) as the initiator, acrylamide (AAm) was grafted onto the membrane surface of poly(acrylonitrile-*co*-methyl methacrylate) (PANCMMA). After grafting, the morphological structure of the membrane did not change, but the wettability was improved [Yuan (1997)]. Grafting of acrylamide onto the surface of an acrylonitrile copolymer (PAN) was studied by using Fe^{2+}/H_2O_2 redox initiator in aqueous medium [Yuan, X. (1998a)]. The result showed improvement in the wettability of the modified membrane. The kinetics and mechanism of acrylamide grafting onto PAN membranes using Fe^{2+}/H_2O_2 initiating system was studied [Yuan, X. (1998b)]. The graft polymerization onto a PAN membrane using redox system was studied by Belfer (1998, 2003), Jimbo (1998). The modification of membranes by surface grafting improved the fouling resistance of sea water reverse osmosis (SWRO) membranes [Belfer (2001)]. Belfer and coworkers reported the bilayered membranes prepared by sequential grafting of oppositely charged monomers by the redox initiator ($K_2S_2O_5$-$K_2S_2O_8$) [Belfer (2003, 2005)]. Layered membranes exhibited a significant decline in water flux in comparison with the initial UF membranes [Belfer (2005)]. It was further stated that the flux could, however, be manipulated by controlling the concentration of monomers, the time of grafting, and the number of layers.

4.1.3. Rejection of arsenic by negatively charged UF membrane

It is reported that the As-V can be rejected by membranes having –ve charge by Donnan exclusion principle [Brandhubar (2001)]. The demonstrated membrane has merely 72% As rejection and is based on sulfonated polysulfone. This polymer has its inherent material drawbacks that could have limited its rejection. Appropriate degree of sulfonation may be limiting this rejection performance. The sulfonation of polysulfone leads to chain scission and ultimately, such polymer could be made water soluble. It was thought that hydrolysis of the PAN membrane by base leading to the formation of carboxylic group ($–COO^{-}\ Na^{+}$) can provide an alternative to sulfonated PSF membrane for this application. As-V rejection by UF membrane would need a small pore size of such membrane (MWCO of 8 kDa as demonstrated by Brandhuber et al. (1998). Literature reports on PAN membrane hydrolysis as reviewed above have shown pore swelling as well as the formation of the carboxyl group on the membrane surface. Thus, PAN hydrolysis leading to these effects was thought to conveniently employ for As-V rejection, while manipulating the pore size by optimizing membrane preparation parameters, especially concentration of the dope solution and solvent.

4.1.3.1. Arsenic in drinking water and its removal

Arsenic is known to be a major pollutant in potable water in certain geological locations. Elevated concentrations of arsenic are found in groundwater in some areas of India, Bangladesh, China, Chile, Argentina, Mexico, Hungary, Taiwan, Vietnam, Japan, New Zealand, Germany and the United States due to naturally occurring arsenic in the aquifer sediment [Bang (2005)]. Though it is necessary as a nutrient in small quantities, it is known to be highly toxic if ingested in large dose. Its consumption through drinking water leads to serious diseases such as cancer in liver, lungs, skin, bladder, kidneys and skin lesions like hyperpigmentation, melanosis, keratosis [Kapaj (2006), Wang (2002), Kartinen (1995), Smith (1992)]. Thus, US Environmental Protection Agency (EPA) approved maximum allowable limit of arsenic in drinking water to be below 10 ppb [Han (2002)]. The predominant forms of arsenic in water are arsenite (As-III) and arsenate (As-V) [Oh (2000)]. At typical pH in natural water (pH 5-8), arsenate exists as an anion, while arsenite remains as fully protonated neutral molecule [Brandhuber (1998)]. It is reported that under oxidizing conditions, $HAsO_4^{-2}$ is dominant at higher pH, H_3AsO_4 is predominant in extremely acidic conditions, and $H_2AsO_4^{-}$ is predominant at low pH, less than pH 6.9 [Shih (2005)]. The removal of As-III is more difficult than the removal of As-V. It needs to be oxidized to As-V using various oxidizing agents like air or pure oxygen, ozone, chlorine, hypochlorite, chlorine dioxide, or H_2O_2 [Bissen (2003)]. Existing methods of arsenic removal are based on co-precipitation (alum coagulation, iron coagulation, lime softening), sorption technique (activated alumina, iron coated sand, ion exchange resin, etc.), exclusion principle (reverse osmosis - RO and nanofiltration - NF type of membranes) and electrodialysis. These methods have their own benefits and drawbacks as given in Table 4.1 [Shih (2005)].

Table 4.1 Advantages and disadvantages of methods used for As removal.

Method	**Advantages**	**Disadvantages**
Co-precipitation		
Alum coagulation	Durable chemicals	Efficient pre-oxidation is must
Iron coagulation	Efficient than alum on weigh basis	Medium removal of As (III)
Lime softening	Most common chemicals	Re-adjustment of pH needed
Sorption techniques		
Activated alumina	Commercially available mtrls	Re-adjustment of pH needed
Iron coated sand	Expected to be cheaper	Yet to be standardized
Ion exchange resin	Well defined medium/capacity	High cost medium, high-tech operation & maintenance
Membrane techniques		
RO/NF	High removal efficiency, no solid wastes, low space requirement, capable of removal of other contaminants	High investment costs, most of the demonstrated membranes do not withstand oxidizing agents

4.1.3.2. Membrane based processes

Reverse osmosis (RO) and nanofiltration (NF) membrane processes have an excellent removal efficiency of arsenic; especially RO, which can have > 95% arsenic removal [Shih (2005)]. However, the percentage of product water that can be produced from the feed water with RO and NF is typically lower than that of product water for UF and MF. The RO and NF membranes consume more energy (thus are more expensive) and are more prone to fouling than UF and MF membranes [Shih (2005)]. The electrodialysis units made up of cation and anion exchange resins are more effective in removing As-V than As-III [Kartinen (1995)]. To achieve higher arsenic removal rates, injection of an oxidizing agent (chloride) into the feed water was necessitated. However, oxidizing agents were said to be harmful to the conventional ion exchange resins (from which the membranes are made), just as they are to the most reverse osmosis membranes. Weng et al. (2005) demonstrated the removal of arsenic and humic substances from water using electro-ultrafiltration (EUF) membrane after applying voltage to the EUF cell. These membranes showed 71% rejection for As-III at pH 10 and > 90% rejection of AS-V at pH 6. Ergican et al. (2005) reported that arsenic (V) was removed from water with cationic surfactant micelles using polyethersulfone (PES) ultrafiltration membrane. With the addition of 10 mM cationic surfactant (cetylpyridiniumchloride, CPC) to the feed water, the arsenic removal efficiency was significantly increased, ranging between 78.1% and 100%. Applicability of UF membrane containing sulfonic and carboxylic acid groups was demonstrated by Brandhuber et al. (1998), exhibiting 72% As-V rejection. This capability of As-V rejection by acid group containing UF membranes was based on Donnan-exclusion principle [Brandhuber (1998, 2001)], wherein, a dilute solution containing ions is brought in contact with a membrane possessing a fixed charge and the passage of ions possessing the same charge as the membrane (co-ions) can be inhibited. The rejection was also shown to be sensitive to the membrane operating conditions and the maximum As-V rejection could be achieved was 88%.

4.2. Experimental

Polyacrylonitrile (PAN) was received from IPCL, Vadodara (viscosity averaged molecular weight: 24800). The NaOH, KOH, ethanolamine (EA), triethylamine (TEA), HCl, *N,N*-dimethyl formamide (DMF), *N*-methyl-2-pyrrolidone (NMP), potassium iodide (KI), iodine (I_2), barium chloride ($BaCl_2$), potassium persulphate ($K_2S_2O_8$), potassium metabisulphite ($K_2S_2O_5$), citric acid and disodium hydrogen orthophosphate anhydrous (Na_2HPO_4), isobutyl alcohol, antimony potassium tartrate ($C_8H_4K_2O_{12}Sb_2{\cdot}3H_2O$) were procured from S.D. Fine Chemicals (India) and sodium borohydride ($NaBH_4$) were procured from J.T. Baker, USA. Zinc chloride ($ZnCl_2$) and sodium arsenate ($Na_2HAsO_4.7H_2O$) were procured from Loba Chemie. L-ascorbic acid ($C_6H_8O_6$), ammonium molybdate ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$) and sulfuric acid ($H_2SO_4$) was obtained from Merck (India). Sodium salt of styrene sulfonic acid (SSA), Bovine Serum Albumin

(BSA, fraction-v, approx, 99%), ovalbumin (grade-V), polyethylene glycol (PEG) of different molecular weights and hydrochloric acid (< 5 ppb As) were obtained from Sigma chemicals (USA). Pepsin was obtained from SRL chemicals (India). The nonwoven support fabric Viledon (H1006) and Hollytex (3324) was procured from Freudenberg, (Germany) and Ahlstrom, respectively. All chemicals were of analytical grade and were used without further purification. The Milli-Q water with 18.3 mΩ.cm resistivity was used for all solution preparation, flux and rejection analysis.

4.2.1. Membrane preparation

Flat sheet PAN based ultrafiltration membranes were prepared by phase inversion method. A dope solution of vacuum dried PAN and additive ($ZnCl_2$, 4 wt. %) in solvent (DMF, NMP) was prepared. It was degassed and then centrifuged at 2500 rpm for 3 hours. Membranes were casted on moving nonwoven support (H1006, 3324) using pilot scale continuous membrane casting facility as shown in Figure 3.1 at 20 °C gelation temperature and 40 °C curing temperature. The formed membrane had an average thickness of ~ 250 μm and stored with aq. formalin solution (0.5%) at 4 ºC until further use. Formed membranes were denoted as PAN_x, where, the subscript 'x' denotes the polymer concentration used in the dope solution.

4.2.2. Flux and rejection analysis

The flux analysis of unmodified and surface modified PAN_{15} and PAN_{23} membranes were done in dead end and cross flow mode as described in Section 3.2.4.1. The PAN_{12} membranes before and after annealing were analyzed in dead end mode.

4.2.2.1. Protein rejection

The rejection analysis of unmodified and NaOH modified PAN_{15} membrane was done by using BSA while the unmodified PAN_{23} membranes were analyzed by using BSA, ovalbumin and pepsin (0.1% w/v concentration in feed) as described in Section 3.2.4.2.

4.2.2.2. PEG rejection

The PEG rejection analysis of membrane was performed in dead end mode by preparing the solution of different molecular weights (0.1% concentration in the feed) in DI water (neutral pH). The concentration of PEG in the feed and permeate was analyzed by following reported procedure [Sims (1980)]. Into a 4 ml feed or permeate sample, 1 ml of reagent A (5% w/v $BaCl_2$ in 1N HCl) and reagent B (0.4 g KI + 0.127 g I_2 + 100 ml water) was added and mixed thoroughly. These samples were allowed to stand for 15 minutes at 40 °C and then absorbance was measured at 535 nm by using double beam UV-visible spectrophotometer (Chemito, Spectrascan UV 2700).

4.2.2.3. Arsenic (As-V) rejection

The membrane performance was studied by varying different feed concentrations of $Na_2HAsO_4.7H_2O$ solution (50 ppb to 1000 ppm of As-V) and different operating conditions like concentration, pH, temperature, cross flow velocity, transmembrane pressure with respect to time. Peristaltic pump was used for varying the cross flow velocity from 0.027 $m.s^{-1}$ to 0.39 $m.s^{-1}$ by varying pump speed from 30 - 90% and back pressure from 0.24 bar to 2 bar. The back pressure was maintained by controlling the recycle flow rate. The experiments were done in the concentration mode, and permeate samples were collected at defined intervals of time. The As-V concentration in feed, permeate and reject samples were analyzed using Atomic Absorption Spectroscope (AAS) from Thermo Electron, M 9 Series. The analysis of arsenic for ppm level was done using flame analysis, while ppb level concentration was measured by making hydride of arsenic. The rejection of arsenic was calculated by using following Equation,

$$\% \mathrm{R} = \left[1 - \left(\frac{C_p}{C_r} \right) \right] \times 100 \tag{4.1}$$

where, C_p is concentration of arsenic in the permeate and C_r is arsenic concentration in the retentate.

4.2.3. Pore size analysis by solute rejection method

The mean pore size was calculated by solute rejection method by plotting graph between PEG rejection of the membrane versus the PEG diameter, a straight line was obtained as described by Singh et al. (1998). From this log-normal plot, mean solute size (μ_s) can be calculated as PEG diameter (d_s) corresponding to 50% PEG rejection and geometric standard deviation about the mean diameter (σ_p) can be determined from the ratio of d_s at 84.13% and at 50%. Stokes radii of PEGs can be obtained from their molecular weights by using Equation 4.2.

$$a = 16.73 \times 10^{-10} M^{0.557} \tag{4.2}$$

where, a is Stokes radius and M is molecular weight of PEG.

4.2.4. Surface modification

4.2.4.1. Dead end mode

PAN membrane surface modification by dead end mode as shown in Figure 3.2 was performed using NaOH, KOH, TEA and EA. The membrane was mounted in a dead end cell and 50 ml of base solution was passed at 1 bar and then membrane was left under the base solution for predetermined time. The membrane was then thoroughly rinsed with water and finally, 100 ml of water was passed through the membrane to remove the base solution left into the pores. Water flux of the modified membrane was recorded at 1 bar transmembrane pressure. In case of membrane treated with NaOH and KOH, a post-treatment of HCl was also performed by passing 30 ml of 0.1N HCl solution through the membrane, followed by thorough water washing till neutral to pH. The water flux after such treatment was again recorded at 1 bar pressure.

4.2.4.2. Cross flow mode

The schematic of the cross flow setup used for this study is shown in the Figure 4.1. The reservoirs R_1 and R_2 filled with 1N aqueous NaOH solution and water respectively were connected to the feed pump through valve V_1 and V_2. The NaOH solution was circulated at defined temperature through the cross flow cell containing PAN membrane having active area 191 cm^2. The transmembrane pressure was kept at 1 bar throughout the treatment period by using throttle valve V_3 fixed at the retentate side of the cell. After predetermined time, the hydrolysis reaction was quenched by closing the valve V_1 and opening the valve V_2. The membrane was washed with water till neutral to pH. The water flux was recorded at 1 bar transmembrane pressure. Minimum 6 repetitions with fresh membranes were done for a particular set of condition. The NaOH treatment was followed by post-HCl treatment by circulating 0.1 N HCl solution kept in reservoir R_2. After collecting 150 ml of HCl solution in the permeate side at 1 bar pressure, the membrane was washed with distilled water by opening the valve V_1 till permeate showed neutral pH and then the water flux was recorded at 1 bar pressure.

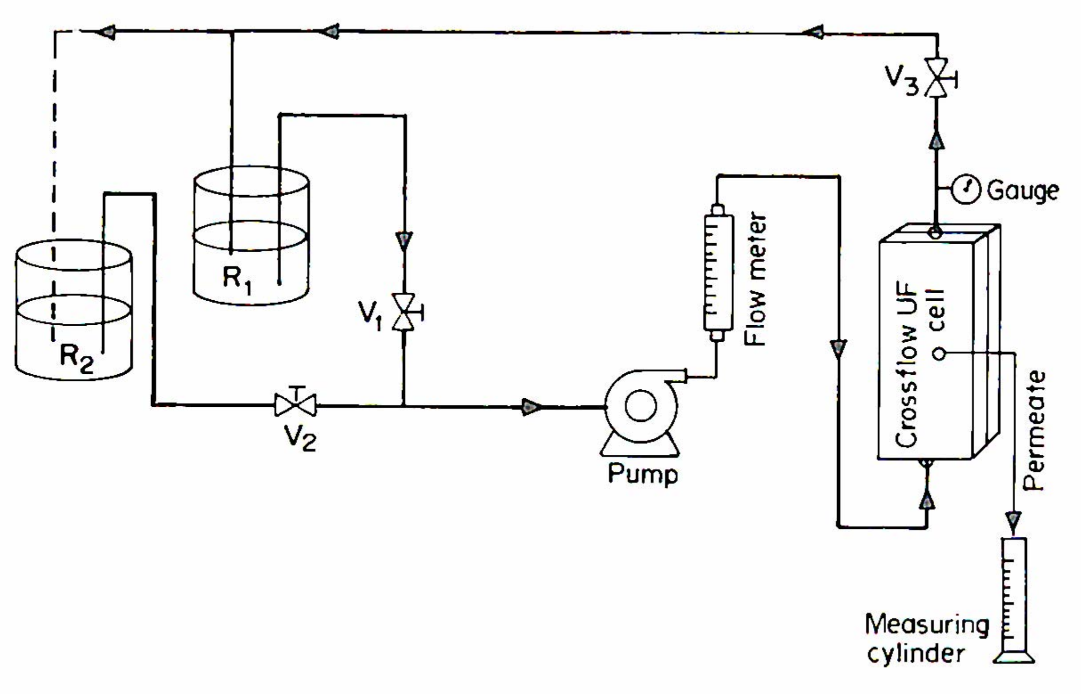


Figure 4.1 Schematics of cross flow set up.

4.2.4.3. Treatment of PAN powder

For IR investigations, the treatment of the PAN powder was done by using 2.5N aqueous NaOH at 45 °C and at varying treatment time of 0.5, 1, 2.5 and 5 hour. The reaction was quenched by discarding the NaOH solution and gentle washing with water till neutral to pH. The 0.1N HCl treatment was also performed at ambient temperature followed by thorough water wash till neutral to pH.

4.2.4.4. Spiral preparation and analysis

The flat sheet PAN_{23} membrane prepared using NMP as a solvent, $ZnCl_2$ as an additive and Viledon H1006 as a porous support fabric was used for spiral preparation. The single leaf spiral wound module was prepared by following the same procedure as described in Section 3.2.10.1.

The water flux of the spiral module was measured in dead end mode at 1 bar transmembrane pressure. The spiral module was mounted vertically, wherein, the feed and permeate side was at the bottom. The water flux was measured after permeating ~ 500 ml of DI water.

The water/air bubble point of the membrane was analyzed as described in the Section 3.2.5.1.

4.2.4.5. Spiral modification and As-V analysis

The spiral modules were modified in a cross flow mode using the assembly as described in Section 4.2.4.2. The spiral module was kept inside the water bath at 45 °C, wherein, the feed side of the module was at the bottom. NaOH solution (1N) maintained at the same temperature was permeated at 0.6 $lit.min.^{-1}$ of retentate flow rate for 3 hours. The hydrolysis reaction was quenched by passing water till neutral to pH.

Water flux analysis of the modified spiral was done in a cross flow mode with 0.6 $lit.min.^{-1}$ of retentate flow rate as described in Section 4.2.4.4. The PEG_{8k} rejection analysis was done using same assembly with 0.6 $lit.\ min.^{-1}$ retentate flow rate at 1 bar transmembrane pressure. The initial permeate of 10 ml was discarded, prior to sampling for analysis. The analysis of PEG was done as described in Section 4.2.2.2.

The modified spiral was used for the As-V analysis. The concentration of As-V in the feed was 1 ppm. The analysis was done at 6.95 and 8.56 pH by using cross flow mode at ambient temperature. The As solution was passed through the assembly and the initial 10 ml permeate was discarded before sampling.

The concentration of arsenic in the feed, retentate and permeate was analyzed by colorimetry [Dhar (2004)]. The coloring reagent was prepared by mixing the aqueous solutions of L-ascorbic acid (10.8% w/v), ammonium molybdate (3% w/v), antimony potassium tartrate (0.56% w/v) and H_2SO_4 (13.98% v/v). The mixing ratio of these four reagents was 2:2:1:5, respectively. The solutions of ascorbic acid, ammonium molybdate and antimony potassium tartrate were first combined together and then H_2SO_4 was added immediately to avoid the turbidity in the colour reagent. Into a 50 ml of As feed, retentate and permeate sample, 5 ml of coloring reagent was added. The solution was stirred immediately and allowed to react for 10 min. at ambient temperature before measuring its absorbance at 880 nm.

4.2.4.6. Grafting of SSA on PAN membrane

The sodium salt of SSA (1 $mol.lit^{-1}$) was dissolved in water. To this aqueous solution, 1N HCl was added dropwise till pH of 1.8 to convert sodium salt into acid form [Belfer (2003)]. The redox initiator used was 0.01 $mol.lit^{-1}$ $K_2S_2O_8$-$K_2S_2O_5$. PAN_{23} membranes (prepared with NMP as a solvent and 3324 as a support) were immersed in aqueous solution of monomer at 30 °C for predetermined time (10, 60 and 120 min). The performance of unmodified and grafted membrane was assessed based on variation in water flux and PEG_{8k} rejection analyzed at 1 bar pressure. At least four different membrane samples were analyzed and the data averaged. The grafted membranes were dipped in 0.1N NaOH for 15 min. at ambient temperature and then washed with water till neutral to pH.

4.2.5. Annealing treatment

For annealing study, PAN_{12} membranes were prepared by using 10% PVP as an additive, NMP as a solvent and 3265 as a support. Formed membranes were annealed by dipping into the water at 80 °C for different time intervals (1, 5, 20 and 60 min.).

4.2.6. Membrane morphology and surface characterizations

4.2.6.1. SEM and EDAX analysis

The scanning electron micrograph (SEM) of unmodified and NaOH modified PAN_{15} and PAN_{23} membrane was recorded. The details of instrument and sample preparation are given in Section 3.2.8. Energy dispersive analysis of X-rays (EDAX) was recorded with Leica, Stereoscan-440.

4.2.6.2. Contact angle

Contact angle of the dried membrane surface (unmodified and surface modified) was measured by the sessile drop method by Digidrop instrument (GBX, France). A water drop of 0.08 μ-lt was placed on a membrane surface. The measurement was repeated with at least 6 membrane samples and the data averaged (variation ± 4°). From the values of the contact angle, work of adhesion (ωA) of dispersion for polymers can be calculated as [Wang, M. (2006b)].

$$\omega A = \gamma_{W} (1 + \mathrm{COS}\,\theta) \tag{4.3}$$

where, γ_w is surface tension of water (7.2×10^{-2} N. m^{-1} at 25 °C).

4.2.6.3. ESCA analysis

Electron spectroscopy for chemical analysis (ESCA) was recorded on a V.G. Scientific (UK) ESCA 3000, using Al K as an X-ray source (1486.6 eV), operated at 250 W of power, 50 eV pass energy, 4 mm slit and a take-off angle of 30° in relation to the sample surface. The residual gas pressure in the spectrometer chamber during the data acquisition was less than 10^{-8} Torr. The ESCA spectra were referenced to the Cl 2p peak (201 eV).

4.2.6.4. FTIR-ATR spectroscopy

The surface analysis of the modified membranes was done by attenuated total reflectance (ATR) spectroscopy (KRS crystal, Perkin-Elmer) at an angle of 45°. The FT-IR spectra of PAN powder before and after modification was recorded on Perkin Elmer 16 PC FT-IR.

4.2.6.5. Atomic force microscopy (AFM)

The atomic force microscopy (AFM) analysis was conducted in a contact mode using silicon nitride tips with Digital instrument (Veeco Metrology Group). The surface morphology of the membrane was expressed in terms of mean surface roughness and it was measured by treating all captured surfaces in the same way.

4.3. Results and discussion

4.3.1. Hydrolysis of PAN_{15} membrane

PAN_{15} membrane prepared with DMF as solvent and Viledon H1006 as a porous support was used for this study.

4.3.1.1. Treatment of organic bases by dead end mode

In order to select an appropriate modification agent and treatment conditions that would improve the water flux without causing the swelling, PAN membrane in this study was modified with ethanolamine, trimethyl amine, NaOH and KOH in dead end mode and the effect on water flux was analyzed. For the modification with ethanolamine or triethylamine, the membrane was first dipped in 15:85 DMF:water (v/v) for 12 hours in order to swell it to ease reaction of swollen PAN with these amines. At ~ 10% aqueous DMF, the degree of acrylamide grafting on PAN-based membrane was reported to be the highest [Yuan (1997)]. Such pretreatment is also known for the reaction of PAN membrane with hydroxylamine and diethylaminoethylmethacrylate [Godjevargova, Z. (1992b)]. The DMF pretreatment did not cause any damage to the pore morphology in the present case. This was confirmed by dipping the swollen membranes again in water for 24 hours to extract back the DMF and then measuring the water flux, which was found to be identical with the initial water flux. After swelling by DMF, the membrane samples were dipped in 15% aqueous solution of ethanolamine or triethylamine for predefined time at an ambient temperature. The results are summarized in Table 4.2.

It was seen that in the case of ethanolamine, water flux was initially increased upto 49% at 6 hour treatment, while it was increased upto 78% after 9 hour triethylamine treatment. The increase in water flux can be attributed to the increased hydrophilicity of the resultant membrane owing to the presence of amide and hydroxyl functionality as shown by Todorov et al. (1996). This led to a marginal reduction in BSA rejection. After 6 hour treatment, water flux of the ethanolamine treated membrane decreased abruptly, due to the formation of cyclic intermediate as proposed by Chiang and Hu [Chiang (1990)], which is less hydrophilic. The reduction in water flux by triethylamine treatment was not as rapid. Though the reaction of PAN with organic bases like monoethanolamine, ethylene diamine and hydroxylamine are well reported in the literature; [Todorov (1996), Godjevargova (1992b), Hu (1991)] the reaction with triethyl amine is not documented, to our knowledge. The PAN membrane modification using organic bases as given in Table 4.1 revealed that 9 hour triethylamine treatment was the best treatment protocol for improving the water flux.

Table 4.2 Change in water flux of PAN based membranes treated with 15 % aqueous EA and TEA in comparison to untreated membrane and their rejection properties.

Treatment time (hour)	**% Change in water flux**		**% BSA rejection**	
	EA treated	**TEA treated**	**EA treated**	**TEA treated**
3	41	28	82	88
6	49	60	85	84
9	-12	78	82	84
12	-44	43	63	82

4.3.1.2. Treatment of inorganic bases by dead end mode

In the case of membrane modification by 1N NaOH or KOH, the water flux initially increased by ~ 50%, regains its original value (at 7.5 hour for NaOH and at 10 hour for KOH) and then decreased continuously by ~ 75% upto 25 hour treatment time as seen in Figure 4.2a and 4.2b.

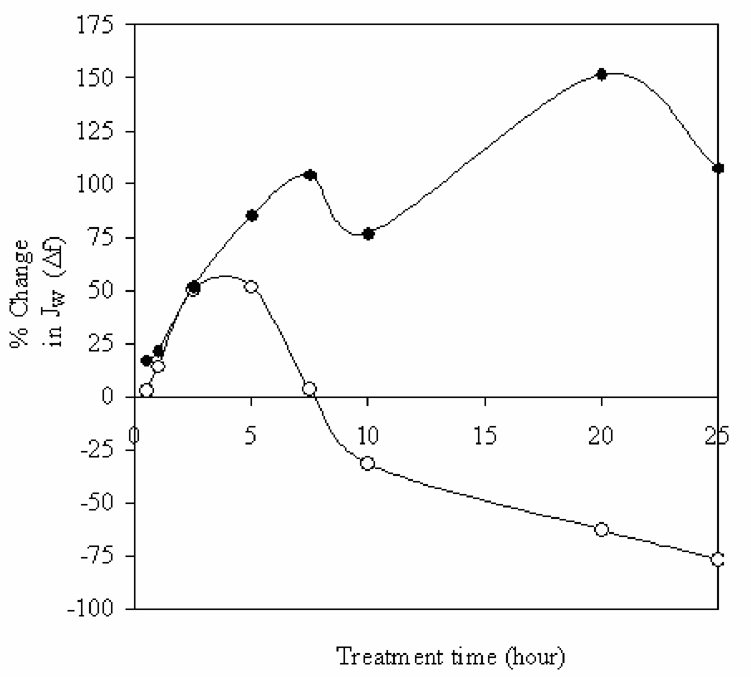


Figure 4.2a Variation in water flux (Δf) caused by treatment with dead end mode in comparison to the untreated membrane; (○) 1N NaOH treatment, (●) 1N NaOH followed by 0.1N HCl treatment.

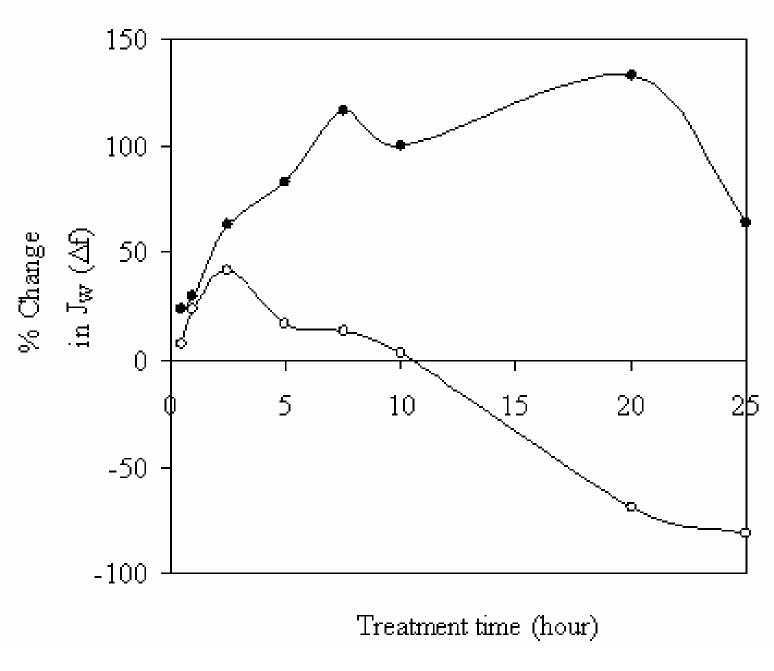


Figure 4.2b Variation in water flux (Δf) caused by treatment with dead end mode in comparison to the untreated membrane; (○) 1N KOH treatment, (●) 1N KOH followed by 0.1N HCl treatment.

The post-HCl treatment to these membranes led to initial enhancement in water flux as revealed by increase in % change in water flux (Δf), which decreased slightly at 7.5 hours treatment duration, again increased upto a maximum value of 152% for NaOH treatment and 133% for KOH treatment for 20 hour duration and then again declined for 25 hours treatment duration for both the cases of NaOH and KOH pretreatments (Figure 4.2a and b). These variations in water flux were associated with marginal changes in BSA rejection (Table 4.3). Among various treatment durations, the lowest BSA rejection was 77-79% for 5 hour treatment duration. The marginal changes in rejection are attributable to the changes in surface properties than to the pore morphological changes. The complex behavior of percent variation in water flux (Δf) and smaller changes in BSA rejection can be explained in terms of effects caused by the various intermediates formed as the reaction products of −CN functionality with NaOH/KOH at respective treatment duration. It is reported that the base initially converts −CN functionality to amide and cyclic intermediates [Litmanovich (2000)]; though the presence of carboxylic groups at lower reaction time is also documented [Oh (2001), Bryjak (1998)].

Table 4.3 Rejection performance of membranes treated with 1N NaOH and 1N KOH, followed by 0.1N HCl at 30 °C by dead end mode.

Treatment time (hour)	**% BSA rejection**	
	NaOH followed by HCl treatment	**KOH followed by HCl treatment**
0.5	92	82
1	93	83
2.5	84	84
5	79	77
7.5	84	85
10	90	99
20	100	87
25	92	91

An initial increase in flux can be attributed to the increased hydrophilicity due to presence of both, amide and carboxyl functionality. The presence of these groups at initial stages of reaction was confirmed by Bryjak et al. (1998) by observing respective C=O bands in the IR spectra. As seen from Figure 4.2a and 4.2b, the difference between percent change in water flux (Δf) for NaOH/KOH treatment and for post-HCl treatment becomes prominent only after the maxima was achieved by the base treatment (which is ~ 4 h for NaOH and 2.5 h for KOH treatment). After this time, a decrease in Δf by base treatment and its increase after post-HCl treatment could not be ascribed just to the surface hydrophilicity, but can better be correlated to the pore morphological changes. It is known that the NaOH treatment to PAN membranes resulted in reduction of pore size caused by swelling [Kim, I. (2002a), Oh (2001), Bryjak (1998), Yang (1997)]; which in turn reduced hydraulic permeability [Yang (1997)] or PEG permeability [Kim, I. (2002a)]. The reduction in pore size was due to the swelling of the labile PAN chains on the membrane pore surface. In present case, this type of swelling though could be speculated for NaOH treatment, was not evident for the post-HCl treatment, since water flux still increased upto 20 hours treatment duration (Figure 4.2a and 4.2b). This could be explained on the basis of reaction products formed after these treatments. During initial stages of treatment, the population of amide and carboxylic groups are moderate and the increased surface hydrophilicity is responsible for the increase in water flux for both, base as well as post-HCl treated membranes. As reaction time progresses, the population of carboxylic groups increases, leading to the decrease in water flux by base treatment (due to swelling). It is postulated that in the case of NaOH/KOH treatment, the swelling is predominantly due to the repulsive interaction of labile polymer chains bearing $–COO^-$ group (as shown in Figure 4.3), and not just by water uptake. The carboxyl functionality would remain in $–COO^-Na^+$ or $–COO^-K^+$ form, which remains ionized, leaving net –ve charge on the membrane surface and causing repulsive interactions among the labile chains bearing these groups. This chain repulsion predominantly causes the swelling, resulting in lowering in pore size and water flux. If it would have been just because of water uptake, the same behavior of swelling should have also been observed in the case of post-HCl treatment, and as a result, water flux would also have decreased.

Conversely, an increased water flux for 5-20 hour post-HCl treated membranes suggests that lowering in porosity caused by base treatment is absent. This is due to the collapse of swollen structure approaching to the original porosity as represented in Figure 4.3.

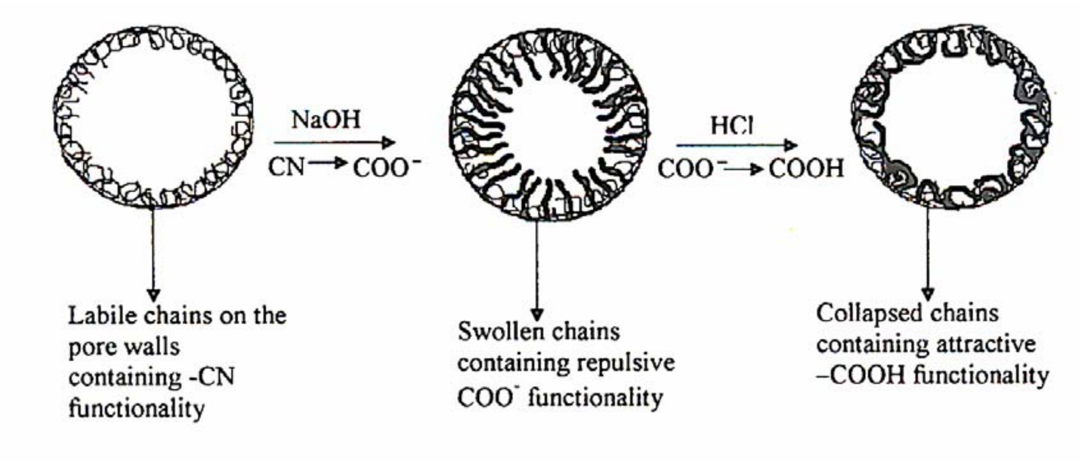


Figure 4.3 Schematic representation of pore swelling by NaOH treatment and regain of porosity by HCl treatment.

This could happen since post-HCl treated membrane now has carboxyl groups in the form of –COOH, which forms H-bonding with neighboring –COOH, creating attractive interactions that results in collapse of swollen structure into coiled one. This leads to an increase in water flux. The highly populated –COOH on labile PAN chains now behaves like a poly(acrylic acid) (PAA) type structure. The postulation is further supported by the observation of PAA grafted onto the pores of a polycarbonate membrane [Ito (1990)], wherein, an increase in pH caused swelling, reducing the pore size and the permeability of the membrane. In the present case, an increase in water flux by post-HCl treatment was seen till moderate reaction has occurred upto 20 hour treatment, after which, the Δf declined again. This could be due to the formation of PAA type layer on the membrane surface, which highly absorbs water, but remained water insoluble. The reason for this PAA insolubility can be as explained by Yang et al. (1997), as not all the nitrile groups on the same molecular chain were converted into carboxylic group or the hydrolyzed molecular chains might be entangled with other non-hydrolyzed PAN chains. This study thus reveals that by carefully controlling hydrolysis conditions of

PAN membranes, pores can be either swollen or unswollen, depending on pH and thus can act as stimuli responsive membranes or as membrane valve. This would need further investigations. The base treatments for longer time/concentration were not done since the membrane surface turned yellow and got delaminated from the support backing.

4.3.1.3. NaOH treatment in cross flow mode

It was thought to analyze effect of base treatment by cross flow mode, wherein the concentration of base at the membrane surface would remain same as that of the bulk concentration. The same may not be true for dead end mode. Since, during dead end treatment NaOH as the base offered higher improvement in flux than that of KOH treatment, it was chosen as the base to be used during cross flow mode of treatment. During these experiments, concentration of the base kept same (1N) as that of cross flow mode. The effect of base treatment by cross flow mode was also studied using 1N NaOH solution. The effect of treatment temperature was thought to be assessed in order to compare the flux performance with that of dead end type treatment. Figure 4.4a and 4.4b show the effect of treatment time on percent change in water flux (Δf) at 30 °C and 45 °C treatment temperature respectively. In both the cases, Δf increases with treatment time. In the case of treatment at 30 °C, the post-HCl treated membrane exhibited higher water flux, except for 0.5 hours treatment. Such overlap of Δf is also seen for the treatment done at 45 °C by cross flow mode (Figure 4.4b) and also for dead end type of treatments (Figure 4.2a and 4.2b). This overlap is observed at lower treatment times, indicating the membrane surface hydrophilicity leading to these enhancement in water flux may not be due to carboxyl groups, but due to the intermediate amide functionality. For 30 °C treatment, the Δf starts rising from 20% and reaches to the maximum of 170% for the treatment period studied. In case of 45 °C treatment, the extent of change in the water flux (Δf) is much higher even at smaller treatment time (Figure 4.4b), owing to high rate of reaction at higher temperature. The Δf reaches its maximum of 230% within 2.5 hours and remains similar till 5 hours time.

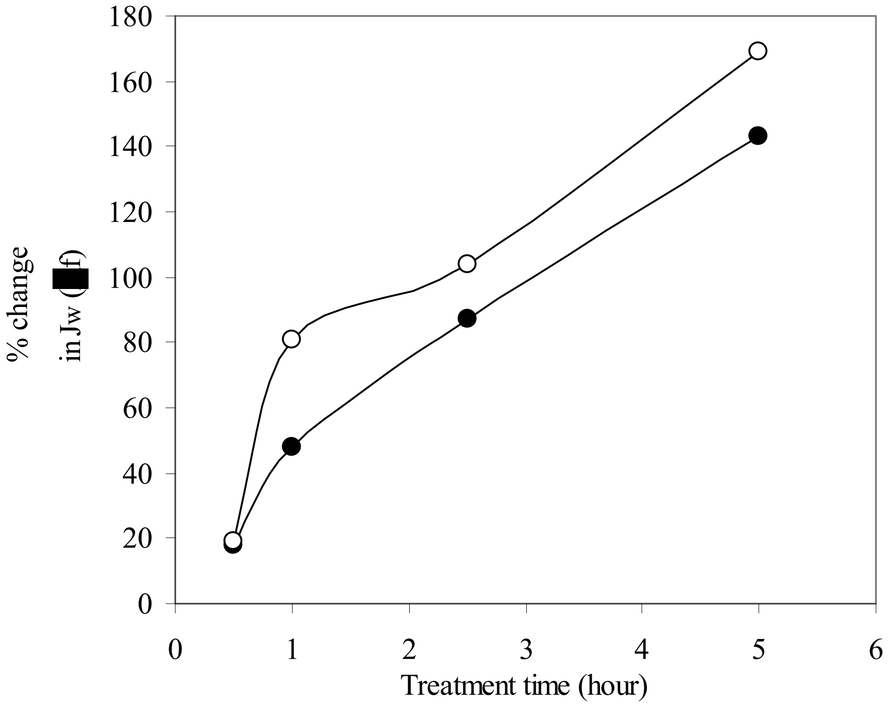


Figure 4.4a Variation in J_w (Δf) caused by treatment at 30 ºC by cross flow mode in comparison to that of untreated membrane; (○) 1N NaOH treatment, (●) 1N NaOH followed by 0.1N HCl treatment.

The percent increase in water flux (Δf) was higher by cross flow type treatment than by dead end type, indicating extent of hydrolysis is higher by earlier mode. This is possible as the base is constantly circulating through the membrane pores. All possible membrane surface as well as pore wall surface gets essentially treated with the same feed concentration, as against depleted concentration at the surface by dead end mode.

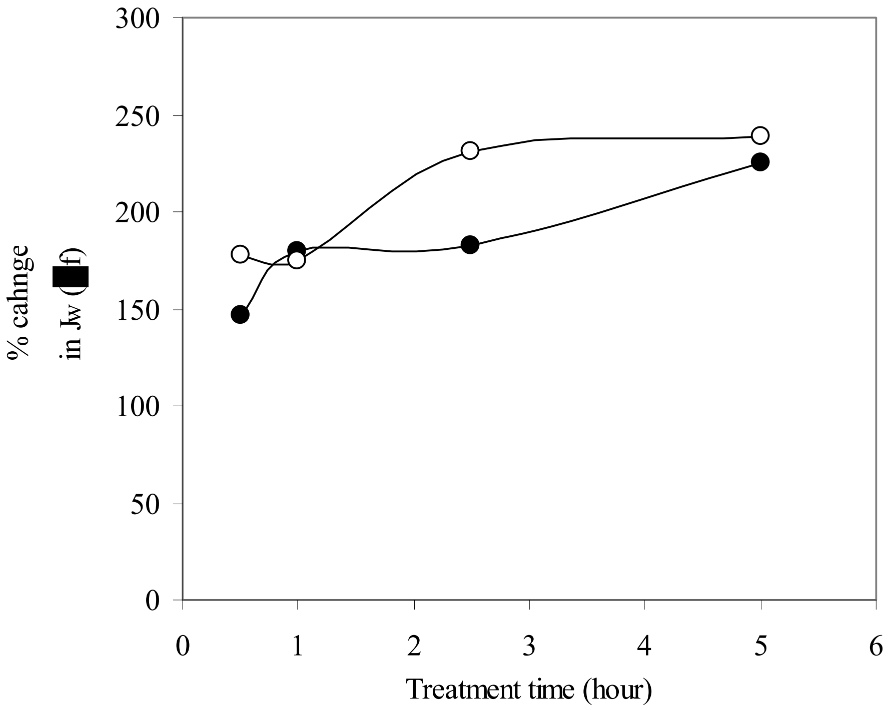


Figure 4.4b Variation in J_w (Δf) caused by treatment at 45 ºC by cross flow mode in comparison to that of untreated membrane; (○) 1N NaOH treatment, (●) 1N NaOH followed by 0.1N HCl treatment.

The BSA rejection showed a general decrease for the membranes treated at 30 °C and 45 °C (Table 4.4). This may be attributed to the changes in the surface hydrophilicity rather than to the pore morphological changes. The extent of decrease in rejection was higher for (i) 45 °C treatment than for 30 °C and for (ii) post-HCl treated than NaOH treated cases; depicting its dependence on extent of reaction as well as treatment type. The decrease in rejection also indicated that there is no considerable pore swelling. The lowering in BSA rejection by cross flow type treatment was higher than by dead end type, which could also be correlated to the higher extent of reaction in earlier case leading to hydrolysis of –CN functionality. The SEM images of membranes treated at various conditions are shown in Figure 4.5. The treatment at even 45 °C did not show appreciable morphological changes.

Table 4.4 Rejection of membranes treated with 1N NaOH by cross flow mode.

Treatment time (h)	% BSA rejection			
	Membrane treated at 30 °C		**Membrane treated at 45 °C**	
	NaOH treatment	**NaOH followed by HCl treatment**	**NaOH treatment**	**NaOH followed by HCl treatment**
0.5	89	84	-	78
1	92	85	73	79
2.5	85	77	57	68
5	79	77	49	59

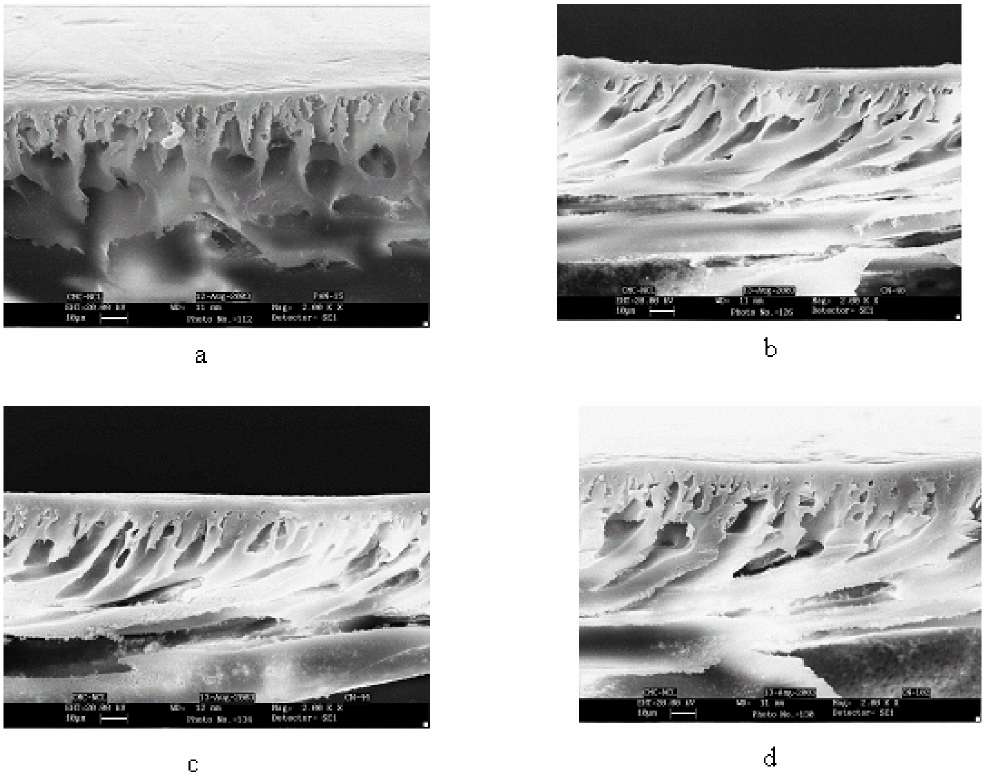


Figure 4.5 SEM of cross section of PAN membranes; (a) unmodified, (b) 1N NaOH treatment at 30 °C for 5 hour, (c) 1N NaOH treatment at 30 °C for 5 hour, followed by 0.1 N HCl, (d) 1N NaOH treatment at 45 ^{o}C for 5 hour, followed by 0.1 N HCl.

4.3.1.4. Contact angle, IR and ESCA studies

The hydrophilicity for surface modified membranes by cross flow mode that showed largest variation in Δf was studied by measuring contact angle of water by sessile drop method. The results are shown in Table 4.5. The decrease in contact angle was observed as the treatment time and temperature was increased, as anticipated due to the formation of hydrophilic amide and carboxylic acid functionality on the membrane surface.

Table 4.5 Contact angle of surface modified membranes.

Time (hour)	**Contact angle for membrane treated at 30 ºC**		**Contact angle for membrane treated at 45 ºC**	
	NaOH treatment	**NaOH followed by HCl treatment**	**NaOH treatment**	**NaOH followed by HCl treatment**
0.5	68	66	-	60
1	61	58	58	58
2.5	59	61	62	54
5	60	61	55	55

The progress of the surface reactions was tried to monitor using FTIR-ATR spectroscopy at incident angle of 45°, but no significant information could be drawn. It is known that the penetration depth of the beam into the sample is variable but of the order of 0.5 to 10 μm [Murphy (1995)]. The chemical modifications in the present case occurred predominantly at the membrane surface, which were masked and not seen in ATR spectra owing to the penetration depth. It was thus thought to treat PAN powder suspended in water by 2.5N NaOH at 45 °C for various time and record the IR spectra. As seen from Figure 6, the characteristic broad –OH stretching peak near 3500 was seen for NaOH as well as post-HCl treated powder. More significantly, a characteristic band for N–H stretching of primary amide ($-CONH_2$) was also observed in this region [Morrison (2003)] till treatment duration of 2.5 hours, confirming the presence of both, amide and carboxylic acid for moderate treatment conditions. This suggests that if the

PAN surface could be evenly treated, presence of both carboxyl and amide functionality would lead to an increased water flux at these moderate treatment conditions. In such case, the behavior of water flux after NaOH as well as post-HCl treated membrane would be as like seen in Figure 4.4a and 4.4b. Conversely, the dead end type treatment would be more focused on membrane surface (and lesser into the pores), converting amide functionality also to carboxylic, leading to different behavior of water flux as seen in Figure 4.2a and 4.2b. The appearance of Na at 1071.8 eV [Briggs (1990), Hammond (1981)] in ESCA as a result of $-COO^{-}Na^{+}$ formation of membrane surface with increasing treatment severity is shown in Figure 4.7. For the membranes treated for 0.5, 2.5, 5 hours at 30 °C and for 5 hours at 45 °C using 1N NaOH solution, the intensity for Na increases. This increasing population of carboxylic groups with the treatment time or temperature led to the observed variations in flux.

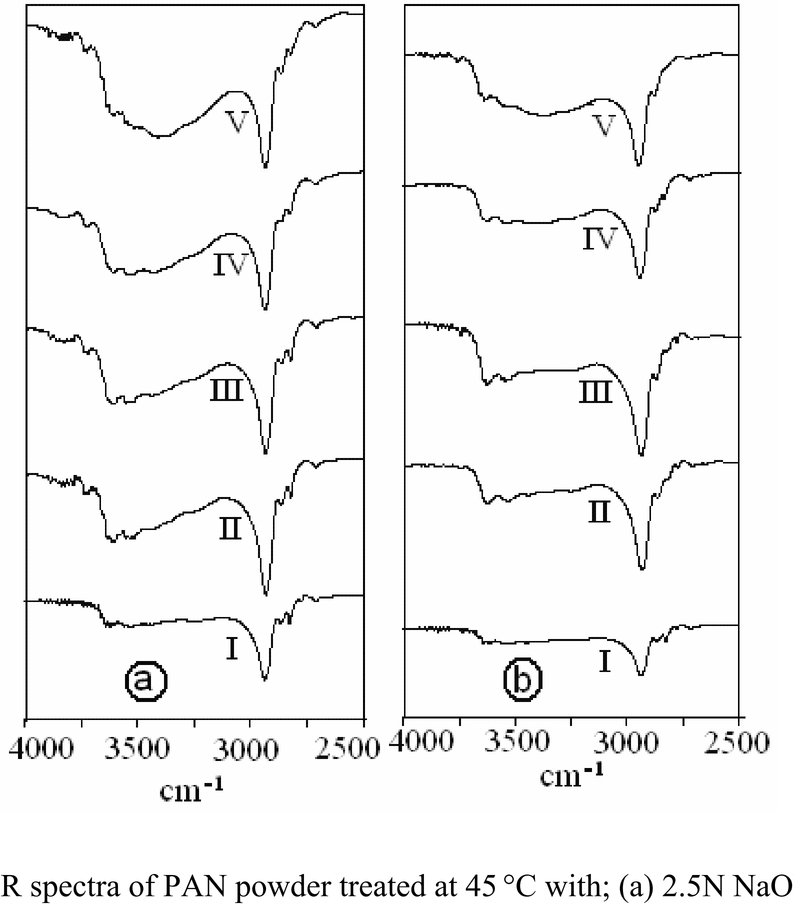


Figure 4.6 FT-IR spectra of PAN powder treated at 45 °C with; (a) 2.5N NaOH solution (b) 2.5N NaOH, followed by 0.1N HCl; I: unmodified, II: 0.5 hour, III. 1 hour, IV: 2.5 hour, V: 5 hour.

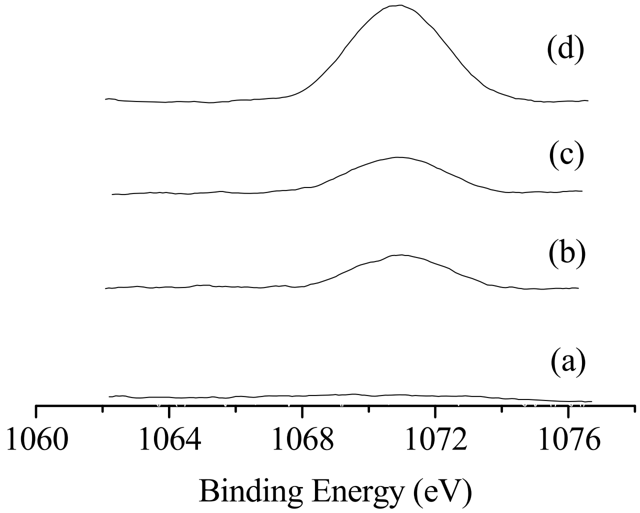


Figure 4.7 Occurrence of Na by ESCA for membranes treated at 30 °C with 1N NaOH at; (a) 0.5 hour, (b) 2.5 hour, (c) 5 hour and (d) 45 °C for 5 hour.

The surface treatment leading to improved fluxes, due to increase in surface hydrophilicity. This is in accordance with the observations by Oh et al. (2001) who found increase in flux. At higher treatment time Figure 4.2a and 4.2b showed decline in flux. This could be because of pore swelling as described in Section 4.3.1.2. This observation is in accordance with Yang et al. (1997). Thus we established a mechanism of surface treatment of PAN and could explain successfully both, flux enhancement as well as reduction because of pore swelling.

It was thought to apply this phenomenon of pore collapse with the formation of –COO^-Na^+ on the membrane surface for As-V rejection by Donnan exclusion principle as proposed by Brandhuber et al. (1998). Author demonstrated sulfonated polysulfone based UF membrane, which showed only 72% rejection. This could be because of inherent material limitation of PSF, which can not be sulfonated beyond certain degree of sulfonation. It was thought that, PAN as a membrane material having negative charge on its membrane surface may not face such limitation. It could be possible to obtain high concentration of negatively charged groups (–COOH) to offer higher arsenic rejection. These investigations are discussed in following section. The work on PAN hydrolysis given in Section 4.3.1 is based on 15% concentration of PAN in the dope solution. These membranes showed > 90% BSA rejection. The Donnan exclusion principle may not work with such high porosity membrane. The porosity of the membrane can be lowered by using following strategies (i) annealing to reduce pore size, followed by hydrolysis to induce –ve charge on the surface (ii) surface hydrolysis of the PAN membrane prepared with smallest porosity possible, using NaOH as a base and (iii) grafting of SSA onto the membrane surface.

4.3.2. Effect of annealing

PAN_{12} membranes (prepared with PVP as an additive, NMP as a solvent and 3265 as a porous support) before annealing showed 90 $l.m.^{-2}h.^{-1}$ flux. The PVP was used as an additive as the blends of PAN/PVP are compatible over all compositions [Guo (1996)] and it is known to suppress macrovoids [Boom (1992)]. After annealing in hot water (80 °C), the water flux drastically decreases. It is known that the annealing process makes the size of pore to be small [Jung (2005)]. The sharp decrease in flux was observed upto 5 min., but after that flux remained unchanged till 60 min (Figure 4.8). Thus, after certain annealing time there was no significant change in the pore size of the membrane. Such reduction in flux after annealing was also observed by Jung et al. (2005), Kim, I. et al. (2002a). It was stated that annealing in hot water led to the rearrangement of amorphous and crystalline domains of PAN. The size of crystallite and the degree of crystallinity were changed when the membrane was annealed in hot water and the water is able to swell the amorphous domain of PAN and causes the change of crystalline structures [Jung (2005)]. In view of ease in inducing crystallinity, it was thought that effects of annealing could be made reversible as the PAN membrane might change its induced crystallinity after some duration or a particular treatment, as done during the hydrolysis. Thus, the investigations were not pursued.

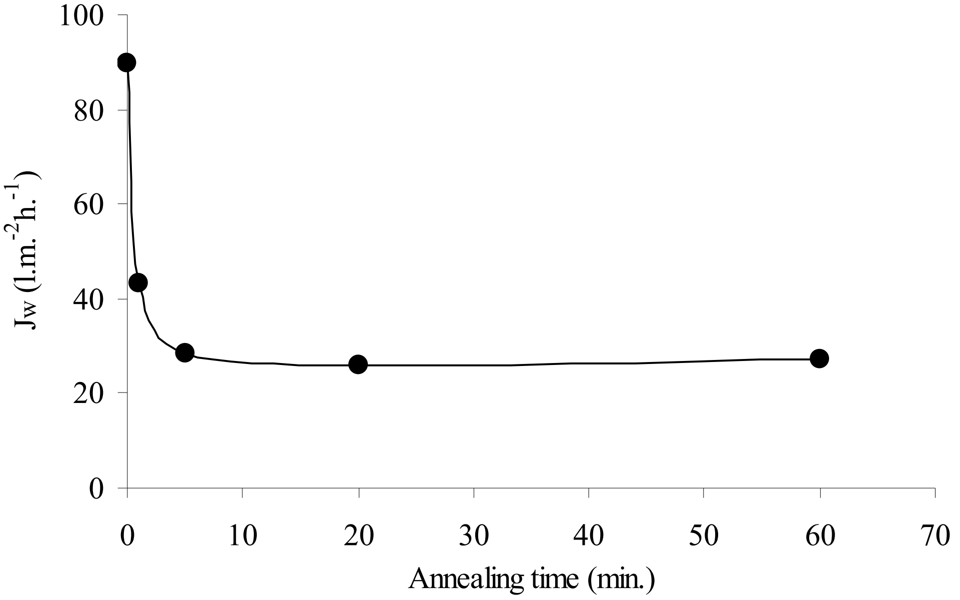


Figure 4.8 Effect of annealing time on flux performance.

4.3.3. Hydrolysis of PAN_{23} membrane and As rejection analysis

The membrane with lower porosity was preferred to achieve effective As-V rejection. Thus, PAN_{23} was chosen as our earlier study (Chapter 3) showed that membrane with 23% polymer concentration and NMP as a solvent showed better selectivity while above this concentration (25%) the membrane showed defects due to higher viscosity of the dope solution. The membrane was prepared using Viledon H1006 as a porous support material. The porosity of PAN_{23} was low enough which after NaOH treatment could reduce further. It was thought these low MWCO membranes will have strong repulsive interactions due to negative charge (due to the formation of $–COO^-$ group on the surface as well as pore walls) which are placed very close to each other as compared to higher porosity membrane. These strong repulsive interactions would be helpful to reject As-V, though it is a very small species following Donnan exclusion principle.

The unmodified membranes exhibited average water flux of 27±5 $l.m^{-2}.h^{-1}$ (cross flow mode) at 1 bar transmembrane pressure for samples of different batches of membrane casting. BSA (68 kDa) and ovalbumin (43 kDa) rejection for these membrane samples was > 95%, while pepsin (33 kDa) rejection was 68%. The rejection for this membrane was from 29% to 45% for varying molecular weight of PEG (6 - 35 kDa) as shown in Figure 4.9.

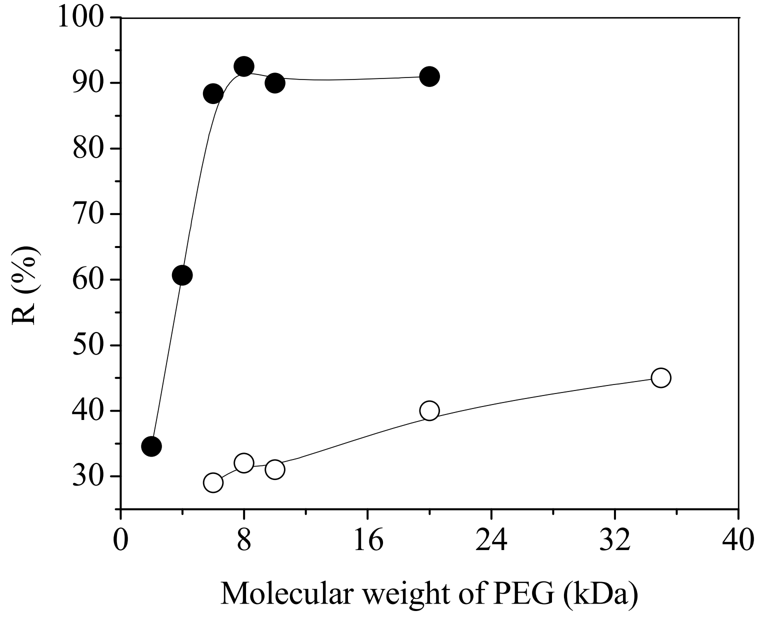


Figure 4.9 Rejection analysis of unmodified (○) and surface modified (●) membrane.

4.3.3.1. Surface modification, flux and rejection characteristics

The unmodified membrane showed 27 ± 5 $l.m^{-2}.h^{-1}$ water flux which was reduced to 8 ± 2 $l.m^{-2}.h^{-1}$ (by cross flow mode) at 1 bar transmembrane pressure after the 1N NaOH treatment for 2.5 hour at 45 °C. This surface modified membrane showed no passage of proteins (ovalbumin and pepsin). The unmodified membrane had shown considerable passage of pepsin (68% rejection). After surface modification, not only this passage was inhibited, but PEG (35 kDa) also showed quantitative rejection. Thus PEGs of different molecular weights were used to determine the rejection by dead end mode. The molecular weight cut off (MWCO) of the surface modified membrane by PEG rejection analysis was found to be ~ 6 kDa (Figure 4.9). This behavior could be attributed to the reduction in pore size, as there is a formation of $–COO^{-}$ groups on the membrane surface as well as on the pore wall. Since the membrane was not subjected to the acid treatment, hydrolysis of the –CN functionality of PAN leading to carboxylic group formation remains in $–COO^{-}$ Na^{+} form. The presence of Na^{+} for similar PAN membrane modification was earlier confirmed by ESCA (Section 4.3.1.4). The negative charge of the $–COO^{-}$ group caused repulsive interactions among the labile chains, leading to swelling of the surface and thus reduction in porosity (Section 4.3.1.2). Such reduction in porosity of PAN based membrane by NaOH treatment was also observed by Bryjak et al. (1998). It was also shown that conversion of $–COO^{-}\,Na^{+}$ to –COOH by acid (0.1N HCl) treatment increased the porosity to some extent, which led to enhancement in water flux (Section 4.3.1.2). In present case also, post-treatment by 0.1 N HCl to the NaOH treated (surface modified) membrane increased water flux by 72%, while rejection of PEG (6 kDa) was 54%, vis-a-vis 88% rejection for NaOH treated membrane (Figure 4.10). This reduction in rejection also supported increase in the pore size after HCl treatment. The values of mean effective pore radius (μ_p) and geometric standard deviation (σ_p) was obtained by plotting solute rejection versus solute diameter (Figure 4.11). The μ_p of modified membrane was 2.8 nm while σ_p was 1.97.

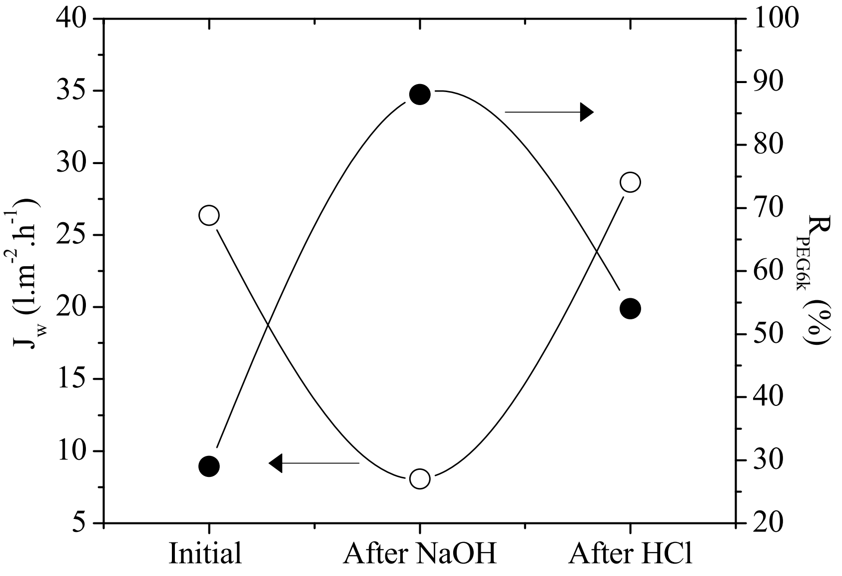


Figure 4.10 Change in water flux (○) and PEG (6 kDa) rejection (●) for membranes with different surface characteristics.

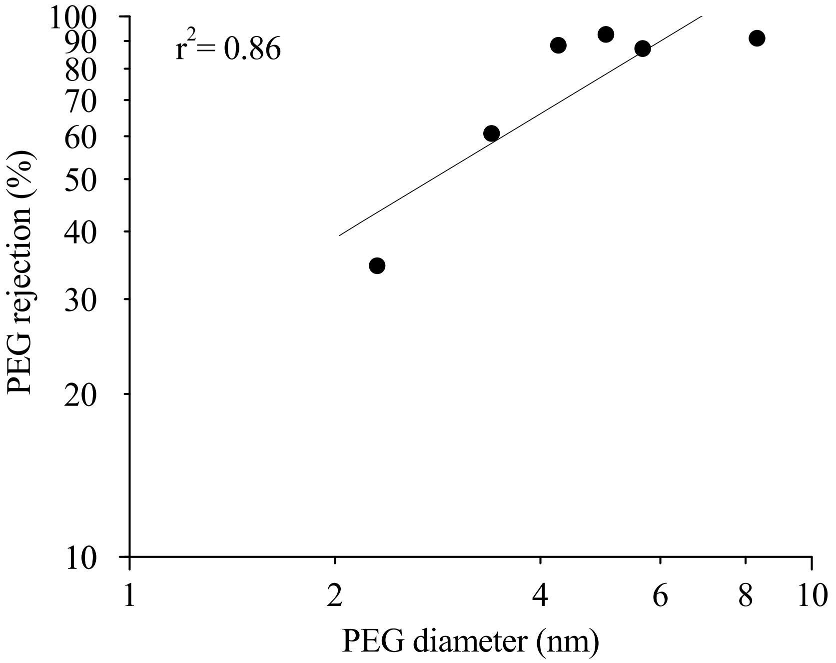


Figure 4.11 PEG rejection versus PEG diameter for surface modified PAN membrane.

4.3.3.2. Contact angle and FTIR-ATR analysis

The water contact angle for unmodified PAN_{23} membrane was 60°, which changed to 33° after the NaOH treatment of 2.5 hour at 45 °C. The work of adhesion (ωA) of dispersion increased from 107.5 $mN.m^{-1}$ to 132.4 $mN.m^{-1}$ for unmodified and modified membrane, respectively. This indicated increase in hydrophilicity after the NaOH treatment. It is reported that the conversion of $–CN$ to $–COO^{-}$ groups proceeds through amide formation [Litmanovich (2000)], as also confirmed by FTIR-ATR analysis in the present case. It could be seen from Figure 4.12 that the amide as well as the carboxyl functionalities were present on the surface of the modified membrane. The peaks emerged at 1654 cm^{-1} and 1724 cm^{-1} which are characteristic of the carbonyl ($C=O$) attached to amine group and hydroxide group, respectively. The formation of $–COO^{-}$ ion was confirmed by appearance of the strong asymmetrical stretching band at 1561 cm^{-1} and weak symmetrical stretching band at 1400 cm^{-1} [Silverstein (2006)]. These peaks were absent in the case of unmodified membrane. Moreover, a characteristic broad peak for primary amine and hydroxide merged together and appeared at 3334 cm^{-1}, which is much broader than that for the unmodified membrane. The appearance of similar peak (though weaker) in this region for unmodified membrane indicated that the starting PAN material used for membrane preparation could be partially hydrolyzed. This was also supported by the contact angle measurement of unmodified membrane, which was found to be 60°. The contact angle for PAN membrane was reported to be 78° [Asatekin (2007)].

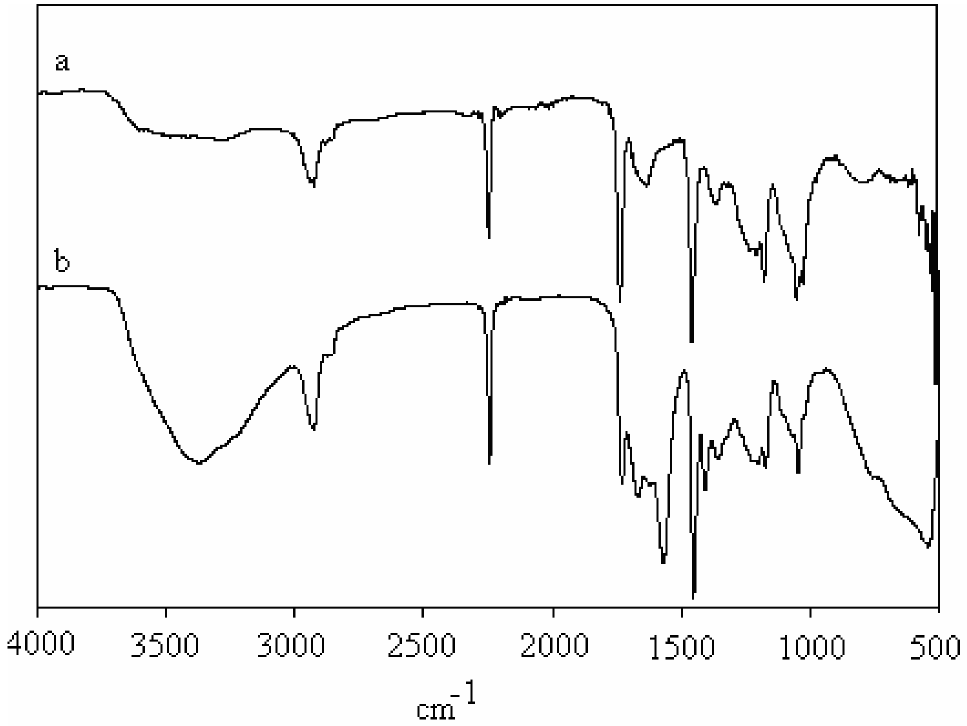


Figure 4.12 FTIR-ATR spectra of (a) unmodified and (b) surface modified PAN membrane.

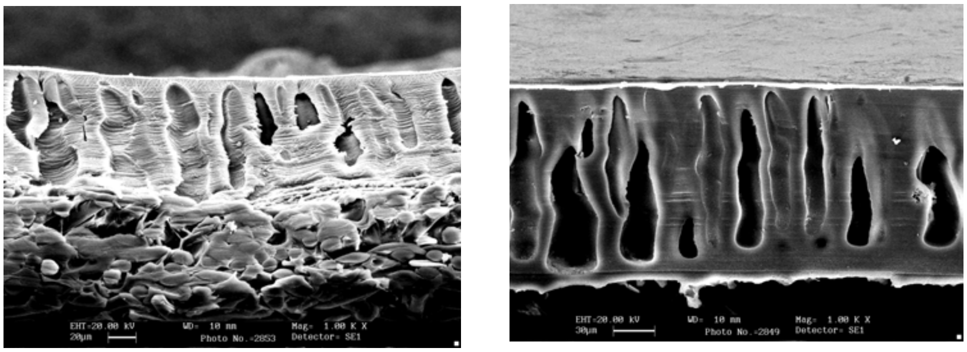
4.3.3.3. EDAX, SEM and AFM studies

The hydrolysis of PAN membrane was confirmed by EDAX analysis. The results obtained are summarized in Table 4.6.

Table 4.6 EDAX analysis of PAN membrane surface.

Element	**Unmodified membrane**		**Modified membrane**
	Theoretical (wt. %)	**Observed (wt. %)**	**Observed (wt. %)**
Carbon	67.9	72.7	68.8
Nitrogen	26.4	19.6	11.2
Oxygen	0	7.7	19.9

The unmodified membrane showed 7.7 wt. % of oxygen, which could be attributed to either the adsorbed oxygen [Zhao (2005)] or its presence due to partial hydrolysis of PAN, or both. Initial PAN used for membrane preparation could be partially hydrolyzed, as revealed by FTIR-ATR and contact angle analysis. After NaOH treatment, an increase in oxygen content from 7.7% to 19.9% and reduction in nitrogen from 19.6% to 11.2% supported the hydrolysis of the nitrile (–CN) to carboxylate (–COO^{-}) group. SEM images of the unmodified and surface modified membranes are shown in Figure 4.13. They clearly reveal reduction in the pore size and smoothening of surface after NaOH treatment. The observed behavior could be attributed to the repulsive interactions of –COO^{-} groups of polymer chains, which force them to move away from each other and from the surface; leading to the reduction in pore size and swollen morphology.



(a) (b)

Figure 4.13 SEM of cross section of (a) unmodified and (b) surface modified PAN membrane.

The surface roughness analysis by AFM was performed to confirm the surface smoothening. Figure 4.14 shows 3D AFM images and the topography for the unmodified and surface modified PAN membrane. The surface topography revealed that the modified membrane surface has low roughness as compared to the unmodified membrane.

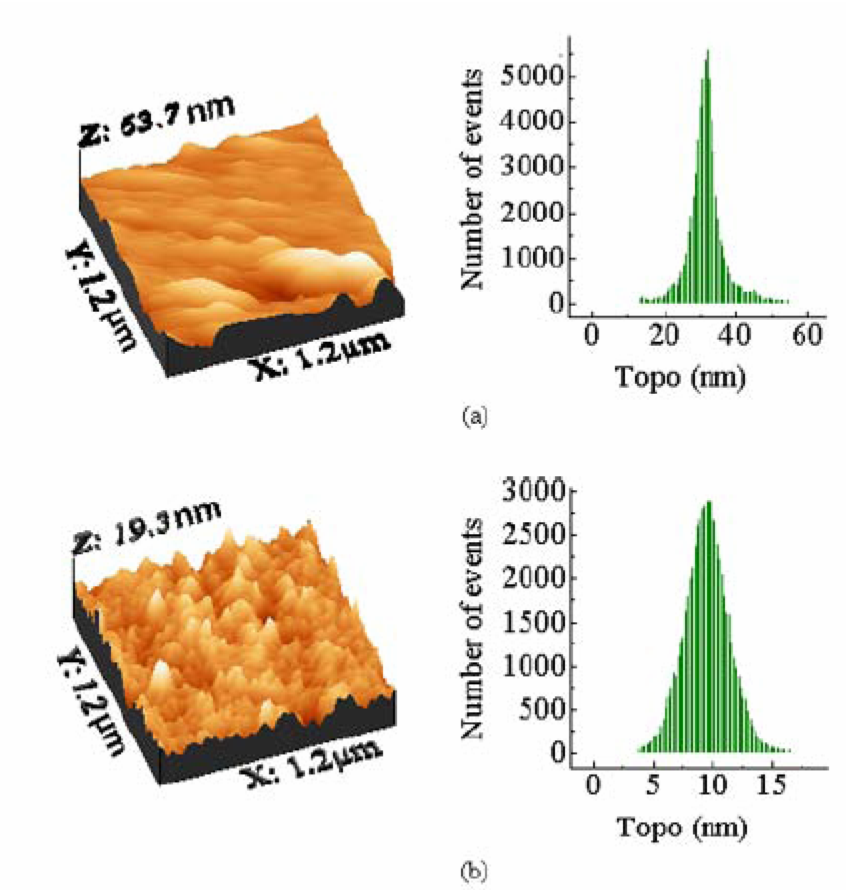


Figure 4.14 AFM analysis of (a) unmodified and (b) surface modified PAN membrane.

4.3.3.4. Arsenic rejection analysis

The effects of physical parameters (temperature, pressure and cross flow velocity) as well as chemical parameters (concentration of feed and pH) on the arsenic rejection of modified membrane were studied as a function of time. The experiments were done in concentration mode and the permeate samples were collected and analyzed for the arsenic content.

a. Effect of feed concentration

The surface modified membranes were analyzed for various feed concentrations of As-V (50 ppb, 250 ppb, 1000 ppb, 50 ppm and 1000 ppm) by cross flow mode and the results were as shown in Figures 4.15 to 4.17. Rejection of As-V was reduced when As-V concentration in the feed was increased. For 1000 ppm arsenic concentration in the feed, the rejection was ~ 60%, which increased to > 95% for 50 ppm (Figure 4.15 and 4.17). For 1000 ppb feed concentration, the arsenic rejection was between 96 to 98%, which further increased to ≥ 98% for 250 ppb and approached almost 100% for 50 ppb (Figure 4.15 and 4.16) . The experimental results of As-V rejection by the modified PAN UF membrane were consistent with Donnan exclusion Principle as the dominant mechanism of rejection. However, the effect of feed concentration of arsenic on its rejection through the membrane can be explained via concentration polarization model. High concentration in the feed leads to high concentration of arsenic at the membrane surface resulting in high concentration polarization and thus reducing the overall rejection.

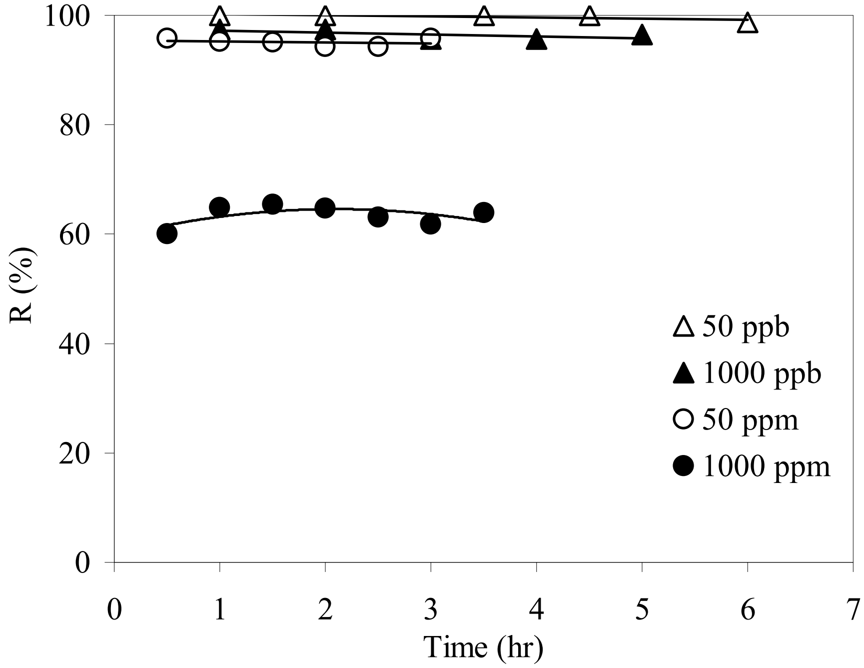


Figure 4.15 Arsenic rejection (R) at different feed concentration (pH: 7, cross flow velocity: 0.29 m.s^{-1}, pressure: 1 bar, temperature: ambient).

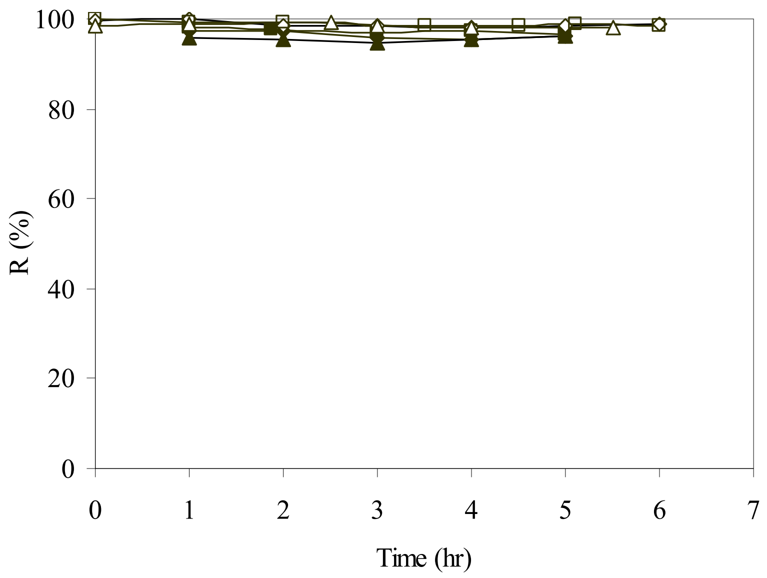


Figure 4.16 Variation in arsenic rejection (R) at 250 ppb (unfilled symbols) and 1000 ppb (filled symbols) as the function of cross flow velocity and pressure (0.24 bar: 0.24 m.s^{-1} (-♦-), 0.39 m.s^{-1} (-◊-); 1 bar: 0.23 m.s^{-1} (-■-), 0.35 m.s^{-1} (-□-); 2 bar: 0.09 m.s^{-1} (-▲-), 0.13 m.s^{-1} (-Δ-).

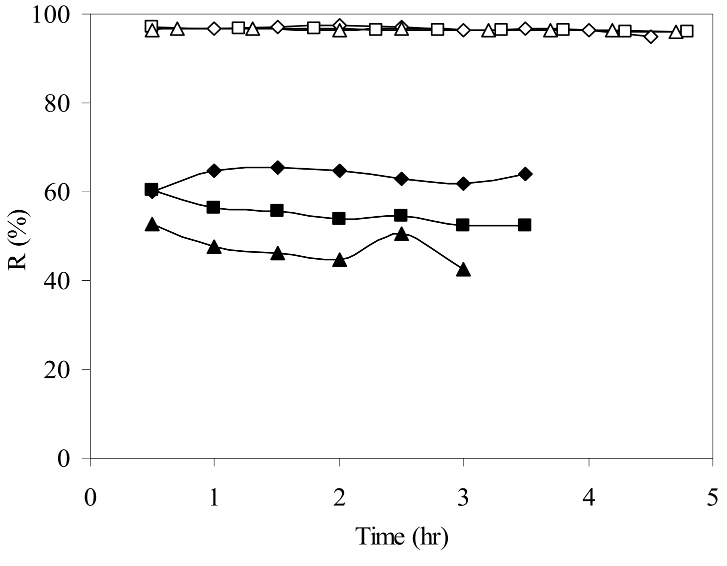


Figure 4.17 Variation in arsenic rejection (R) at 50 ppm (unfilled symbols) and 1000 ppm (filled symbols) as the function of cross flow velocity and pressure (0.29 m.s^{-1}, 0.24 bar: -◊-, -♦-; 0.28 m.s^{-1}, 1 bar: -□-, -■-; 0.027 m.s^{-1}, 2 bar: -Δ-, -▲-).

b. Effect of pressure and cross flow velocity

Figures 4.16 and 4.17 show the variation in arsenic rejection at 250 ppb, 1000 ppb, 50 ppm and 1000 ppm feed concentration of As-V with transmembrane pressure of 0.24 bar to 2 bar and cross flow velocity of 0.027 $m.s^{-1}$ to 0.39 $m.s^{-1}$. For concentration ≤ 50 ppm of arsenic, concentration polarization at membrane surface was expected to be negligible so that the cross flow velocity and TMP variation did not change the As-V rejection performance. However, for 1000 ppm feed concentration, the observed rejection varied from as low as 40% to as high as 65%. The lower % rejection for arsenic was observed for lower cross flow velocity and higher pressure and high % rejection was observed for high cross flow and low pressure (Figure 4.17). For 0.29 $m.s^{-1}$ cross flow velocity and 0.24 bar TMP, the % rejection was higher (around 65%) as shown in Figure 4.16. But by decreasing the cross flow velocity to 0.027 $m.s^{-1}$ and increasing TMP to 2 bar, the rejection decreased to around 40% (shown in Figure 4.17).

c. Effect of feed pH

Variation in permeate flux and As-V rejection were observed with the change in pH of feed solution for NaOH modified membrane (Figure 4.18). At pH 4 and 5, the As-V rejection was initially 64% and 82% respectively, which was reduced to 46%, after 2 hours and 78%, after 2.5 hours. At pH 6, the rejection varied within a short range (83-86%); while at pH 7, initial rejection (≥ 95%) was almost constant up to 2.5 hours. Along with the rejection, corresponding permeate flux at the same pH was also determined. The permeate flux was 20±4 and 17±2 $l.m^{-2}.h^{-1}$ at pH 4 and pH 5, respectively. For pH 6 and pH 7, changes in permeate flux were not so significant as a function of time and were 11±1 and 9±1 $l.m^{-2}.h^{-1}$, respectively. Although difference in permeate fluxes were not high at pH 6 and pH 7, the significant enhanced rejection was observed at pH 7, compared to that of pH 6. The rejection was found to be inversely proportional to the permeate flux. This could be ascribed to both, the change in membrane porosity with pH (as discussed in Section 4.3.1.2 above) as well as the state of the arsenic in the feed solution at certain pH. Initially, As-V would be in monovalent anion or divalent anion state [Urase (1998)]. It is reported [Brabdhuber (2001)] that the trend of increased rejection with increase in pH corresponds to the degree of de-protonation of the monovalent arsenic anion to the divalent anion $HAsO_4^{-2}$, which gives better rejection than the monovalent anion H_2AsO_4. As the pH lowers, the conversion of $-COO^{-}$ present on the membrane surface to –COOH is enhanced. This favors attractive interactions among the chains on the membrane surface, leading to the contraction of chains. This in turn increases membrane pore size than for the case wherein solely $-COO^{-}$ (basic conditions) is present on the surface (Section 4.3.1.2). This increase in porosity could lead to the reduction in rejection and increase in flux. Moreover, the conversion of $-COO^{-}$ to –COOH reduces the negative charge density on membrane surface and thus also the capability of membrane to repel As-V to cause rejection by Donnan exclusion principle.

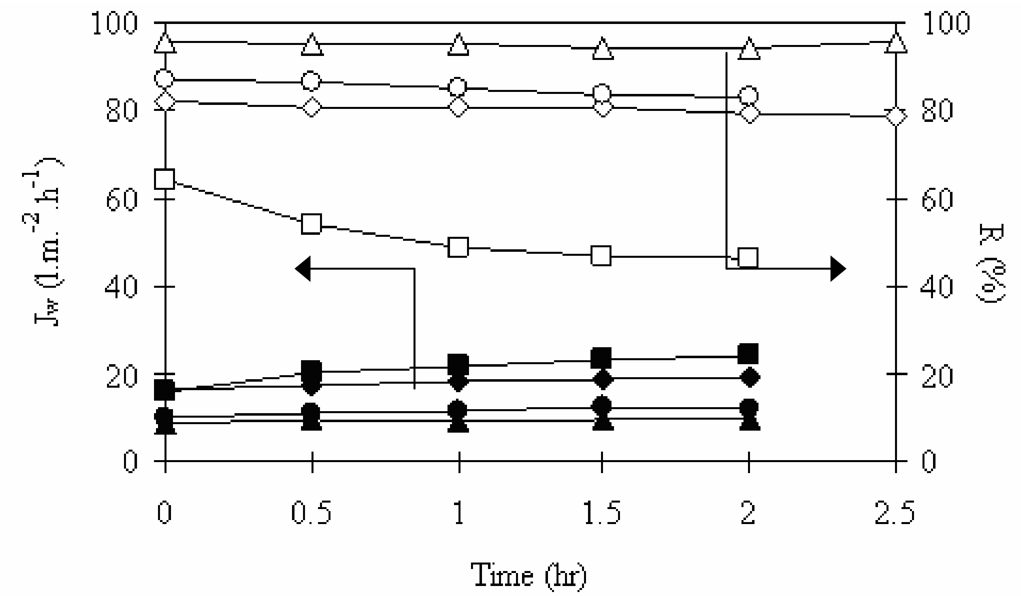


Figure 4.18 Variation in arsenic rejection (R, unfilled symbols) and permeate flux (filled symbols) with time and feed solution pH for 50 ppm As-V concentration in feed, (pH = 4: -□-, -■-; pH = 5: -◊-, -♦-; pH = 6: -○-, -●-; pH = 7: -Δ-, -▲-).

d. Effect of feed temperature

The influence of feed temperature on As-V rejection using 50 ppm feed concentration was as plotted in Figure 4.19. Increase in temperature generally results in beneficial effects of lowering viscosity and increasing diffusion from transport point of view. The experiments were therefore carried out at different temperature for a constant pressure, cross flow velocity and pH. Figure 4.19 clearly indicates that the rejection coefficient was dependent on the temperature. As the feed temperature increased from 4 to 30 °C, As-V rejection increased. It was closer at 24 °C and 30 °C. Since overall transport of the solute (As-V) under the experimental conditions is dominated by convective transport rather than the diffusive transport, the overall change in rejection could be small [Brandhuber (2001)]. The effect of temperature on polymer chain dynamics could also play a role here, which needs further investigations. At lower temperature, chain movements could be anticipated to be lower than those at higher temperature. The effect could be more significant when $-COO^-$ containing chains exhibit repulsive interactions.

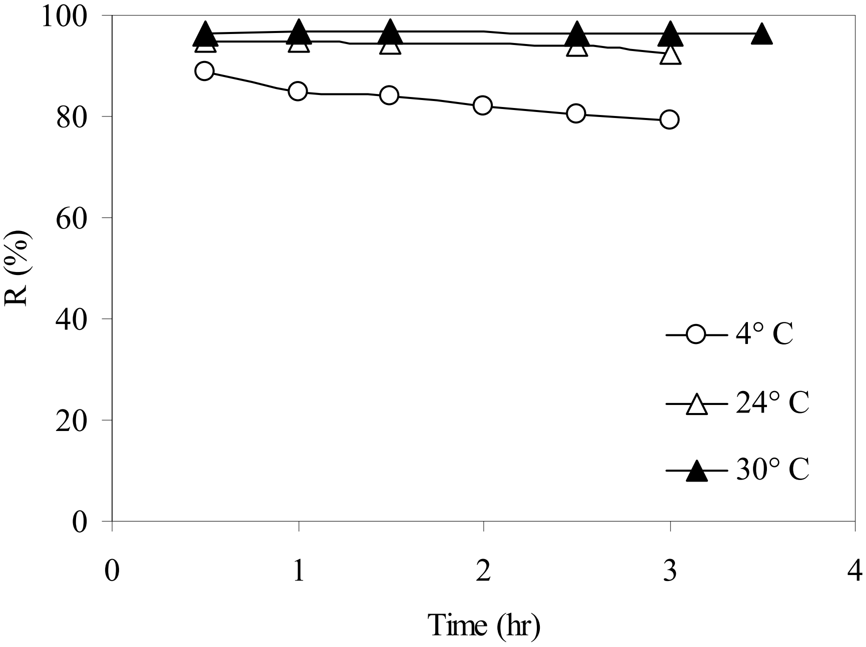


Figure 4.19 Variation in arsenic rejection (R) with feed temperature (feed concentration: 50 ppm of As-V, pH: 7).

4.3.4. Spiral analysis and its modification

The flat sheet PAN_{23} membrane showed quantitative retention of As-V (Section 4.3.3.4). For assessing feasibility at larger scale, the spiral wound modules were prepared using PAN_{23} membranes prepared with $ZnCl_2$ as an additive. The water flow rate of these modules was analyzed using assembly as discussed earlier (Section 4.2.4.5). The results are given in Table 4.7.

Table 4.7 Spiral wound module analysis.

PAN_{23} unmodified membrane	Water flow rate (lit.hr.$^{-1}$)		NaOH flux after 3 hour treatment (lit.hr.$^{-1}$)	Water flow rate after modification (lit.hr.$^{-1}$)	PEG_{8k} rejection after modification (%R)
	Average	Variation (%)			
$ZnCl_2$ additive	4.2	17	1.5	0.9	96

The average water flow rate of 15 spiral modules analyzed was 4.2 lit.hr.$^{-1}$. Since the initial flow rate was lower and the spirals were prepared with single leaf, the variation in water flow rate could be higher. Since the gluing was done manually, it may also contribute to this observed variation as a result of deviation in active membrane area.

The surface modification of these spirals was done with 1N NaOH at 45 °C. Initially, the treatment time was kept same as that of the flat sheet membrane modification by cross flow mode (Section 4.3.3.1). It was found that the rejection of PEG_{8k} was 77%, which was much lesser as that of the rejection of flat sheet membrane. Thus the treatment period was increased to 3 hour. The rejection of PEG_{8k} after this variation could be achieved to 96%, which is in line with the rejection of flat sheet membrane. The water flow rate for modified membrane was 0.9 lit. hr.$^{-1}$.

4.3.4.1. As-V rejection analysis

The surface modified spiral was analyzed for arsenic rejection by using cross flow mode at different pH. The feed concentration was kept as 1 ppm. The permeate sample was collected immediately after circulation and the other sample was collected after 15 min. circulation. The modified spiral at pH 6.95 showed 94% arsenic rejection initially, which after circulation for 15 min. reduced to 79%. At higher pH 8.56, the spiral showed 88% rejection after circulating the feed solution for 15 min. (Table 4.8). Though the flat sheet membrane showed > 95% rejection under similar conditions, the spiral module showed slightly lower rejection. This could be attributed to various reasons. One of them could be the defects in the spiral module originating from large scale membrane area. Secondly, the effect of large volume circulation, maintaining pH conditions, etc. could also be responsible and need further investigations.

Table 4.8 Arsenic rejection analysis of surface modified spiral wound module.

Membrane code	pH of feed solution	As-V rejection (%R)	
		Initial	After 15 min.
PAN_{23} module (E-98-1)	6.95	93.5	79
	8.56	99	88

4.3.5. Grafting of SSA on PAN_{23} membrane

A phenomenon of pore swelling and deswelling due to change in pH was observed as given in Section 4.3.1.2. At lower pH, the swollen polymer chains got collapsed due to H-bonding interactions after the formation of –COOH functionality. This leads to increase in pore size of the membrane. It was anticipated that the formation of –COOH functionality would lower the rejection of As-V in acidic condition (as a result of reduction in the negative charge density on the membrane surface and increase in pore size). In view of lower pKa value of sulfonic acid group (1.8) [Belfer (2003)] as compared to carboxylic acid (4.25) group [Oliviero (2000)], it was thought that the sulfonation of PAN would result a membrane that could exhibit As rejection capability at even lower pH range also. In case of PAN based membrane, introduction of $–SO_3H$ functionality can be done by grafting PAN membrane by monomeric styrene sulfonic acid by using redox initiators, as reported by Belfer et al. (2003).

For grafting of SSA on the membrane surface, PAN_{23} membrane with 20 $l.m.^{-2}h.^{-1}$ flux and 24% PEG_{8k} rejection were used. The grafting was done at 30 °C by using redox initiator and by varying grafting time, viz., 10, 60 and 120 min. The grafted coupons were dipped in DI water for 6 days to remove excess of the monomer as well as polymer, those were not grafted onto the PAN membrane surface. The performance of grafted membrane was analyzed by water flux and PEG_{8k} rejection analysis and was compared with the base unmodified membrane. After 10 min. grafting time, the water flux reduced upto 59%; while at 60 min. it was reduced by 83% and remained almost constant for 120 min

(Figure 4.20). Belfer et al. (2005) also observed such decline in water flux after grafting. The PEG_{8k} rejection was 36%, 40% and 55% at 10, 60 and 120 min. grafting time, respectively (Figure 4.21). The decrease in flux and increase in rejection performance indicated the grafting of SSA on the PAN membrane surface. The grafted membranes were further dipped in 0.1N NaOH solution for 15 min. at ambient temperature to study the pore swelling due to the conversion of $–SO_3H$ groups to $–SO_3^{-}Na^{+}$, as was observed in case of carboxylic acid functionality (Section 4.3.1.2). It was observed that, at 10 min. grafting time the flux reduced further, while it was almost similar at 60 and 120 min. grafting time as shown in Figure 4.20. These NaOH treated grafted membrane showed increase in PEG_{8k} rejection performance upto 60 min., while at 120 min. it remained unchanged (Figure 4.21). Thus, the study shows that the effect of grafting upto 60 min. was significant. The rate of grafting decreased after this duration, as all monomer might have got polymerized.

It would have been interesting to investigate the As-V rejection capability of these membranes, but was not attempted since the observed PEG rejection was lower. In order to improve the membrane performance for this application, more investigations are necessary.

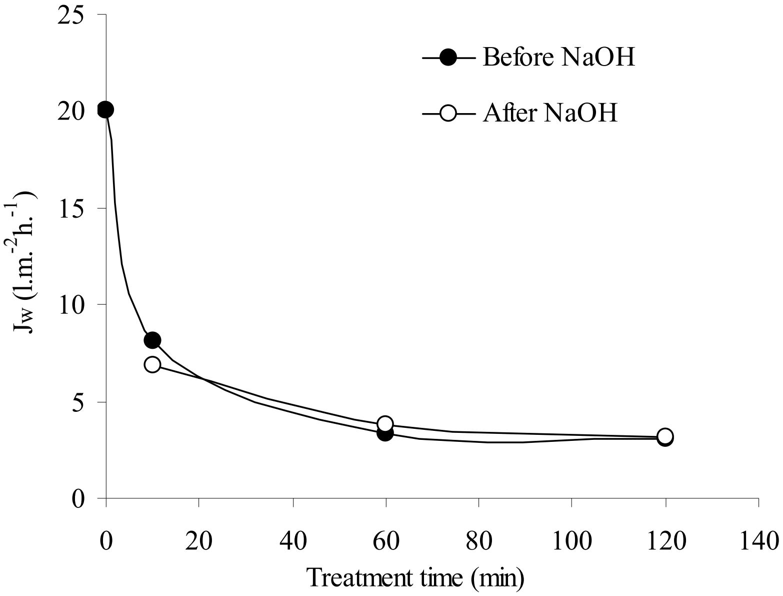


Figure 4.20 Flux analysis of grafted membrane; (●) before NaOH treatment and (○) after NaOH treatment.

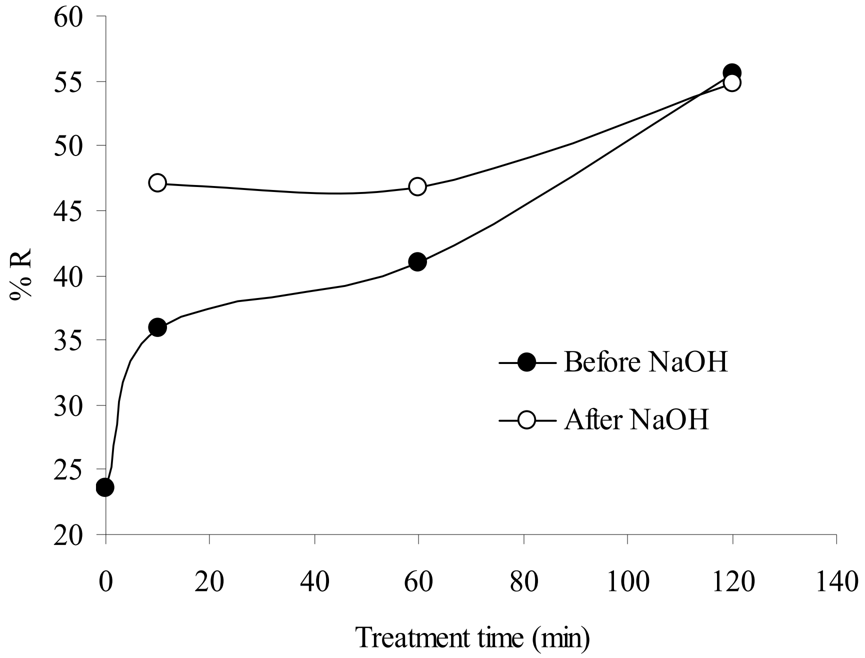


Figure 4.21 PEG_{8k} rejection analysis of grafted membrane; (●) before NaOH treatment and (○) after NaOH treatment.

4.4. Conclusions

An increase in the water flux for PAN_{15} membrane was achieved by surface treatment of PAN membranes either by organic bases (TEA, EA) or by inorganic bases (NaOH, KOH), the latter being more effective. The flux improvement was attributed to the hydrolysis of –CN functionality to amide and carboxylic acid groups. SEM did not show any variation in membrane porosity after the treatment. A maximum increase of 152% in water flux was achieved by dead end mode type of treatment within 20 hours, while cross flow offered maximum increase of 230% within just 2.5 hours duration at 45 °C. Smaller variation observed in BSA rejection with substantial improvement in the water flux was attributable mainly to the changes in surface hydrophilicity.

PAN membranes were prepared using PVP as an additive with an objective of obtaining low porosity membrane by annealing of such membrane. The annealed membrane showed sharp decrease in flux within 5 min. annealing time, which reduced further after 10 min. and remained constant upto 60 min. treatment time; revealing limited success of this approach for reducing pore size.

In another attempt of reducing membrane pore size, PAN_{23} membranes were prepared having ~ 33 kDa MWCO. These membranes after hydrolysis by NaOH showed decrease pore size and thus in water flux. The MWCO of this membrane was ~ 6 kDa. The reduction in pore size was attributed to the formation of $–COO^{-}$ groups on the membrane as well as pore wall surface. These groups caused repulsive interactions among the labile chains present on the surface, leading to swelling of the pore. The presence of carboxylic group after the modification was confirmed by FTIR-ATR and EDAX analysis. SEM images showed pore size reduction and pore smoothening after the NaOH treatment. The surface smoothening was confirmed by AFM analysis, as surface roughness of the membrane was reduced after the modification. These modified membranes showed excellent As-V rejection following Donnan exclusion principle. The $–COO^{-}$ groups present on the surface as well as on the pore wall repel negatively charged arsenic efficiently and size exclusion mechanism of conventional UF has a little contribution to arsenic removal. On the other hand, porosity of UF membrane allowed operational pressure to be lower than conventional RO or NF membranes used for As removal. Variation of pH had a strong role on rejection efficiency. More than 95% rejection was achieved for pH ≥ 7 at a low arsenic concentration (i.e. ≤ 50 ppm) in feed; which approached to beyond detectable limits for concentration of 50 ppb. The effect of cross flow velocity and transmembrane pressure on the arsenic rejection was negligible for feed concentration ≤ 50 ppm. For 1000 ppm feed concentration of arsenic, rejection was varied from 40 - 65% and was a function of cross flow velocity and transmembrane pressure. The membrane showed consistent rejection of arsenic till 6 hours of continuous operation. The single leaf spiral wound module for this purpose was prepared, which offered 4.6 $lit.hr.^{-1}$ flow rate with 2.7 bar bubble point. The NaOH modified spiral module (3 hour, 45 °C) showed reduction in flow rate (0.9 $lit.hr.^{-1}$) with 96% PEG_{8k} rejection. At 6.95 pH, the module showed 79% rejection while at 8.56 pH, it was 88%.

SSA was grafted on the membrane surface using redox initiator. Effect of grafting time on the membrane performance (flux and PEG_{8k}) rejection was analyzed. The base membrane showed 20 $l.m.^{-2}h.^{-1}$ flux and 24% PEG_{8k} rejection. The flux after grafting decreased sharply upto 60 min. and remained same till 120 min. treatment duration. The grafted membrane showed maximum 55% PEG_{8k} rejection at 120 min. grafting time.

Chapter 5: ABPBI based UF membranes

5.1. Introduction

Numerous separation technologies for solutions polluted by organic solvents could be improved or optimized by the application of solvent resistant polymeric membranes [Hicke (2002)]. The use of UF membranes for treatment of spent solvent cleaning rinses from nickel plating operations was studied by Qin et al. (2004). It was observed that membranes made of CA and PAN could tolerate the organic solvent(s) present in the cleaner and were suitable for treating the spent solvent rinses, whereas PES and PSF membranes were not suitable. Chemically and thermally resistant composite membranes based on poly(acrylonitrile) and poly(amideimide) were prepared by coating hydroxy propyl methyl cellulose (HPMC) and polyether-block-polyamides [Peinemann (2001)]. The formed composite membranes were suitable for the separation of low molecular weight substances from organic solvents. Hicke et al. (2002) reported that membranes from copolymers of acrylonitrile with maleic anhydride were not autoclavable because of hydrolysis. These authors prepared membrane based on poly(acrylonitrile-co-glycidyl methacrylate) (PANGMA) followed by post treatment with ammonia. The resultant membrane due to extensive cross-linking showed solvent stability, especially towards DMF. Furthermore, that membrane could be safely sterilized by hot steam at 121 or 140 °C and drying of the membrane on air is possible without any additives.

The PAN/Chitosan composite UF membranes were found to be stable in aqueous acidic (pH 3) and basic (pH 11) medium [Musale (1999)]. Solvent resistant UF membranes based on copolysulfoneimide showed stability towards alcohols, acetone and hexane was reported [Kim, I. (2002d)]. Poly(vinylidene fluoride) (PVDF), polyethersulfone (PES) and poly(sulfone) (PSF) based UF membranes were used for vegitable oil degumming (removal of phospholipids) by Ochoa et al. (2001). Results showed that PVDF based membranes were more stable with hexane than PES and PSF. Chung et al. (1996) manufactured PAN hollow fibers resistant to chloroform for the development of high-performance composite membranes [Qin (2004)]. Singh et al.

(1996) investigated the removal of volatile organic compounds using different UF membranes and obtained above 98% rejection for toluene with a poly(vinylidene fluoride) membrane of a molecular weight cut-off (MWCO) of 18,000 [Qin (2004)]. The poly(imide) based membrane was studied by Iwama et al. (1982). This membrane exhibited excellent stability and high fluxes with most common organic solvents, even when tested at elevated temperatures. Poly(p-phenylene-terephthalamide) based UF membranes were developed by Zschocke et al. (1980), which showed stability in almost all organic solvents including DMSO, NMP and DMAc.

The above literature reports indicate that the presently available membranes have limited stability under harsher environment. Polybenzimidazole (PBI) which is known as the high performance polymer owing to its excellent chemical [Wang, K. 2006c), Chung (1997)] thermal [Wang, K. (2006c), Tsur (1974)] and mechanical stability [Cho (2004)] was investigated as a membrane material for this work. PBI is a generic name of a class of heterocyclic polymers, and the most commonly cited member of this family in the literature is poly-2,2′-(m-phenylene)-5,5′-bibenzimidazole (PBI-I). It is widely investigated as the proton exchange membrane (PEM) material [Li (2003, 2004), Fu (2004), Schuster (2003)] and is synthesized by condensation of diaminobenzidine (DAB) and isophthalic acid (IPA) [Vogel (1961)] or their derivatives [Iwakura (1964)]. The applicability of this PBI-I as a membrane material for reverse osmosis (RO) and hemodialysis was demonstrated [Brinegar (1974), Model (1972a, 1972b)]. Its asymmetric [Chung (1998, 1999)] and ultrafiltration (UF) membranes are documented [Cherdron (1994), Sansone (1987)]. The surface of first generation reverse osmosis PBI membranes was characterized by optical microscopy, scanning electron microscopy, transmission electron microscopy and high resolution scanning electron imaging [Sawyer (1984)]. It was observed that top 20 nm layer had no resolvable pores, whereas the bulk membrane exhibited pores of about 100 nm across. These membranes revealed finger-like macrovoids below the top 500 nm layer. Wang, K. et al. (2006d) reported PBI-I based NF membranes (hollow fibers) with mean effective pore radius of 0.348 nm for cephalexin separation, which was dependent on the pore size and the electrostatic interactions between solute and the membrane. PBI-I based NF membranes with molecular weight cut-off (MWCO) of 525 Da exhibited V-shaped chromate rejection curve with an increase in pH [Wang, K. (2006e)]. A 98.4% sulfate and 97.2% chromate rejection with less than 4% chloride rejection at pH 13 from chlor-alkali brine [Wang (2007)] and effective removal of divalent heavy metal cations from their sulfate salt and chloride salt solutions [Lv (2008)] was also demonstrated using NF membranes. PBI-I and polyarylate blend membranes showed 60 - 80 gfd flux at 50 psi and 90 - 99% rejection of cytochrome-C (MW = 12,000) [Chung (2004)].

ABPBI, a member of PBI family is prepared by self condensation of 3,4-diaminobenzoic acid [Asensio (2004, 2005), Wolfe (1985)]. It has excellent thermo-chemical and mechanical stability [Cho (2004)] and is demonstrated for PEM application [G´omez-Romero (2005), Kim (2004), Wereta (1978)]. Neither glass transition nor crystalline melting point was observed in the temperature range of -150 to 400 °C for this polymer [Wereta (1978)]. Except PEM, other types of membranes based on ABPBI are not documented, in spite of its excellent thermo-chemical properties. One of the reasons could be that it is soluble only in strong acids such as sulfuric acid, formic acid, trifluoroacetic acid, phosphoric and poly(phosphoric acid) [Asensio (2005)]; while PBI-I based on DAB and IPA is soluble in polar aprotic solvents and the most widely used is *N,N*-dimethyl acetamide [Li (2003)]. Monomer cost and synthesis time for ABPBI are much lower than that for PBI-I.

Present work investigated ABPBI based phase inversion membranes. Effects of various parameters viz., porous support, nonsolvent and polymer concentration on the membrane performance in terms of water flux, MWCO and pore size distribution was studied. The stability of ABPBI membrane towards organic solvents, concentrated acid and base was evaluated. Capability of glycerol treatment to prevent pore collapse was analyzed.

5.2. Experimental

3,4-Diaminobenzoic acid (DABA, 97%) and poly(ethyleneglycol) (PEG) of different molecular weights were obtained from Aldrich chemicals (USA). Poly(phosphoric acid) (PPA, ca 84% as phosphorus pentoxide) was procured from Alfa Aesar (USA). NaOH, H_2SO_4 (98%), methane sulfonic acid (MSA), HCl, glycerol, *N,N*-dimethyl formamide (DMF), *N,N*-dimethyl acetamide (DMAc), toluene, tetrahydrofuran

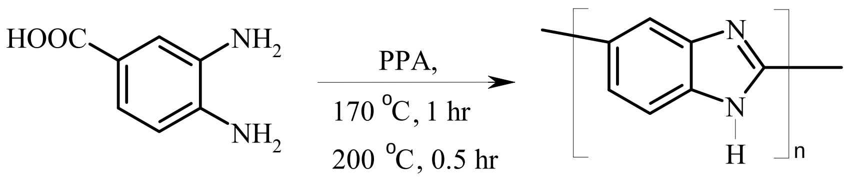
(THF), chloroform ($CHCl_3$), hexane, isopropyl alcohol (IPA) and isobutyl alcohol (IBA) were procured from SD fine chemicals (India). All these chemicals were of AR/GR grade and were used without further purification. The nonwoven support fabrics, viz., Viledon H3160 and FO2470 were procured from Freudenberg (Germany), while Hollytex 3324 and 3265 were procured from Ahlstrom (USA). Properties of these supports available from suppliers are given in Table 5.1.

Table 5.1 Physical properties of porous supports.

Porous support	**Weight (g.m^{-2})**	**Thickness (mm)**	**Air permeability**	**Tensile strength**	**Elongation (%)**
FO2470	60	0.12	200 (dm^3.s^{-1}.m^{-2})	200 -100 N/5 cm	28 - 33
H3160	60	0.07	30 (dm^3.s^{-1}.m^{-2})	210 N/50 mm	22
3324	99.9	0.13	9 cfm	CD 28 lbs.in^{-1} MD 60 lbs.in^{-1}	CD 80
3265	81.2	0.13	20 cfm	CD 21 lbs.yd^{-2} MD 65 lbs.in^{-1}	CD 70

5.2.1. Synthesis and characterization of ABPBI

ABPBI was synthesized by condensation of DABA in PPA [Asensio (2005)] as shown in Scheme 5.1 below.



3,4-Diaminobenzoic acid

Scheme 5.1 Synthesis route of ABPBI.

A three necked 1 liter round-bottom flask equipped with an overhead stirrer, N_2 inlet and $CaCl_2$ guard tube was charged with PPA (500 g) and heated upto 170 °C. 25 g of DABA (0.1644 mol) was added while stirring and heating continued for an hour. The temperature was raised to 200 °C and allowed to stir for 30 minutes. The reaction mixture was precipitated into stirred water; obtained polymer was crushed and thoroughly washed till neutral to pH. It was then kept under 10% aq. NaOH solution for 24 hours, washed with water till neutral to pH, soaked in acetone for 15 hours and dried in vacuum oven at 80 °C for a week. It was preserved in the desiccator until use.

Inherent viscosity of ABPBI was determined by using Ubbelhode viscometer with 0.2 $g.dL^{-1}$ solution in conc. H_2SO_4 at 35 °C. Wide-angle X-ray diffraction (WAXD) spectra of polymer was recorded using PANalytical X'pert Pro MPD X-ray diffractometer with Cu-K_α radiation in 2θ range of 5-40°. Thermogravimetric analysis (TGA) of polymer was performed by using Perkin Elmer TGA-7 under nitrogen atmosphere at the heating rate of 10 $°C.min^{-1}$.

5.2.2. Membrane preparation

The dope solutions of ABPBI were prepared while varying polymer concentration (4% and 6% w/w) using MSA as the solvent at 70 °C and stirring under dry atmosphere for 48 hours. Higher concentration led to a gel formation and was not pursued further. The formed solution was allowed to cool to the ambient temperature and then degassed to remove trapped gases. The dope solution viscosity was measured using Brookfield digital viscometer (Model DV-I) at 0.5 RPM at the ambient temperature. Membranes were prepared using Sheen Automatic Film Applicator-1132 on different non-woven support fabrics as shown in Figure 5.1. The knife movement was set to 15 $cm.sec^{-1}$ transverse speed with a gap of 250 μm. The membranes were casted on porous fabric supports (FO2470, H3160, 3324 and 3265) at 20 °C gelation temperature and exposed in air for 8 seconds prior to dipping in nonsolvent bath. Water or 0.5N NaOH was used as the nonsolvent. The total thickness (along with support) of the supported membrane was ~ 200 μm. These membranes were washed with running water till neutral to pH and then stored at 4 °C until use. The identification of membranes is given in Table 5.2.

Figure 5.1 Sheen automatic film applicator.

5.2.3. Membrane characterization

5.2.3.1. Flux analysis

The flux analysis of ABPBI membrane was done in dead end cell with active area 14.5 cm^2 as described in Section 3.2.4.1.

5.2.3.2. Rejection analysis

The rejection analysis of ABPBI membranes was done using various molecular weight PEGs (0.1% w/v concentration in feed) in dead end cell with active area of 14.5 cm^2. The analysis of PEG was done as described in Section 4.2.2.2.

5.2.3.3. Pore size analysis

The ABPBI membrane pore size and its distribution were determined by liquid-liquid displacement method as described in Section 3.2.5.2.

The mean pore diameter of ABPBI membranes was determined by solute rejection method as described in Section 4.2.3.

5.2.3.4. Scanning Electron Microscopy (SEM)

The membrane cross sections were analyzed by using SEM and low vacuum SEM mode. The details of SEM instrument and sample preparation are given in Section 3.2.8. The cross section of ABPBI membrane in low vacuum SEM mode was analyzed by Quanta 200 3D SEM using large field detector (LFD). The sample chamber pressure was 200 Pascal. The membrane sample was treated with 10, 20 and 50% glycerol (in each glycerol concentration for 24 hours), sequentially and used for imaging.

5.2.3.5. Stability of ABPBI membrane in organic solvents, acid and base solution

Membrane stability was analyzed in DMF, DMAc, IPA, toluene, THF, $CHCl_3$ hexane, H_2SO_4 (25N) and NaOH (2.5N) at the ambient temperature. Membranes were also autoclaved at 15 psi pressure and 121 °C for 20 min. Membranes with known water flux were dipped in the respective solvent for 24 hours at the ambient temperature and flux of organic solvents was measured. For water immiscible solvents, the membranes were initially dipped in IPA for 24 hours and then in respective solvent for 24 hours, and again in IPA for the same time, before measuring the water flux for the comparison with the initial flux. The change in thickness before and after solvent treatment was also measured. Results were repeated at least for three coupons and then averaged.

5.2.3.6. Effect of glycerol treatment

Two concentrations of glycerol, 10 and 50% (v/v) were used for assessing their capability to refrain from pore collapse. Membranes were dipped into 10% glycerol solution for 24 hours. The 50% glycerol treatment was done by sequential dipping in 10% (8 hours), 20% (16 hours) and finally in 50% glycerol solution (24 hours). After the glycerol treatment, these membranes were allowed to dry in the oven at 60 ºC for 24 hours. These dried membranes were dipped in water overnight before measuring the flux. The effect of repeated 50% glycerol treatment (removal and recharge) on water flux of the membrane was also analyzed.

5.3. Results and discussion

5.3.1. ABPBI synthesis and characterization

The self polycondensation of DABA (Scheme 5.1) in PPA, which acts as a solvent as well as dehydrating agent [Harris (1993)] offered ABPBI. The reaction time of an hour at 170 °C and 30 minutes at 200 °C was enough to offer polymer with inherent viscosity of 1.72 - 2.17 dL.g^{-1}. The WAXD analysis of the polymer in powder form indicated its amorphous nature (Figure 5.2) having average interchain spacing (d-spacing) of 3.01 Å. It is reported that films of ABPBI prepared from methanesulfonic acid, chlorosulfonic acid or formic acid/m- cresol induces crystallinity [Wereta (1978)], owing to the nature of solvents and heating conditions [Sannigrahi (2006), Wainright (2003)]. Amorphous nature of phosphoric acid doped as well as undoped ABPBI dense membranes with *d* spacing of 3.4 Å is reported [Asensio (2004)]. Thermogravimetric analysis of ABPBI showed initial loss up to ~ 355 °C, which could be attributed to the loss of absorbed water. The polymer was stable up to 610 °C, while char yield at 900 °C was 45% as shown in Figure 5.3.

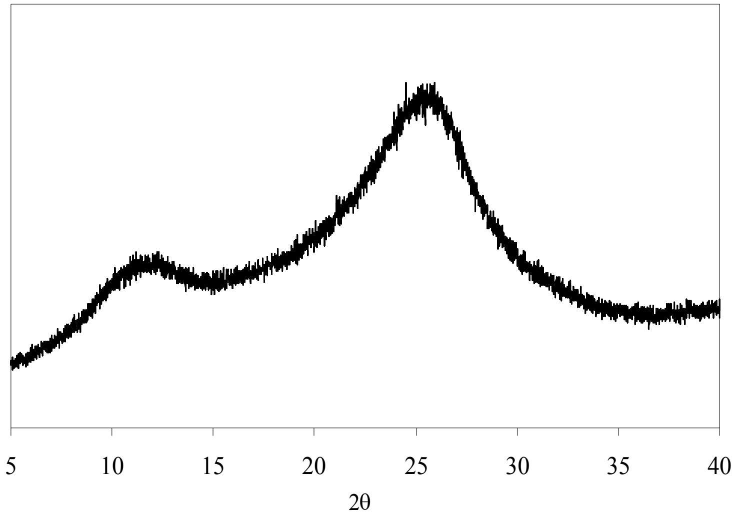


Figure 5.2 WAXD spectrum of ABPBI.

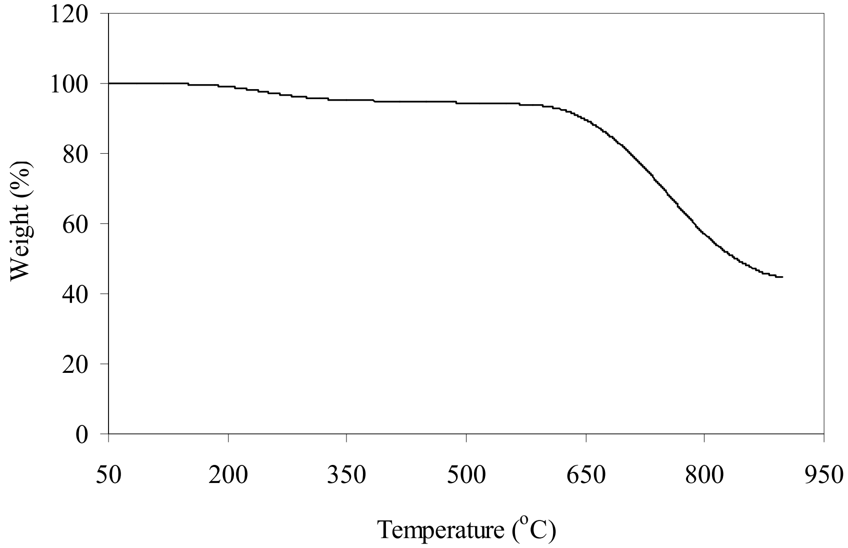


Figure 5.3 TGA spectrum of ABPBI.

5.3.2. Membrane preparation

ABPBI based UF membranes were prepared by varying porous supports, nonsolvent and polymer concentration in the dope solution. Supported membranes using two different dope solution concentrations (4% and 6%) were prepared using MSA as the solvent. The dope solution viscosity of 6% and 4% polymer concentration was 3040 cP and 17255 cP at 5 RPM, respectively. The phase inversion membranes using these solutions were prepared with either water or 0.5N NaOH as the nonsolvent at the ambient temperature. The effect of these variants on membrane performance is discussed in following sections.

5.3.2.1. Effect of porous support material

The effect of support material was studied as their properties are known to affect the membrane performance [Section (3.3.4), Munari (1990)]. Membranes with 6% dope solution concentration were prepared by using polypropylene support FO2470 and polyester supports H3160, 3324 and 3265. Formed membranes were designated as M-1, M-2, M-3 and M-4, respectively. Water flux at 2 bar transmembrane pressure for M-1 was 16.3 $l.m^{-2}.h.^{-1}$, while for M-2, M-3 and M-4 it was 3, 3.2 and 5.3 $l.m^{-2}.h.^{-1}$, respectively (Table 5.2). The lower flux in case of membranes prepared using polyester support than with polypropylene support was an outcome of the lower number of pores and lower surface porosity of these type membranes (Table 5.2). The pore size distribution analysis (Figure 5.4) showed that the membrane M-1 prepared with FO 2470 (polypropylene) support offered more number of pores near to smaller pore size. The total number of pores in this case were 3.92×10^7 and surface porosity was 0.0055% (Table 5.2). Mosqueda-Jimenez et al. (2004) reported ~ 0.05% surface porosity for the PES based UF membrane with ~ 19 $l.m.^{-2}h.^{-1}$ flux at 3.45 bar. In comparison to this porosity, the porosity of M-1 (0.0055%) is much lower, though the membrane offered similar water flux. In order to investigate the reasons behind observed lower porosity, SEM analysis was performed. The delamination of membrane from its support occurred when the membranes were exposed to the vacuum conditions during SEM analysis, offering no clue on porosity (Figure 5.5a). Thus SEM was performed under low vacuum mode of E-SEM. This effort also could not indicated any porosity (Figure 5.5b). Thus, unsupported membrane was analyzed, which shows sponge-like structure (Figure 5.5c). It is reported by Wang et al. that the delayed demixing during membrane formation can lead to the sponge-like structure [Wang (2007)]. In present case, a basic PBI was dissolved in highly acidic solvent. The resultant acid-base complex may not be easily broken by water used as a nonsolvent, since it is not stronger base than PBI. This could result in delayed demixing during membrane formation resulting in sponge-like pore structure. With this kind of nature of the pores (sponge type), high surface porosity should have been obtained. On the contrary, PSD analysis showed very low porosity. This indicates that pores in the sponge type open structure could not be interconnected, resulting in overall low surface porosity. The calculations of the pore size in liquid-liquid displacement method were done on the assumption that the pores are parallel and are not interconnected [Gijsbertsen (2004)]. It is also reported that the sublayer resistance is always larger than the unconnected pore resistance in an isotropic membrane with interconnected pores and thus the estimated pore size distribution is always shifted towards smaller pore sizes than they really are. This also could be one of the reasons for lower observed surface porosity.

Secondly, for PSD analysis of UF membranes with finger-like porosity, the membrane thickness (skin layer thickness) is assumed to be equal to the thickness of dense layer of the membrane usually ~ 0.1 μm [Capennelli (1983)]. This may not be essentially true for present membrane possessing sponge- like structure. If the PSD analysis is done with actual membrane thickness (excluding support thickness), obtained results on surface porosity are far apart from the one obtained by assuming ~ 1 μm as the membrane thickness. This data is given in the Table 5.2. This higher surface porosity can be correlated to the observed water flux.

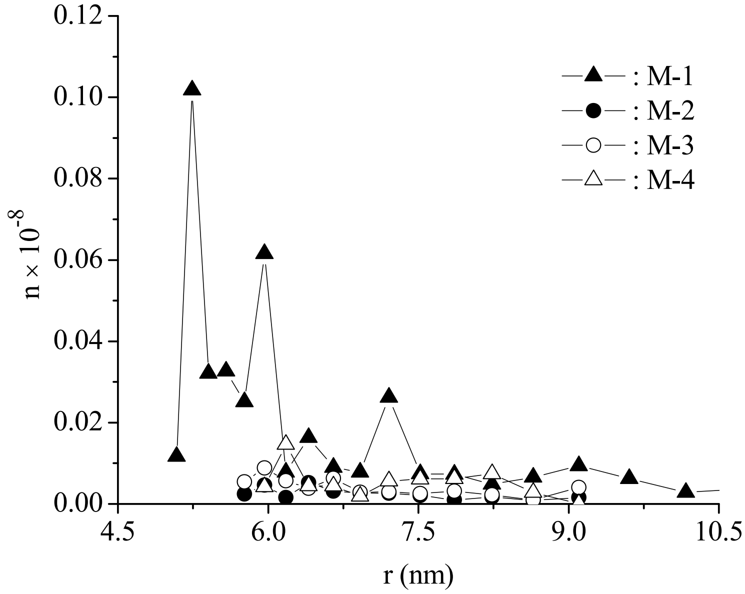
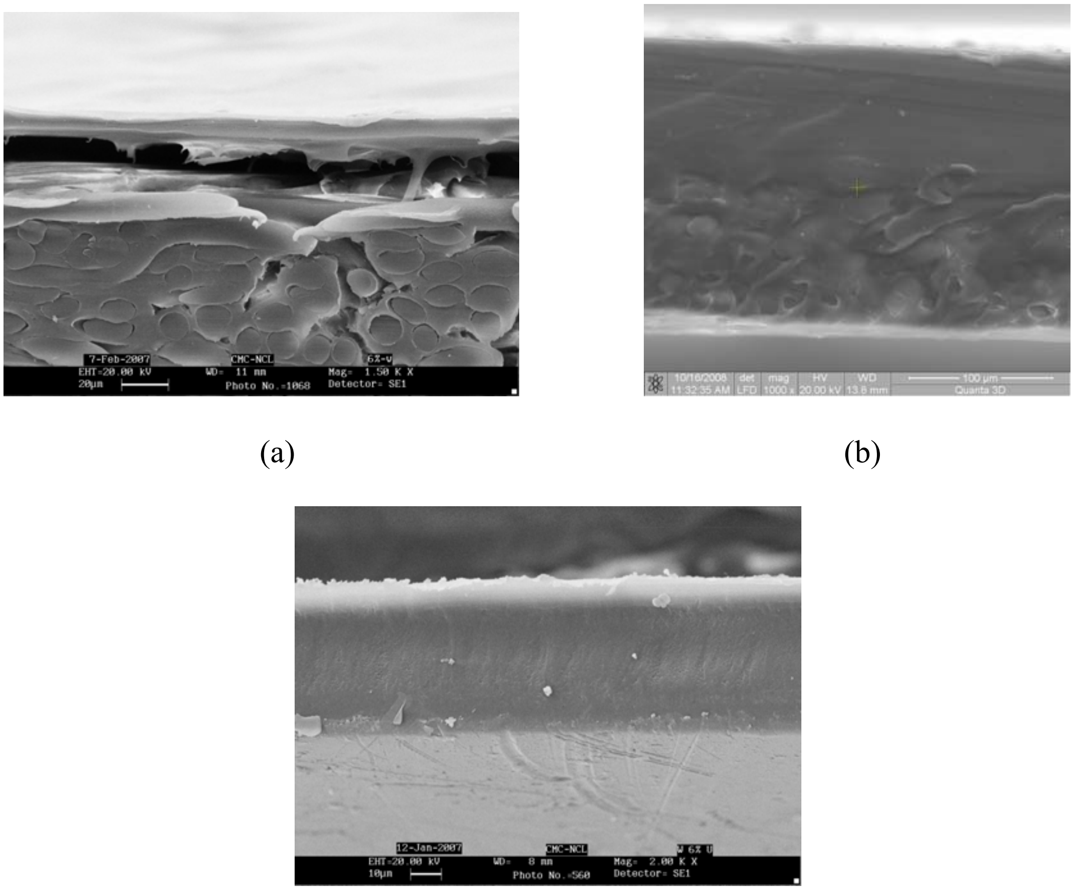


Figure 5.4 Pore size distribution of membranes prepared using different supports and 6% ABPBI in dope solution.

The surface porosity can also be determined by solute rejection method [Singh (1998), Aimar (1990)]. In present case, the fluxes after the PEG rejection even after washing with 0.1N NaOH could not regained. Thus, surface porosity was not determined by this method.

Air permeability of the polypropylene support is higher than the polyester supports used (Table 5.1). This could be one of the reasons for higher flux obtained in case of earlier support. Among the membranes prepared using polyester supports, 3265 porous support (M-4) exhibited maximum total number of pores and surface porosity due to the more open porous structure of 3265 support.



(a) (b)

(c)

Figure 5.5 SEM cross section images of (a), (b) supported and (c) unsupported ABPBI membrane.

Table 5.2 Water flux, rejection and pore size analysis by solute rejection method of membranes prepared using different porous supports.

				Properties studied						
						By liquid-liquid displacement method			By solute rejection method	
Polymer concentration in dope solution (%)	**Membrane code**	**Support used**	**Nonsolvent used**	**Water flux, J_w, at 2 bar ($l.m^{-2}.h^{-1}$)**	**PEG_{6k} rejection (%)**	**Total no. of pores per unit surface**	**Mean pore diameter (nm)**	**Surface porosity (%)**	**Mean pore diameter, μ_p (nm)**	**Geometric standard deviation, σ_p**
6	M-1	FO2470	Water	16.3 ± 2.8	93.3	3.92×10^{7} $(3.37\times10^{10})^{b}$	12.7	0.0055 (4.58)	3.21	1.51
	M-2	H3160	Water	3.0 ± 0.6	37.9	2.80×10^{6} $(2.41\times10^{9})^{b}$	13.45	0.0004 (0.38)	5.66	1.68
	M-3	3324	Water	3.2 ± 0.1	38	5.39×10^{6} $(4.65\times10^{9})^{b}$	12.80	0.0003 (0.27)	5.33	1.78
	M-4	3265	Water	5.3 ± 0.8	52	5.50×10^{6} $(4.73\times10^{9})^{b}$	14.85	0.0012 (1.05)	4.22	1.95
	M-5	FO2470	NaOH	9.3^{a} ± 0.7	83.8	-	-	-	-	-
4	M-6	FO2470	Water	30.2 ± 6.6	90.8	7.47×10^{7} $(6.23\times10^{10})^{b}$	13.2	0.011 (9.87)	3.38	1.37

[a]: At 1 bar pressure, [b]: Values determined using 86.2 μm pore length.

Figure 5.6 shows that MWCO of membranes prepared with polyester supports (M-2, M-3 and M-4) was higher (~ 35 kDa) than that of membrane prepared with polypropylene support (~ 6 kDa). This could be explained on the basis of porosity of these membranes. The mean pore diameter determined by using liquid-liquid displacement method and solute rejection method showed that M-1 offered lower mean pore diameter as compared to the membranes M-2, M-3 and M-4 (Table 5.2). Higher number of pores in case of M-1 than that for M-2, M-3 or M-4 could be responsible for the higher water flux of this membrane. The values of mean pore diameter and σ_p were determined by solute rejection method by plotting the graph between PEG diameter versus PEG rejection (Figure 5.7). This analysis is also in good agreement with the lower pore size for the membrane M-1 than that of other types as obtained by liquid-liquid displacement method. In comparison to the mean pore diameters of membranes obtained by solute rejection method, the liquid liquid displacement method showed higher values. This is also observed by Kim et al. (1994) and stated that the controlling pore dimension for separation is the surface skin dimension. On the basis of these analyses, polypropylene appears to be the better choice than polyester as the support fabric.

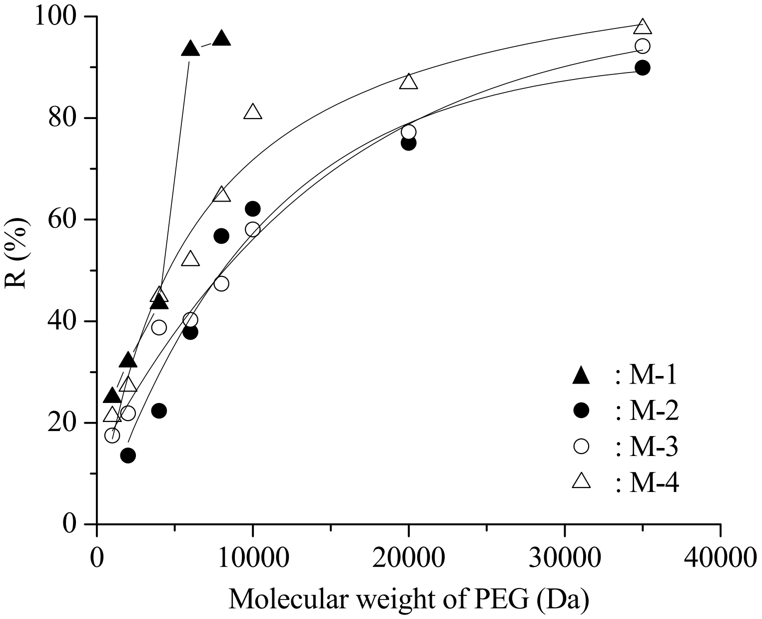


Figure 5.6 Rejection (R) of membranes prepared using different supports and 6% ABPBI in dope solution.

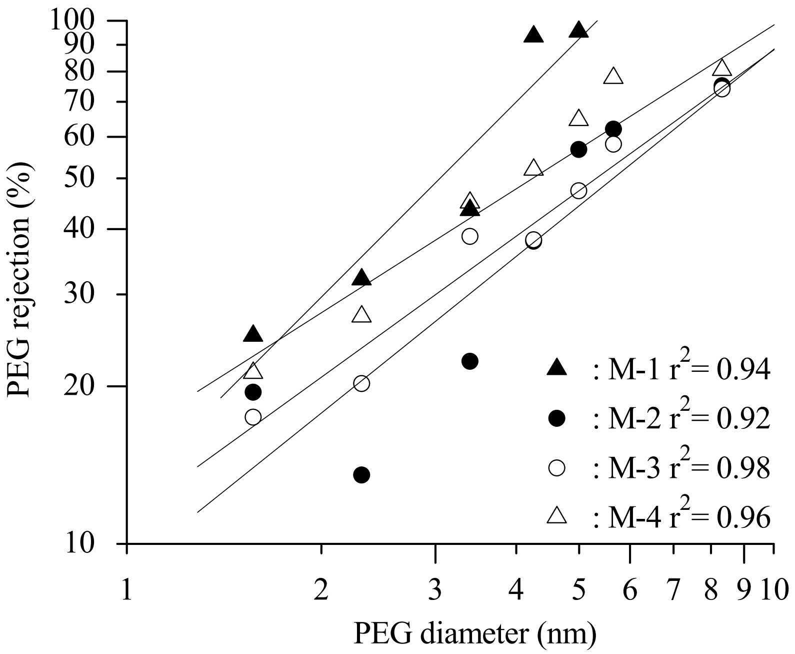


Figure 5.7 PEG rejection versus PEG diameter for membranes prepared using 6% dope solution concentration on different supports.

5.3.2.2. Effect of nonsolvent

The dope solution for membrane casting was prepared with MSA as the solvent. Since ABPBI is a basic polymer owing to the presence of two nitrogen atoms carrying lone pair of electrons per repeat unit, the acid molecules are anticipated to be associated with the polymer matrix. It is well known that ABPBI sorbs H_3PO_4 [Asensio (2002)]. During the phase separation process, if NaOH is used as the nonsolvent, instead of water, it is possible that the sorbed acid can also be taken away by using NaOH since it is a stronger base than the −NH functionality of ABPBI. Membranes M-1 and M-5 offered 8.6 $l.m.^{-2}h.^{-1}$, 9.3 $l.m.^{-2}h.^{-1}$ water flux at 1 bar transmembrane pressure, respectively (Table 5.2). The MWCO of these membranes was 6 kDa as shown in Figure 5.8. Since the porosity is same as that of membrane prepared with water as nonsolvent, the factor controlling pore formation is not the type of nonsolvent. In view of low concentration of the dope solution, microfiltration type of membranes could have been expected. On the contrary, the porosity obtained is in the range of low MWCO UF type. The polymer concentration, nonsolvent used seems to have negligible effect on porosity.

5.3.2.3. Effect of polymer concentration

Membranes were prepared by using 6% (M-1) and 4% (M-6) dope solution concentration by using water as a nonsolvent. M-1 and M-6 exhibited 8.6 and 17 $l.m^{-2}.h^{-1}$ dead end flux at 1 bar transmembrane pressure, respectively. It is known that the membrane prepared with higher polymer concentration shows lower flux [Nouzaki (2002), Paul (1992)]. M-6 offered almost double flux than M-1, but they exhibited similar MWCO (6 kDa) as shown in Figure 5.8. This behavior can be explained on the basis of pore size distribution analysis of the membrane (Figure 5.9). The difference in flux performance can be correlated with pore density and surface porosity of the membrane.

The membrane M-1 offered lower pore density and surface porosity than M-6 as given in Table 5.2. Thus, the membrane M-1 exhibited lower water flux than the membrane M-6. The mean pore diameter of M-1 determined by liquid- liquid displacement method as well as solute by rejection method is comparable to that of M-6 (Table 5.2) and thus exhibited similar MWCO. The mean pore diameter and σ_p was calculated by plotting graph between PEG diameter versus PEG rejection (Figure 5.10). It was observed that the value of σ_p in case of membrane M-1 and M-6 are close to each other. Michael et al. (1980) stated that, due to close values of σ_p, virtually all the membranes were quite similar in their microstructure. Membrane M-6 showed higher flux as compared to membrane M-1 with similar rejection performance, thus for further analysis M-6 was used.

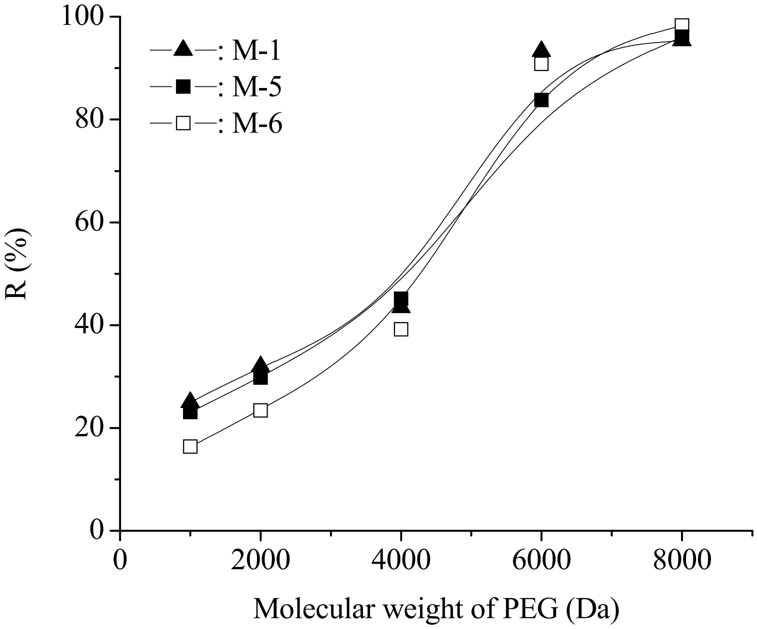


Figure 5.8 Rejection (R) of ABPBI membranes prepared by varying polymer concentration in dope solution and nonsolvent.

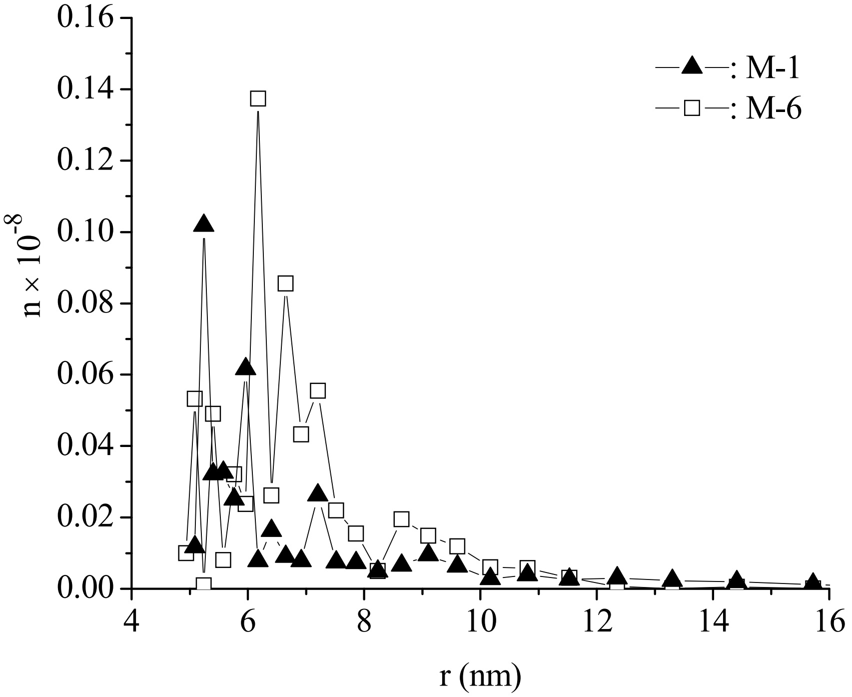


Figure 5.9 Pore size distribution of ABPBI based membranes.

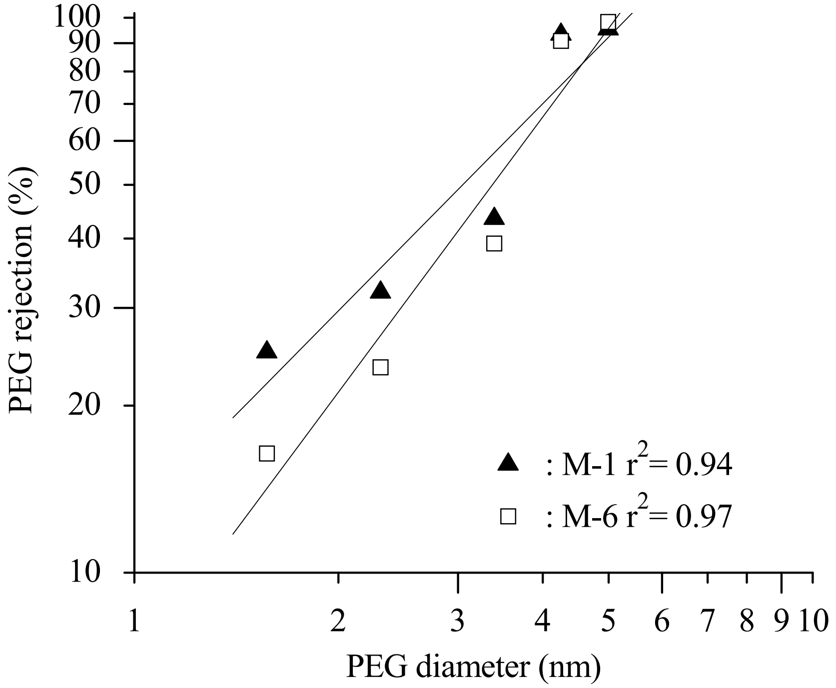


Figure 5.10 PEG rejection versus PEG diameter for M-1 and M-6.

5.3.3. Membrane stability in organic solvents

The membrane prepared using polypropylene support (M-6) was used to evaluate the stability of ABPBI based membranes in various organic solvents, autoclaving conditions as well as concentrated acid (H_2SO_4) and base (NaOH). The polypropylene support was chosen as it is more stable in basic environment than the polyester support [Daisley (2006)]. The solvent flux through the membrane was measured after dipping into the respective solvent for 24 hours. In case of water immiscible solvents like chloroform, toluene and hexane, membranes were dipped initially in IPA (24 hours) and then in the respective solvents (24 hours). The properties of solvent and their flux through the membrane are given in Table 5.3. Higher solvent fluxes were obtained in case of non polar solvents than that of polar solvents. No correlation was seen between the solvent flux and dielectric constant of the solvent. Machado et al. (1999) observed that there is relatively small effect of dielectric constant on the solvent flux due to the difference in dielectric constant of solvent and polymeric membrane material. It is known that the solvent with higher viscosity exhibited lower flux through polyimide based ultrafiltration membranes [Iwama (1982)]. M-6 showed highest flux for THF having viscosity of 0.55 cP, which is lowest among other solvents. Though the viscosity of THF is comparable with that of chloroform and toluene, membrane showed lower solvent fluxes for the later solvents. This shows that polarity of the solvent could also be important. No clear correlation could be observed between solvent flux and solubility parameters or surface tension. In hexane, the membrane was delaminated from the support, which could be due to its nonpolar nature.

The effect of solvent treatment on the membrane morphology was analyzed by measuring water flux after the solvent treatment and compared with initial flux. The membrane showed 59.4% and 59.2% reduction in water flux after chloroform and toluene treatment, respectively. In aqueous environment (polar solvents), strong hydrogen bonding due to nitrogen associated with hydrogen atom [Wang, K. (2006c)] is favourable. This is not possible in case of non polar solvents. Thus, there could be shrinkage of pores in presence of these non polar solvents. Such change in pore size due to shrinkage was analyzed by PEG rejection. PEG_{4k} was selected for the rejection analysis as the untreated membrane showed 39% rejection. The membranes treated with chloroform and toluene offered 85% and 55% rejection, respectively. The increase in rejection performance confirmed the reduction in pore size after the solvent treatment. Effect of chloroform and toluene treatment was also analyzed in case of the membrane M-1. But membrane showed delamination from the support after treated with chloroform and just 16% change in water flux after the toluene treatment. The membrane M-6 showed large decrease in water flux after the toluene treatment as compared to M-1. It may be due to high porosity of M-6, which led to more shrinkage as compared to M-1 having low porosity. The membrane prepared using polypropylene support was delaminated; while polyester support based membranes were stable after the hexane treatment. This could be because of good adherence of polymer film with hydrophilic polyester support as compared to the hydrophobic polypropylene support.

The membranes M-2 and M-4 offered up to 62% and 69% reduction in water flux, respectively, after the hexane treatment as shown in Table 5.4. Among the polyester based membranes, 3324 was a better support as M-3 showed 41% decrease in water flux, which is lowest variation as compared to the same for M-2 and M-4. This decrease in flux is due to the non polar nature of hexane. Membranes treated with polar solvents (DMF, DMAc, IPA and THF) showed marginal change in water flux and showed excellent stability towards these solvents.

M-6 showed good stability after autoclaving with marginal change in water flux (Table 5.3). This showed additional advantage of ABPBI membrane towards thermal stability in presence of steam. Especially for membrane application in medicine, pharmaceutical and food industry there is a strong demand for safely sterilizable membranes [Hicke (2002)].

Table 5.3 Stability of membrane M-6 towards organic solvents.

Solvent used	**$\eta_{solvent}^{b}$ (cP)**	**δ^{b} (cal.cm^{-3})$^{1/2}$**	**ε^{b} at 20°C**	**σ^{b} Dyne.cm^{-1} at 20°C**	**$J_{solvent}$ (l.m^{-2}.h^{-1}.bar^{-1})**	**% Reduction in membrane thickness**	**% Change in J_w**
DMF	0.82	12.1	36.7	35	14.7	8	13.46
DMAc	0.92	11.0	37.8	34	6.6	15	10.11
IPA	2	11.5	18.3	21.7	7.0	4	8.68
Chloroform	0.57	9.3	4.8	27.16	13.6	33	-59.42 (85%)^{a}
THF	0.55	9.1	7.6	2.8	33.3	9	-12.84
Toluene	0.59	8.9	2.38	28.5	12.7	27	-59.23 (55%)^{a}
Hexane	0.31	6.9	1.9	18.4	^{c}	20	-
Autoclaving	-	-	-	-	-	13	-14.51

^{a}: PEG_{4k} rejection

^{b}: From reference [Smallwood, 1996]

^{c}: Membrane delaminated from support.

Table 5.4 Hexane stability of membranes prepared using different porous supports.

Membrane code	**% Reduction in membrane thickness**	**% Change in J_w**
M-1	16.0	Delaminated
M-2	57.5	-61.6
M-3	22.6	-41.1
M-4	28.8	-69.3

5.3.4. Membrane stability in concentrated acid and base

The ABPBI membrane (M-6) stability towards concentrated acid (25N H_2SO_4) and base (2.5N NaOH) was analyzed. In 30N H_2SO_4 solution membrane was stable only for 10 seconds with 14.6% decrease in flux. After prolonged exposure, polymer ultimately started dissolving. Thus, lower concentration of H_2SO_4 was evaluated. On visual observation, it was found that in 25N H_2SO_4 solution membranes (M-1, M-6) were stable, for long time (24 hours). Thus, this concentration was used for the further study. Membranes M-1 and M-6 exhibited marginal decrease in water flux after treatments with 25N H_2SO_4 and 2.5N NaOH as shown in Table 5.5. All these membranes after the concentrated acid and base treatment showed marginal reduction in thickness (11 to 26%). ABPBI based UF membranes offered excellent stability in concentrated acid and base. On the other hand, solvent resistant membranes based on poly-(*p*-phenyleneterephthalamide) showed limited stability, i.e. towards 2N H_2SO_4 and NaOH at pH 12 [Zschocke (1980)].

Table 5.5 Change in water flux after treatment of concentrated acid and base.

Membrane code	**25N H_2SO_4 treatment**		**2.5N NaOH treatment**	
	% Reduction in membrane thickness	**% Change in J_w**	**% Reduction in membrane thickness**	**% Change in J_w**
M-1	22.9	-23.7	12.7	-7.3
M-6	26.0	-36.1	11.5	-1.5

5.3.5. Effect of drying and glycerol treatment

In view of studying the effect of drying on the membrane porosity, M-6 was dried at 60 °C in oven for 24 hours. The membrane showed 98% and 34% decrease in flux and thickness, respectively (Table 5.6) due to shrinkage. This membrane after immersing in water for prolonged time (24 hours) did not regain thickness or flux. Such irreversible shrinkage after drying in case of poly-(*p*- phenylenetere-phthalamide) based membrane was observed by Zschocke et al. (1980). Pore morphology of the dried membrane was analyzed by SEM. The delamination of polymer film from the support was observed after drying as shown in Figure 5.5a. SEM cross section images of dried membrane clearly shows collapsed pore structure, which led to the decrease in flux and membrane thickness.

Table 5.6 Effect of drying on water flux.

Treatment protocol	**Drying at 60 °C**	**Dipped in 10% Glycerol + 60 °C**	**Dipped in 50% Glycerol[a] + 60 °C**
% Change in J_w	-97.96	-92.51	-17.6
% Change in thickness	-34.18	-22.03	-3.50

[a]: Initially dipped in 10% (8 hour) + 20% (16 hour) + 50% (24 hour)

To avoid pore collapse, membranes were dipped in 10% glycerol and then dried at 60 °C. The decrease in water flux was upto 93% and indicates that 10% glycerol treatment is not sufficient to avoid pore collapse. Thus, membranes were treated with 10%, 20% and 50% glycerol solution sequentially, and dried at 60 °C. The membrane showed only 17.6% decrease in water flux with marginal decrease in thickness as given in Table 5.6. Thus, the pore collapsing of ABPBI membrane can be avoided by 50% glycerol treatment as shown in Figure 5.5b. This imaging was done by using 50% glycerol treated membrane without any prior treatment in low vacuum SEM mode.

To study the effect of glycerol treatment, the glycerol in the pores was replaced by water and the flux was measured. Such replacement of glycerol by water in the pores was repeated four times. The reduction in flux was observed for the first treatment and then it became almost constant as shown in Figure 5.11.

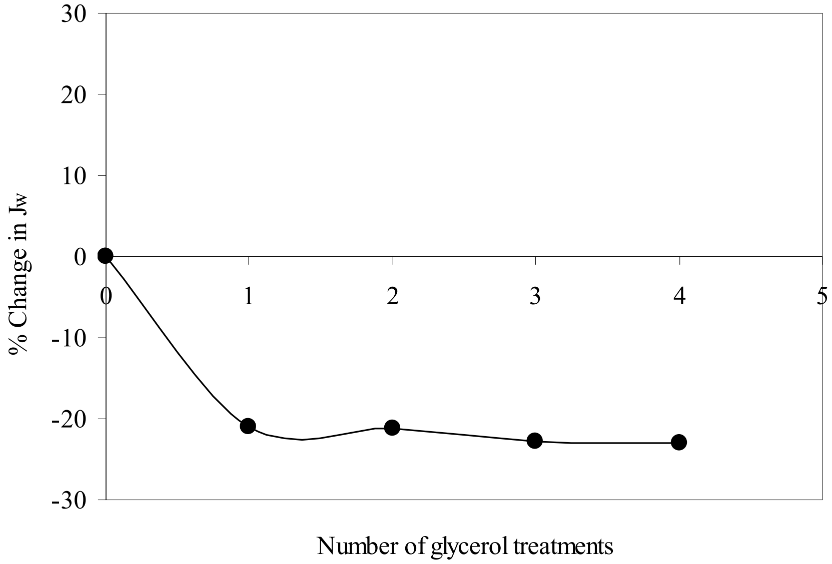


Figure 5.11 Change in J_w after repeated glycerol treatment for membrane M-6.

5.4. Conclusions

The ABPBI was synthesized by self condensation of 3,4-diaminobenzoic acid with inherent viscosity of 1.72 – 2.17 $dL.g^{-1}$. ABPBI based membranes were prepared by phase inversion method by varying porous support material, polymer concentration and non solvent. The membrane prepared using polypropylene support offered higher flux than polyester based membranes. The polypropylene based membrane (M-1 and M-6) showed 6 kDa MWCO while it was 35 kDa for polyester based membranes (M-2, M-3 and M-4). The pore size and the surface porosity of the membrane are the governing factors. On the basis of flux, MWCO and pore size distribution the polypropylene appeared to be the better porous support. The non solvent (water/0.5N NaOH) had negligible effect as the membrane M-1 and M-5 showed similar performance. The M-6 showed higher flux due to its higher surface porosity than M-1 while both the membrane showed 6 kDa MWCO as their pore diameters are comparable. The membrane M-6 showed excellent stability towards organic solvents, autoclave condition, concentrated acid (25 N H_2SO_4) and base (2.5N NaOH). The dried membrane showed pore collapse as clearly seen in SEM which can be avoided by 10%, 20% and 50% glycerol treatment. This was confirmed by flux analysis.

Chapter 6: Conclusions

Investigations towards effects of membrane preparation parameters on the performance of resulting PAN based UF membranes led to an understanding towards use of adequate concentration, solvent, additive and support fabric to be used for obtaining a combination of good water flux and rejection performance. Protein rejection analysis revealed that PAN_{15} and PAN_{17} membranes exhibited MWCO of ~ 68 kDa. Increasing the PAN concentration in the dope solution to 23 wt. % (in case of PAN_{23} membrane) could lower the MWCO just upto 33 kDa. This indicated that merely increasing polymer concentration in the dope solution does not necessarily lead to lowering of the pore size.

The effect of solvents (DMF, DMAc, DMSO and NMP) was studied on membranes prepared using different polymer concentration (15, 18.5, 20.5 and 23%) in the dope solution. The membrane prepared by using DMF and DMAc as solvent exhibited similar fluxes at all PAN concentration and were lower as compared to that of membrane casted using DMSO and NMP as the solvent. The protein rejection analysis showed that membrane prepared with DMSO as a solvent showed poor control on its porosity. Among these solvents, the NMP emerged as better solvent as it offered high flux as well as appreciable rejection for all membranes prepared by varying polymer concentration.

Out of multicarboxylic acids studied as an additive in the dope solution, citric acid and tartaric acid based membranes offered ~ 2.5 times higher flux than that of $ZnCl_2$ based membranes, without any sacrifice in BSA rejection for two PAN concentrations studied (PAN_{15} and PAN_{13}). The supporting evidence for interactions between basic solvent and carboxylic acid additives was provided by FT-IR spectroscopy. The blue shift in >C=O, O–C–N stretching and –OH frequency was observed. The potential of these membranes for large scale applicability was assessed by preparing spiral modules. They exhibited not only the BSA rejection, but also a complete bacteria (*E.Coli*) rejection, as that of small size membrane coupons analyzed for these crucial characteristics; as far as application of drinking water purification is concerned.

Support fabric properties were found to play a crucial role in determining resulting membrane properties. Though material of construction of these supports was polyester, their properties like porosity and type (woven vs. nonwoven) was found to be crucial in governing properties of resulting membranes. Membranes casted on 3265 support showed higher water flux but wider BSA rejection than membranes casted on the H1006 support. The membrane casted with support 3324 though offered lower flux than that of 3265 based membranes, variation in its flux and rejection was smaller. The pore size distribution analysis showed that membranes prepared with 3265 and PES-111 supports exhibited wider pore size distribution and lower compaction pressure than the same for other cases.

Modification of PAN based membrane surface by different bases while varying treatment conditions (time, temperature, etc.) led to a maximum of 152% and 230% increase in water flux without sacrifice in rejection performance by dead end and cross flow mode of treatment, respectively, depicted potential of surface modification in improving membrane performance. A decrease in contact angle of modified membranes in comparison to the unmodified membrane due to increase in hydrophilicity by virtue of formation of amide and carboxylic group by the transformation of –CN functionality of PAN was confirmed by IR and ESCA analysis. A mechanism was proposed based on the swelling and deswelling of the pore caused by base and acid treatment, respectively.

It was thought to extend the potential of negative charge formation on the membrane surface by the base treatment for an application of As-V rejection by Donnan exclusion principle. The surface of the membrane with lowest possible porosity (PAN_{23}) was treated with NaOH in cross flow mode for 2.5 hour at 45 °C to obtain MWCO of 8 kDa and shown to offer quantitative As-V rejection from ppb to a ppm level. The feed conditions such as pH, temperature and concentration had their own effect in governing As-V rejection performance. In addition to FTIR-ATR and contact angle analysis for assessing effects of surface treatment, SEM and AFM analysis confirmed the pore swelling and smoothening, respectively.

Though PAN based membranes are known to sustain certain organic solvents, ABPBI based membranes were shown to be stable with almost all the organic solvents including DMF and DMAc. In addition, these membranes showed excellent stability to 2.5N NaOH and 25N H_2SO_4. These membranes showed excellent water flux at lower MWCO of ~ 6 kDa. The inability of these membranes to retain porosity when dried was resolved by glycerol treatment, which could be done repeatedly, without a large sacrifice in the flux of the membrane.

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Synopsis of the thesis entitled:

"Investigations in ultrafiltration membranes based on polyacrylonitrile and AB-polybenzimidazole"

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Preamble

Ultrafiltration (UF) is a pressure driven membrane separation process primarily based on the size exclusion principle. The pore size of UF membranes vary in the range of 100 – 1000 Å. Applicability of UF membrane technology is wide-spreading owing to its usefulness in various industries such as textile, chemical, food, dairy, pharmaceutical, metallurgy, paper, leather, water and waste water treatment, etc.

The majority of UF membranes are prepared by phase inversion method. Various parameters like dope solution composition, additives used, casting temperature, evaporation time, chemical treatment, etc. are known to play a crucial role in determining membrane porosity (size and density) [1-5]. In present study, some of these parameters are investigated using polyacrylonitrile (PAN) as the membrane material. PAN hydrolysis using bases is documented in the literature [6-9]. When this phenomenon is applied to UF membranes, most of the studies indicated flux decline due to pore size reduction [9-11]. It is known that PAN hydrolysis proceeds through intermediates [12]. If the hydrolysis of the UF membrane surface could be carried out in a controlled manner leading to only increased hydrophilicity and not to pore size reduction, water flux can be increased to advantage overall membrane productivity. This issue is addressed with PAN membranes, which led to significant increase in water flux (up to 230 %) without large variation in the rejection performance. During the course of this work, pore size reduction was also observed, which was conveniently extended to synthesize negatively charged membranes that have arsenic (As-V) rejection capability following Donnan exclusion principle [13].

Use of UF membranes remained mostly confined to aqueous solutions. In view of wide-spreading applicability, investigations in UF membranes those would withstand stringent environments of acids, bases and solvent need to be broadened. With this aim, UF membranes based on polybenzimidazole were prepared and evaluated for their characteristics. Their stability towards organic solvents, concentrated acid (H_2SO_4) and base (NaOH) was investigated.

The work done is presented in following 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 is presented.

Chapter 2: Literature survey

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

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

This chapter begins with introduction and reviews various parameters affecting membrane performance. Experimental section describes the preparation of PAN based membranes by optimizing some of the crucial parameters. The rejection and bubble point analysis of membranes prepared while increasing dope solution concentration suggested that the decrease in water flux is not monotonous. The membranes prepared using NMP as a solvent and dope solution concentration of $\leq$ 20.5 % offered better combination of flux and rejection as compared to membranes prepared using other solvents (DMF, DMAc and DMSO). Organic acids as additive in dope solution showed significant improvement in the performance of resulting membranes. Improved flux (up to 2.5 times) without sacrificing BSA rejection in comparison to the membranes prepared with $ZnCl_2$ as an additive demonstrated importance of organic acids additives. The properties of porous fabric (woven and non-woven) used for the preparation of supported UF membranes was shown to have significant effect on the membrane performance in terms of flux, rejection, bubble point and membrane compaction. Potential of some of above membranes was examined for water disinfection through 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. PAN membrane surface modification was done with an aim of improving water flux of resulting membranes. Some of the results on pore size reduction were thought to be beneficial for rendering As rejection capability, while tuning initial (unmodified) membrane properties.

The hydrolysis of PAN_{15} (subscript denotes polymer concentration in the dope) membrane surface was performed by using organic and inorganic bases with an objective of enhancement in the flux. Effects of treatment mode (dead end vs cross flow), nature of base, temperature and duration of hydrolysis was assessed. Results showed that inorganic bases are better than organic bases towards improving water flux. A maximum increase in flux of 152 % was achieved by dead end mode within 20 hours, while 230 % increase could be obtained by cross flow mode within 2.5 hours at 45 °C.

The manipulation of membrane porosity for arsenic (As-V) removal by UF membranes was explored with PAN_{23} membranes. The surface hydrolysis of this membrane by NaOH offered pore size of ~ 6 kDa molecular weight cut off (MWCO). The surface modification leading to the formation of $-COO^{-}Na^{+}$ on the membrane surface caused repulsive interactions and thus pore size reduction. This membrane showed almost quantitative rejection of As-V by following Donnan exclusion principle [13]. Variation in pH was found to have a strong effect on As-rejection. To address this drawback, grafting of styrene sulfonic acid on PAN_{23} membrane surface was done. Though reduction in water flux was observed indicating reduction in porosity as that of untreated PAN_{23} membrane, inferior rejection performance indicated that more work is required to pursue this approach.

Chapter 5: ABPBI based UF membranes

This chapter begins with literature survey on solvent resistant membranes. Few available explorations on PBI as a membrane material for nanofiltration (NF) and UF applications are presented. Experimental section describes synthesis and characterization of ABPBI, its membrane preparations and characterization methods. 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 was studied. The stability of ABPBI membrane towards organic solvents, concentrated acid and base was evaluated. The membrane was found to be stable towards common organic solvents (DMF, DMAc, IPA, THF, chloroform, toluene and hexane), 25N H_2SO_4 and 2.5N NaOH. This excellent membrane stability could be attributed to the rigid nature and inherent material stability of ABPBI. 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.

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Signature of the Candidate	Signature of the Research Guide
(Ms. Harshada R. Lohokare)	(Dr. U. K. Kharul)

List of Publications

1. **H.R. Lohokare**, S.C. Kumbharkar, Y.S. Bhole, U.K. Kharul, "Surface modification of polyacrylonitrile based ultrafiltration membranes", *J. Appl. Polym. Sci.* **101** (2006) 4378-4385.
2. **H.R. Lohokare**, Y.S. Bhole, U.K. Kharul, "Effect of support material on ultrafiltration membrane performance", *J. Appl. Polym. Sci.* **99** (2006) 3389–3395.
3. **H.R. Lohokare**, M.R. Muthu, G.P. Agarwal, U.K. Kharul, "Effective arsenic removal using polyacrylonitrile based ultrafiltration (UF) membrane", *J. Membr. Sci.* **320** (2008) 159-166.
4. **H.R. Lohokare**, Y. S. Bhole, S.V. Taralkar, U.K. Kharul, "Polyacrylonitrile based ultrafiltration membranes: Effects of preparation parameters", Manuscript under preparation.
5. **H.R. Lohokare**, U.K. Kharul, "Solvent and acid-base resistant ultrafiltration membranes based on AB-polybenzimidazole", Manuscript under preparation.

Patents

1. **H.R. Lohokare**, U.K. Kharul, "Solvent resistant ultrafiltration (UF) membranes based on ABPBI", Applied.

Presentations

1. **H.R. Lohokare**, Y.S. Bhole and U.K. Kharul, "Surface modification of PAN based Ultrafiltration membranes and performance evaluations", Poster presented in '*National workshop on Priority Research and Technology Program for Rural Water Supply and Sanitation'*, held at NEERI, Nagpur, India; February 2003.
2. **H.R. Lohokare**, U.K. Kharul, Y.S. Bhole, S.V. Taralkar, "Investigations towards factors governing Ultrafiltration (UF) membrane performance", Poster presented in *Macro-2004*, International Symposium, held at Trivandrum, India; December 15 - 17 2004.

3. **H.R. Lohokare**, P. Karadkar, U.K. Kharul, “PAN based UF membranes with different porosity”, Poster presented in ‘*National seminar on Membrane Science and Technology: Challenges and Opportunities’*, held at Jorhat, India; 12 - 13 February 2004.
4. **H.R. Lohokare**, U.K. Kharul, “Tuning ultrafiltration membrane porosity by surface modification”, Poster presented in international symposium *‘Macro-2006’*, held at Pune, India; 17 - 20 December 2006.
5. **H.R. Lohokare**, M.R. Muthu, G.P. Agarwal, U.K. Kharul, “Charged Ultrafiltration membrane for arsenic rejection”, Oral presentation in ‘*8th International Conference on Catalysis in Membrane Reactors (ICCMR8)’*, Central Glass & Ceramic Research Institute (CGCRI), held at Kolkata, India; 18 - 21 December 2007.