Preparation, characterization, modification of ultrafiltration membrane for wastewater treatment

Thesis

Submitted By

Somakraj Banerjee

[Exam Roll No. M4CHE19008]

[Class Roll No. 001710302012]

[Reg. No. 119484 of 2012 – 2013]

Under the Guidance of

Prof. (Dr.) Chiranjib Bhattacharjee

In the partial fulfillment for the award of the degree of

MASTER OF CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL ENGINEERING

JADAVPUR UNIVERSITY

Jadavpur, Kolkata-700032

INDIA

May 2019

Declaration of Originality and Compliance of Academic Ethics

I hereby declare that this thesis contains literature survey and original research work by the undersigned candidate, as part of his Master of Chemical Engineering studies. All information in this document have been obtained and presented in accordance with academic rules and ethical conduct.

I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name: Somakraj Banerjee

Roll Number: 001710302012

Thesis Title**:** ***Preparation, characterization, modification of ultrafiltration membrane for wastewater treatment***

Signature:

Date:

CERTIFICATE

This is to certify that the thesis entitled "***Preparation, characterization, modification of ultrafiltration membrane for wastewater treatment***" has been carried out by Somakraj Banerjee in the partial fulfillment of the requirements for the degree of the Master of Chemical Engineering from Jadavpur University, Kolkata is recorded as bona fide work that has been conducted under the supervision of Prof. (Dr.) Chiranjib Bhattacharjee. The contents embodied in the thesis have not been submitted to any other university for the award of any degree or diploma.

_____

Prof. (Dr.) Chiranjib Bhattacharjee
Thesis Supervisor
Chemical Engineering Department
Jadavpur University
Kolkata – 700032

_____

Prof. (Dr.) Debashis Roy
Head of Department
Chemical Engineering Department
Jadavpur University
Kolkata – 700032

CERTIFICATE OF APPROVAL*

The foregoing thesis is hereby approved as a creditable study of an engineering subject and presented in a manner satisfactory to warrant acceptance as pre requisite to the degree for which it has been submitted. It is understood that by this approval the undersigned do not necessarily endorse or approve any statement made, opinion expressed or conclusion drawn there in but approve the thesis only for which it is submitted.

Committee on final examination
for the evaluation of the Thesis

_____

Signature of the Examiner

_____

Signature of the Supervisor

Only in case Thesis is approved

ACKNOWLEDGEMENT

This thesis would not have been possible without the guidance and the help of several individuals during the preparation and completion of this study.

First and foremost, I would like to show my sincere and utmost gratitude to my supervisor ***Dr. Chiranjib Bhattacharjee, Professor, Department of Chemical Engineering, Jadavpur University, Kolkata, India*** for his kind and valuable advices during the completion of this research work.

I am also very much grateful to research scholars of Chemical Engineering Department, Dr. Arijit Mondal, Souptik Bhattacharya, Ankita Mazumder Sarkar, Pallavi Chakraborty for their kind and heartily cooperation. Whenever I found myself in difficulty, their ever-helping attitudes have given me the courage to proceed further.

I am grateful to my colleagues, seniors and staffs in the Department of Chemical Engineering, Jadavpur University, Kolkata, India for their kind cooperation and moral support.

It would be incomplete if I do not mention my affable gratitude and thankfulness towards my family especially to my parents without whose constant support and enthusiasm this thesis would not have been completed.

Somakraj Banerjee

Department of Chemical Engineering

Jadavpur University

Kolkata – 700032

Date:

CONTENTS

ABBREVIATIONS

PSF	Polysulfone
PVP	Polyvinylpyrrolidone
DMAc	Dimethylacetamide
FESEM	Field emission scanning electron microscope
LLDP	Liquid-Liquid Displacement Porosimetry
MWCO	Molecular weight cut-off
PWF	Pure water flux
EWC	Equilibrium water content
BSA	Bovine serum albumin
TMP	Transmembrane pressure
IP	Isoelectric point
CF	Compaction factor
P_m	Hydraulic permeability
L_n	Total hydraulic permeability coefficient
R_m	Mean pore radius
N_t	Total no. of pores
A_t	Total area of pores
WPC	Whey protein concentrate
MDW	Model dairy wastewater

Abstract

Asymmetric polymeric ultrafiltration (UF) membranes were prepared from homogeneous Polysulfone (PSF) solution in Dimethylacetamide (DMAc) solvent with Polyvinylpyrrolidone (PVP) as an additive using phase inversion method. PSF, DMAc and PVP were mixed in a weight ratio of x:84:y. Structural parameters of prepared membrane were examined using field emission scanning electron microscope (FESEM). Liquid-Liquid Displacement Porosimetry (LLDP) method has been used for membrane characterization. Pore number, membrane permeability, pore distribution, average pore size was determined using LLDP data. Molecular weight cut-off (MWCO) of the membrane as it should be found by dextran rejection was estimated using pore size distribution data. Permeation performance of the membrane was evaluated through parameters like pure water flux (PWF) and hydraulic permeability. The hydrophilic nature of the membranes was evaluated by determining water contact angle and equilibrium water content (EWC). Solute rejection tests of resulting membrane were done using Bovine serum albumin (BSA) of molecular weight 68,000 Da in a dead-end filtration module with a capacity of 200 ml. Sodium hypochlorite solution was used for chemical cleaning after permeation test which gave 104% flux recovery. BSA rejection performance of membranes was observed subjected to different transmembrane pressure. From the above investigations best membrane was chosen for treatment of model dairy wastewater. Reduction in total protein content and total carbohydrate content was investigated using UV-vis spectroscopy.

Chapter 1.

Introduction

1. Introduction

Wastewater (or waste water) is any water that has been affected by human use. Wastewater is "used water from any combination of domestic, industrial, commercial or agricultural activities, surface runoff or stormwater, and any sewer inflow or sewer infiltration".[1] Therefore, wastewater is a byproduct of domestic, industrial, commercial or agricultural activities. The characteristics of wastewater vary depending on the source. Types of wastewater include: **domestic wastewater** from households, **municipal wastewater** from communities (also called sewage) or **industrial wastewater** from industrial activities. Wastewater can contain physical, chemical and biological pollutants. Wastewater is the combination of liquid and water-transported wastes from homes, commercial buildings, industrial facilities, and institutions, along with any groundwater infiltration and surface water and storm water inflow that may enter the sewer system. Domestic wastewater is the spent water originating from all aspects of human sanitary water usage. It typically constitutes a combination of flows from the kitchen, bathroom and laundry, toilets, baths, kitchen sinks, garbage grinders, dishwashers, washing machines and water softeners. Domestic wastewater, as the name implies, principally originates in residences and is also referred to as sanitary sewage. As such, commercial, institutional and industrial establishments contribute a domestic wastewater component to the sewer system resulting from human sanitary activity. Industrial wastewater emanates from the myriad of industrial processes that utilize water for a variety of purposes. This water is usually altered considerably in the process and may contain contaminants that degrade the water quality such as nutrients, suspended sediments, bacteria, oxygen demanding matter, and perhaps toxic substances. The amount of solid component in wastewater is expressed as a concentration in milligrams per liter or parts per million. Considered chemically, wastewater is a very complex mixture of components that would be difficult to completely define. In broad terms, it consists of an organic and an inorganic component. Probably the most often measured characteristics of wastewater are suspended solids and biological oxygen demand (BOD). [2]

1.1 Sources of wastewater

The sources of wastewater include the following domestic or household activities: [3]

- Human excreta (feces and urine) often mixed with used toilet paper or wipes; this is known as blackwater if it is collected with flush toilets

- Washing water (personal, clothes, floors, dishes, cars, etc.), also known as greywater or sullage
- Surplus manufactured liquids from domestic sources (drinks, cooking oil, pesticides, lubricating oil, paint, cleaning liquids, etc.)

Activities producing industrial wastewater:

- Industrial site drainage (silt, sand, alkali, oil, chemical residues);
- Industrial cooling waters (biocides, heat, slimes, silt)
- Industrial processing waters
- Organic or biodegradable waste, including waste from hospitals, abattoirs, creameries, and food factories.
- Organic or non-bio-degradable waste that is difficult-to-treat from pharmaceutical or pesticide manufacturing
- Extreme pH waste from acid and alkali manufacturing
- Toxic waste from metal plating, cyanide production, pesticide manufacturing, etc.
- Solids and emulsions from paper mills, factories producing lubricants or hydraulic oils, foodstuffs, etc.
- Water used in hydraulic fracturing
- Produced water from oil & natural gas production

Other activities or events:

- Urban runoff from highways, roads, carparks, roofs, sidewalks/pavements (contains oils, animal feces, litter, gasoline/petrol, diesel or rubber residues from tires, soap scum, metals from vehicle exhausts, de-icing agents, herbicides and pesticides from gardens, etc.)
- Agricultural pollution, direct and diffuse

Wastewater can be diluted or mixed with other types of water by the following mechanisms:

- Seawater ingress (high volumes of salt and microbes)
- Direct ingress of river water
- Rainfall collected on roofs, yards, hard-standings, etc. (generally clean with traces of oils and fuel)
- Groundwater infiltrated into sewage
- Mixing with other types of wastewater or fecal sludge

1.2 Organic matter in wastewater

The discussion of chemical characteristics of wastewater is presented in three parts:

(i)Organic matter

(ii) Inorganic matter

(iii) Gases

In a wastewater of medium strength, about 75 percent of the suspended solids and 40 percent of the filterable solids are organic in nature. These solids are derived from both the animal and plant kingdoms and the activities of man as related to the synthesis of organic compounds. Organic compounds are normally composed of a combination of carbon, hydrogen, and oxygen, together with nitrogen in some cases. The principal groups of organic substances found in wastewater are proteins (40 to 60 percent), carbohydrates (25 to 50 percent), and fats and oils (10 percent). Urea, the chief constituent of urine, is another important organic compound contributing to wastewater. Because it decomposes so rapidly, undecomposed urea is seldom found in other than very fresh wastewater. Along with the proteins, carbohydrates, fats and oils, and urea, wastewater contains small quantities of a large number of different synthetic organic molecules ranging from simple to extremely complex in structure. Typical examples, discussed in this section, include surfactants, organic priority pollutants, volatile pollutants compounds, and agricultural pesticides. Further, the number of such compounds is growing yearly as more and more organic molecules are being synthesized.

1.3 Dairy wastewater

The milk processing industry is one of the world's staple industries, thus the treatment possibilities of dairy effluents have been attracting more and more attention. The dairy industry includes the transformation of raw milk into pasteurized and sour milk, yoghurt, hard, soft and cottage cheese, cream and butter products, ice cream, milk and whey powders, lactose, condensed milk, as well as various types of desserts. With the rapid industrialization observed in the last century and the growing rate of milk production (around 2.8% per annum), dairy processing is usually considered the largest industrial food wastewater source. Moreover, in around 50% of the world's whey production, especially concerning acid whey,

it is untreated prior to disposal [4]. Water can be severely polluted by dairy wastewater without proper treatment. Traditional physical-chemical and biological approaches for dairy wastewater treatment like coagulation/flocculation, anaerobic and aerobic processes have many disadvantages, such as nutrients loss, generations of greenhouse gases (i.e., carbon dioxide and methane) and sludge. In case of treatment of wastewater, specifically with biological, dairy, pharmaceutical wastes rich in protein molecules, from an environmental protection point of view, the high content of lactose and proteins in post-production wastes, like whey, is harmful for the environment. From another point of view, whey is a source of very valuable, active proteins, particularly lactoferrin and serum albumin. Their modulatory potential is exhibited in their pure form and improves after partial, controlled hydrolysis. Unfortunately, the fractionation of this multicomponent medium is not an easy task. [5] The composition of
proteins in a typical dairy wastewater is given.

Protein	**Concentration (g/L)**	**Molecular weight (kDa)**	**Isoelectric pH**
β-lactoglobulin (monomer, often present as a dimer)	2.7	18.4	5.2
α-lactoalbumin	1.2	14.1	4.5-4.8
Immunoglobulin G	0.65	150-1000	5.5-8.3
Serum albumin	0.4	66	4.7-4.9
Lactoferrin	0.1	78	9.0
Lactoperoxidase	0.02	89	9.5
Glycomacropeptides	Varies	<7.0	Various

Table 1.1 Proteins in dairy wastewater

1.3.1 *Whey as pollutant*

Wastewater of food industry usually contains high concentrations of carbonaceous organic chemicals in form of carbohydrates and no toxic compounds which make them emendable for biological conversions. Wastewaters of dairy industry (milk-cheese-yoghurt), meat-poultry, starch, and fruit juice-soft drinks industry contain significant amounts of carbohydrates,

proteins, fats-lipids that can easily be metabolized by special organisms and converted to useful products under special conditions. By using proper organisms and conditions it is possible to produce some commercial products such as ethanol, organic acids (lactic, acetic etc), and high protein animal feedstuff (single cell protein) from these wastewaters some of which may require pre- treatment before bio-conversion [15]. Actual market trends point to a gradual increase in cheese production that generates more than 145 × 106t of liquid whey per year, with 6 × 106t corresponding to lactose. To make 1 kg of cheese, 9 kg of whey is generated [6]. Because of its low concentration of milk constituents (whey is only 6-7% dry matter), whey has commonly been considered a waste product. A dairy farm processing 100 t of milk per day produces approximately the same quantity of organic products in its effluent as would a town with 55 000 residents. Although several possibilities for cheese-whey exploitation have been assayed over the last 50 years, approximately half of world cheese-whey production is not treated, but is discarded as effluent. Therefore, cheese whey represents an important environmental problem because of the high volumes produced and its high organic matter content, exhibiting a BOD5 = 30000-50 000 ppm and COD =60000-80000ppm, with lactose being largely responsible for the high BOD and COD, seeing that protein recovery reduces the COD of the whey only by about 10000 ppm. Bioconversion of whey lactose to SCP (single cell protein), ethanol or methane reduces more than 75% of the BOD while producing marketable products, but in most cases the ensuing effluent is not then ready for disposal. A solution to this water-pollution problem has now become urgent due to the increasing volumes of whey produced, the centralization of production plants and stricter legislative requirements regarding effluent quality.

1.3.2 *Utilization of whey*

Whey proteins are nutritionally the most valuable components in whey. They are composed of thermo sensitive fractions, such as β-lactoglobulin (β-Lg), α-lactalbumin (α-La), blood serum albumin and immunoglobulin as well as thermo stable proteose-peptone. Whey proteins have a compact globular structure that accounts for their solubility (unlike caseins that exist as a micellar suspension, with a relatively uniform distribution of non-polar, polar and charged groups). These proteins have amino acid profiles quite different from caseins: they have a smaller fraction of Glu and Pro, but a greater fraction of Sulphur-containing amino acid residues (i.e. Cys and Met). These proteins are dephosphorylated, easily denatured by heat, insensitive to Ca2+, and susceptible to intra molecular bond formation via disulfide bridges between Cys sulfhydryl groups. Nutritionally whey proteins fractions are

most valuable proteins because they contain high concentration of essential amino acids (especially lysine, cysteine and methionine) and high concentration of cystine. Because of the desirable amino

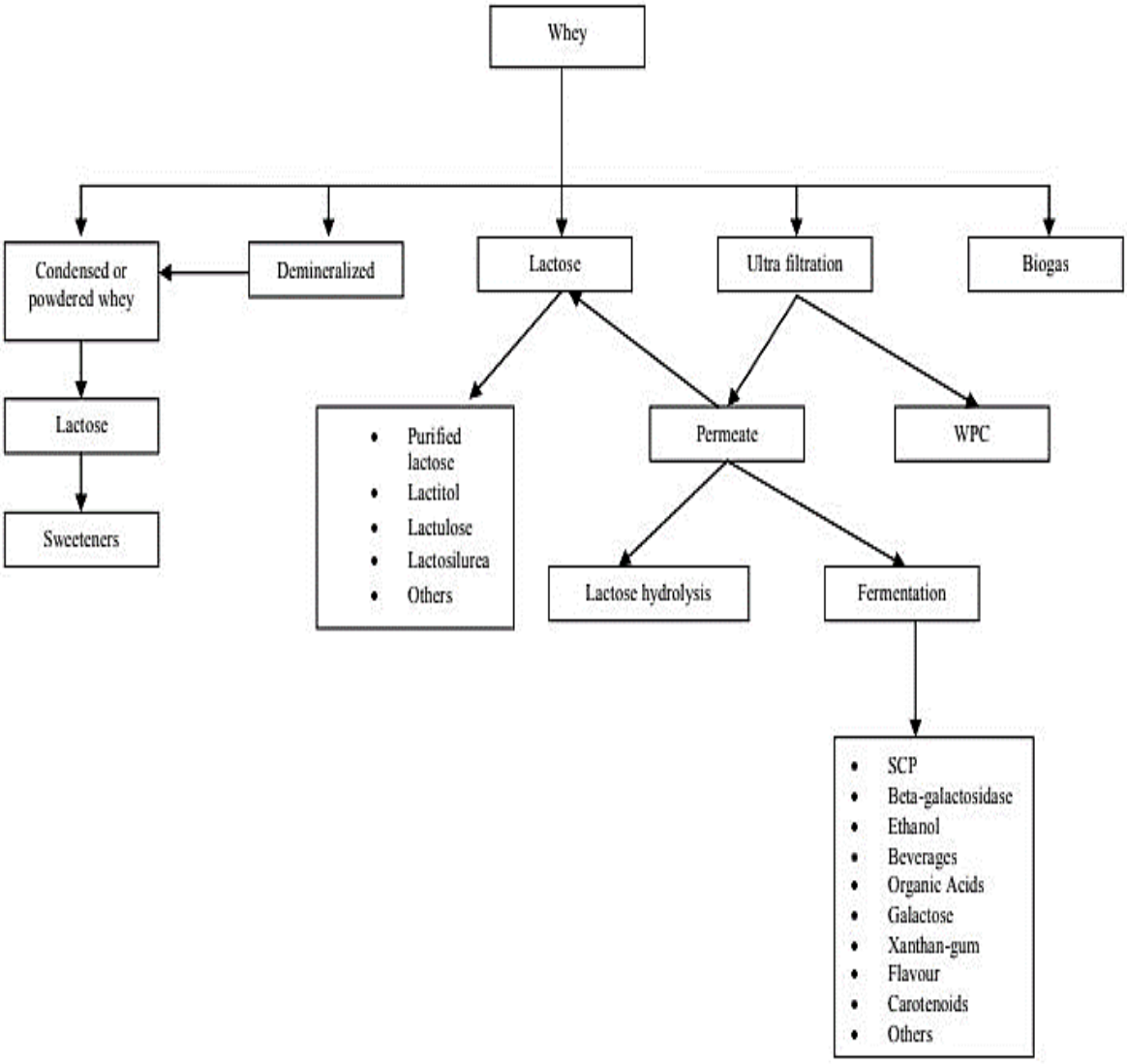


Fig.1.1 Utilization of whey

acid composition, whey proteins have higher biological value when compared to casein, and other proteins of animal origin, including egg, which were considered for a long time as a referent protein. Utilization of proteins in the body is closely related to the ratio of cysteine/methionine, which is about 10 times higher in whey proteins than in casein. Thermally denatured α-la is almost completely absorbed in the digestive system compared to case in which one is absorbed only 75%. Daily requirements for the most essential amino acids may be obtained by consuming ~1.5 L of whey or 0.5 L of milk. Whey also can be pool of bioactive peptides. Bioactive peptides have been defined as specific protein fragments that have a positive impact on body functions or conditions and may ultimately influence health. Upon oral administration, bioactive peptides, may affect the major body systems—namely, the cardiovascular, digestive, immune and nervous systems. The beneficial health effects may be classified as antimicrobial, antioxidative, antithrombotic, antihypertensive, antimicrobial or immunomodulatory. In addition, whey proteins have excellent functional properties, such as good solubility, viscosity, gelling and emulsifying properties, and their concentrates are widely used in the food industry. Since whey proteins are easier to digest than casein, they are used for purposes such as the manufacture of infant formulas or to increase the nutritional value of dairy and other food products. Also, immunoglobulin and other glycoprotein's (lactoferrin, transferrin) and enzymes (lysozyme, lactoperoxidase) are very important factors that contribute to human immunoactive system. They exert antimicrobial properties, and may reduce or inhibit allergic reactions.

1.4 Methods of protein recovery

Various technologies like **Ultracentrifugation, Zone Electrophoresis, Chromatographic Processes** have been employed for separating proteins from whey solution among them **Membrane separation** has been proved to be an efficient procedure due to low cost and a substantial permeate flux value.

1.4.1 *Ultracentrifugation*

An important tool in biochemical research is the centrifuge, which through rapid spinning imposes high centrifugal forces on suspended particles, or even molecules in solution, and causes separations of such matter on the basis ultracentrifugation of differences in weight. Proteins are separated by ultracentrifugation—very high-speed spinning; with possibility of

appropriate photography of the protein layers as they form in the centrifugal field, it is possible to determine the molecular weights of proteins. The ultracentrifuge is a centrifuge optimized for spinning a rotor at very high speeds, capable of generating acceleration as high as 19600 km/s² (around 50000 rpm). Analytical Ultracentrifugation (AUC) experiments give us a method for the direct measurement of basic thermodynamic properties of macromolecules in solution. Since sedimentation relies on the principal property of mass and centrifugal force, it is a valuable technique for a wide variety of solution conditions. Examples of molecules that can be analyzed are Proteins, Polysaccharides, Nucleic acids, Small molecules: drugs, ligands, gasses, Large aggregates: viruses, organelles.

1.4.2 *Zone electrophoresis*

Zone electrophoresis (ZE) is an electrophoretic separation technique typically used for analyzing proteins, nucleic acids, and biopolymers. During the process, different species in a sample are transported in a continuous electrolyte buffer system, subject to a potential gradient. Due to differences in the mobilities, the species in the samples will eventually separate into different, well-resolved peaks.

1.4.3 *Membrane separation*

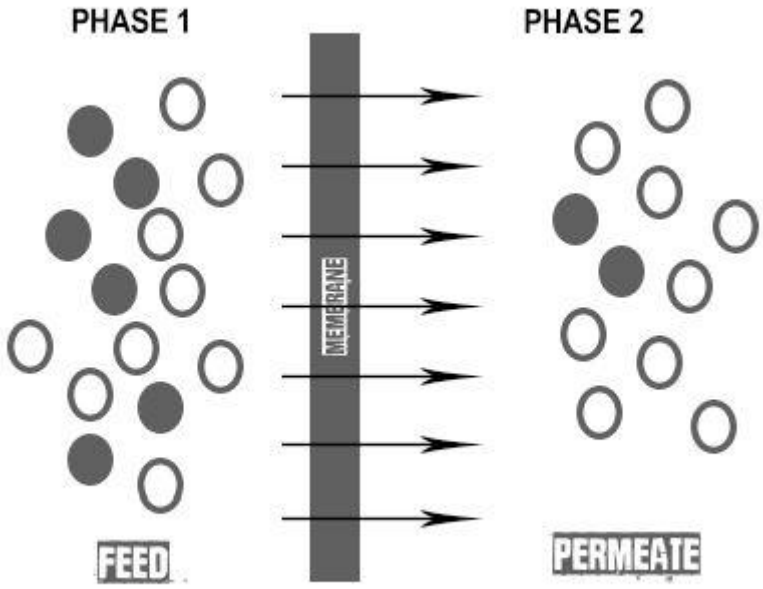


Fig1.2 Membrane separation process

If we start with technology as an attempt to recreate natural or biological systems engineered in a way to put those systems work according to daily life or industrial needs, Membrane technology emerges as a lucrative way of doing that. The membranes need very little or almost no energy to function and these can come with great reusability. Use of membrane in various applications like waste water treatment, food processing, desalination and many other separations is increasing every day. Thus, membrane separation technology is become a very popular alternative to existing separation procedures with continuous research. Membranes are widely categorized by pore size, morphological structure and separation mechanism. Ultrafiltration (UF), Microfiltration (MF) membranes work with sieving mechanism where Reverse Osmosis (RO), Nanofiltration (NF) membranes work with Solution-diffusion mechanism.

1.4.3.1 Microfiltration

MF has numerous small applications. It is essentially a sterile filtration with pores (0.1-10 μm) so small that micro-organisms cannot pass through them. MF is a process of separating material of colloidal size and larger than true solutions. MF membrane is generally porous enough to pass molecules of true solutions, even if they are large. Micro filters (MF's) can also be used to sterilize solutions, as they are prepared with pores smaller than 0,3 μm, the diameter of the smallest bacterium, *pseudomonas diminuta*. The MF's are made from natural or synthetic polymers such as cellulose nitrate or acetate, polyvinylidene difluoride (PVDF), polyamides, polysulfone, polycarbonate, polypropylene. The inorganic materials such as metal oxides, glass, zirconia coated carbon are also used for manufacturing the MF's.

1.4.3.2 Ultrafiltration

Ultrafiltration (UF) is most commonly used to separate a solution that has a mixture of some desirable components and some that are not desirable. UF is somewhat dependent on charge of the particle, and is much more concerned with the size of the particle. Typical rejected species include sugars, bio-molecules, polymers and colloidal particles. UF processes operate at 2-10 bars though in some cases up to 25-30 bars have been used. UF processes perform feed clarification, concentration of rejected solutes and fractionation of solutes. UF is typically not effective at separating organic streams. UF throughput depends on physical properties of the membrane, such as permeability, thickness, process and system variables like feed consumption, feed concentration, system pressure, velocity and temperature. Polymeric materials, polysulfone, polypropylene, nylon 6, polytetrafluoroethylene (PTFE),

PVC and acrylic copolymer have been used successfully as UF membranes. Inorganic materials such as ceramics, carbon based on membranes, zirconia, have been commercialized by several vendors.

UF has a wide range of applications as shown below:

- Oil emulsion waste treatment
- Treatment of whey in dairy industry
- Concentration of biological macromolecules
- Electrocoat paint recovery
- Concentration of textile sizing
- Concentration of heat sensitive proteins for food additives
- Concentration of gelatin
- Enzyme and pharmaceutical preparations
- Pulp mill waste treatment
- Production of ultrapure water for electronics industry
- Macromolecular separations replacing the conventional change of phase methods.

1.4.3.3 Nanofiltration

Nanofiltration (NF) is a form of filtration that uses membranes to separate different fluids or ions. NF is typically referred to as ―loose‖ RO due to its larger membrane pore structure as compared to the membranes used in RO, and allows more salt passage through the membrane. Because it can operate at much lower pressures, and passes some of the inorganic salts, NF is used in applications where high organic removal and moderate inorganic removals are desired. NF is capable of concentrating sugars, divalent salts, bacteria, proteins, particles, dyes and other constituents that have a molecular weight greater than 1000 Daltons. An advantage of NF over RO is that NF can typically operate at higher recoveries, thereby conserving total water usage due to a lower concentrate stream flow rate. NF is not effective on small molecular weight organics, such as methanol. Membranes used for NF are cellulose acetate and aromatic polyamide type having characteristics as salt rejections.

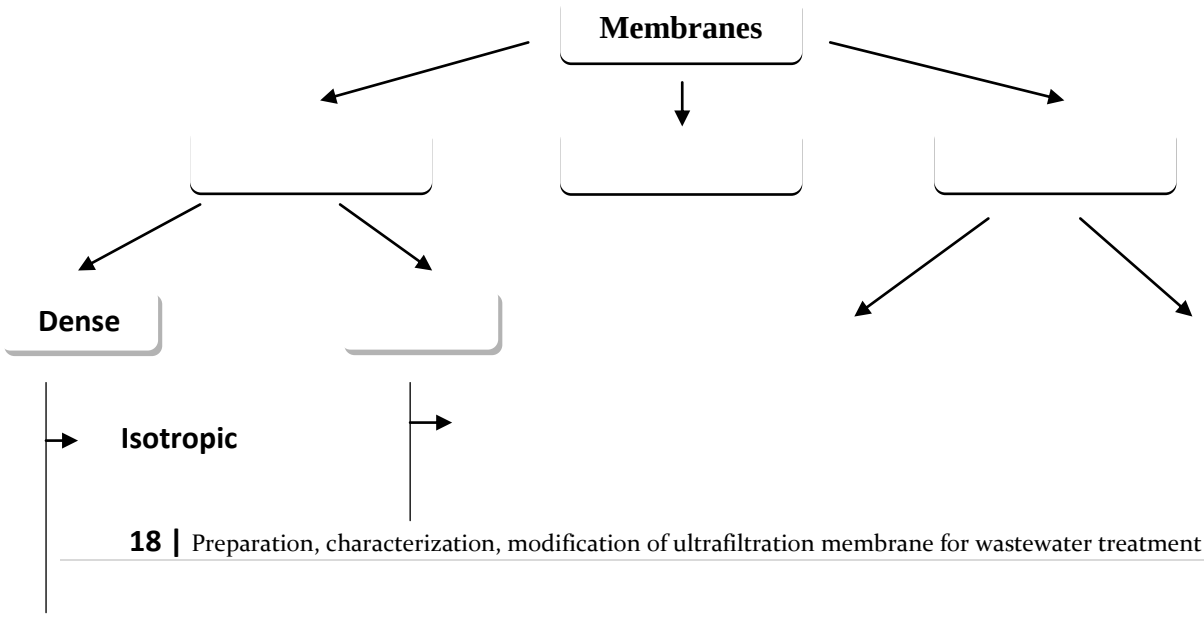
1.4.3.4 Reverse Osmosis

Unlike ultrafiltration, that can only remove some suspended materials larger than 1 micron, the process of RO will eliminate the dissolved solids, bacteria, viruses and other germs contained in the water. RO is essentially a pressure driven membrane diffusion process for

separating dissolved solutes. The RO is generally used for desalination seawater for its conversion into potable water. The salient features of the process are that it involves no phase change and it is relatively a low energy process. RO is the most widely used of the membrane techniques. Although superficially similar to ultrafiltration and hyperfiltration, it operates on a different principle in that the membrane is selectively permeable to water and excludes ionic solutions. RO uses high pressures to force permeate through the membrane, producing a concentrate containing high levels of dissolved salts. RO is a separation process that uses selective semi permeable membrane to remove dissolved solids, such as metal salts, from water. The membrane is more permeable to water than to contaminants or impurities. The water in the feed is forced through a membrane by applied pressure which exceeds the osmotic pressure of the feed and becomes permeate consisting of treated wastewater. Molecules of water pass through the membrane while contaminants are flushed along the surface of the membrane and exit as concentrate. The concentrate flow from a reverse osmosis system ranges from 10 to 50 percent of the feed flow, with concentrations of dissolved solids and contaminants approaching 10 times that of the feed water. RO membranes are made polymers, cellulose acetates and Polysulfone, polyamide types. RO finds extensive applications in the following:

- Potable water from sea or brackish water
- Ultrapure water for food processing and electronic industries
- Pharmaceutical grade water
- Water for chemical, pulp and paper industry
- Advanced wastewater treatment

1.5 Types of membranes



1.5.1 *Asymmetric Membranes*

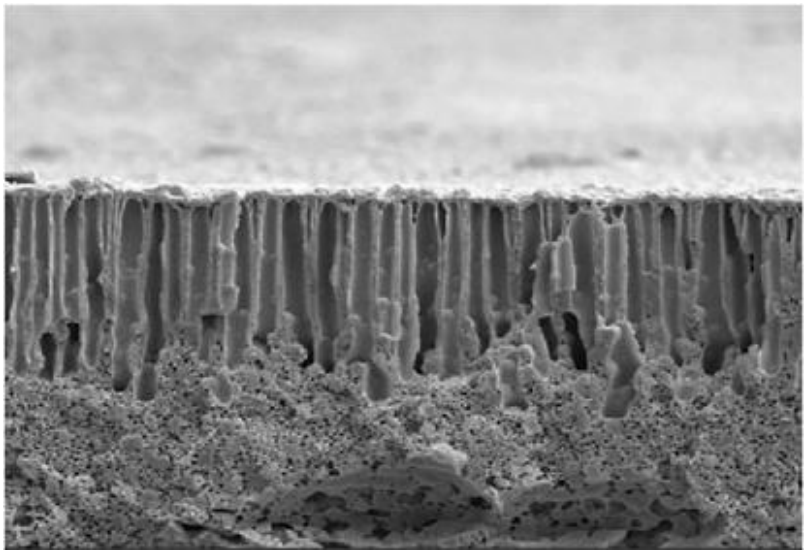


Fig 1.3 SEM image of a typical asymmetric membrane [16]

A membrane should be as thin as possible if a high permeation flux is to be achieved. Membrane separation may not be economical if the flux is low. But for all practical purposes, a membrane must have reasonable mechanical strength and should be defect-free (large-size pores and fissures in a membrane are called *membrane defects*, defects may appear during fabrication of a membrane). If the membrane is too thin and mechanically weak, it becomes difficult to handle it and to fabricate a membrane separation module. It is Dense skin layer practically impossible to cast a membrane less than about 20 μm in thickness. But an isotropic porous membrane of this thickness (for ultrafiltration, for example) offers too much resistance to solvent flow and the flux does not become acceptable. This seemingly difficult problem was solved by fabrication of the 'asymmetric membrane, which is maybe the greatest breakthrough in membrane research. An asymmetric membrane has a thin (0.1 to 1 m) permselective layer supported on a highly porous substructure. The thin layer may be non-porous (for use as 30 μm an RO membrane) or may have very fine pores for use as a UF membrane). But the entire membrane is an integral piece of the same material. The thick

highly porous substructure offers necessary mechanical strength but does not offer any appreciable resistance to permeation since it has much larger pores and a high porosity [17]. From the figure the porous substructure with fingerlike cylindrical pores and a thin permselective layer below that can be clearly seen.

1.6 Membrane modules

A 'membrane module is a compact unit housing the membrane as a barrier between the feed and permeate flow regions, and fitted with the inlet and outlet nozzles on both feed and permeate sides. Compared with conventional separation devices, a membrane module has a small size but a large packing density (the membrane area per unit volume of a module is called packing density). A number of modules can be used in parallel if the feed rate is large. It is never built as a big unit because of practical limitations. Four types of modules are in common use:

1) plate and-frame
2) spiral-wound
3) hollow-fiber
4) tubular

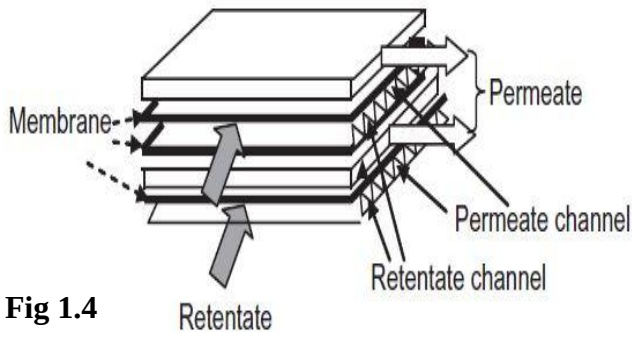


Fig 1.4

The **plate-and-frame configuration** resembles the plate-and-frame filter press, with the filter media replaced by membranes. The membranes may be square or circular, arranged in vertical or horizontal stacks. Plate-and-frame modules cannot withstand very high pressure and are therefore limited to MF and UF duty. The surface area to volume ratio of plate-and-frame modules is not high.

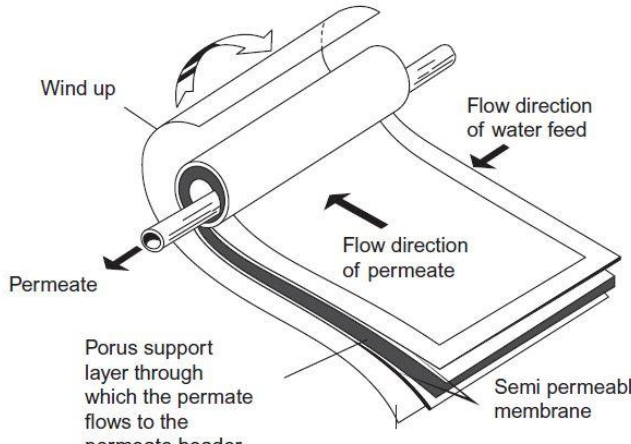


Fig 1.5

In the **spirally wound configuration**, two large sheets of

membrane are heat-sealed on three sides, forming a bag. A flexible spacer mesh or a porous support layer is inserted into the bag, creating between the two membrane layers a free space for permeate flow. The sandwich assembly thus formed is wounded spirally, forming a cylindrical module. The open side of the bag is connected to a central perforated tube serving as a collector for the permeate. The rolled-up membrane sheets are separated by a mesh spacer, thus providing a flow channel for the retentate. Spirally wound membranes are sold as cylindrical assemblies or cartridges, complete with central tube, spacers, and connections. Their surface area to volume ratio is high.

Hollow fiber configurations are, in principle, similar to the tubular setup. The tubes, however, are much thinner with diameters from 1 mm. down to capillary size, hence the name of hollow fibers. The small diameter imparts to the tubes, sufficient mechanical strength so that an external rigid support is not necessary. A very large number of hollow fibers (or lumens) are connected to perforated end plates and the entire bundle is inserted in a vessel or jacket. Flow direction may be inside-out or outside-in. The main advantage of hollow-fiber modules is their compactness, attaining thousands of square meters of membrane area per cubic meter of module bulk volume. Their disadvantage is their high susceptibility to fouling and clogging, limiting their use to clear fluids of relatively low viscosity [18].

The **tubular membrane configuration** resembles a shell-and-tube heat exchanger. The membrane is cast on the inner wall of rigid porous tubes, made of polymer or ceramic. The tubes are connected to end plates and installed as parallel bundles inside a shell. The tubes may have diameters in the range of 10–25 mm. Flow direction is usually inside-out, that is,

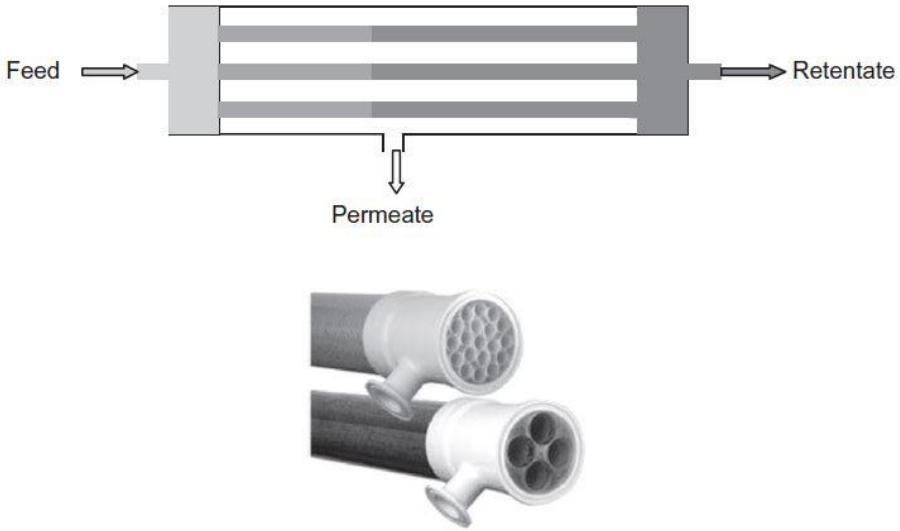


Fig 1.6

the retentate flows inside the tubes and the permeate is collected at the shell-side. It is often possible to reverse the flow (outside-in) for cleaning and unclogging of the membrane. Tubular configurations provide the possibility of maintaining high tangential velocity in the feed stream and are therefore particularly suitable for applications where the feed contains a high proportion of suspended solids or must be strongly concentrated. Owing to their relatively large diameter, tubular membranes are easy to clean and inspect. The surface area to volume ratio of tubular modules, however, is not high.

According to flow-configuration, membrane modules can be mainly grouped into following types:

1) Dead-end or batch filtration module
2) Cross-flow module
3) Hybrid-flow module
4) Rotating disk module

1.6.1 *Dead-end or batch filtration module*

Dead-end filtration is one of the main flow configurations of membrane processes. In dead-end filtration the direction of the fluid flow is normal to the membrane surface. The dead-end membranes are relatively easy to fabricate which reduces the cost of the separation process. The dead-end membrane separation process is easy to implement and the process is usually cheaper than cross-flow membrane filtration. The dead-end filtration process is usually a batch-type process, where the filtering solution is loaded (or slowly fed) into membrane device, which then allows passage of some particles subject to the driving force. Dead-end management is applied because the energy loss is less than when one applies a cross-flow filtration. This is because all energy enters the water that actually passed the membrane. The pressure that is needed to press water through a membrane is called Trans Membrane Pressure (TMP).

During cleaning of a membrane, components are removed hydraulically, chemically or physically. When the cleaning process is performed, a module is temporarily out of order. As a result, dead-end management is a discontinuous process.

1.6.2 *Cross-flow module*

Cross flow filtration is when the flow is applied tangentially across the membrane surface. As feed flows across the membrane surface, filtrate passes through while concentrate accumulates at the opposite end of the membrane. The tangential flow of the membrane creates a shearing effect on the surface of the membrane, which in turn reduces fouling. Because cross flow removes build up from the surface of the membrane, the permeate flux does not drop as fast when compared to dead end filtration. Cross flow technology also provides the benefit of an improved membrane lifespan by helping to prevent irreversible fouling.

1.6.3 *Hybrid-flow module*

The hybrid flow process combines the dead-end and the cross-flow principle. As in the cross-flow filtration tubular membranes are with the filtration layer on the inside wall are used. The filtration process has two phases: the production phase and the flushing phase. During the production phase, the tubes are closed on one side and a dead-end filtration is performed. During the flushing phase, the tube is open on both sides and the fraction that did not pass through the membranes is removed in order to clean the membrane surface as in cross-flow filtration. This filtration technique is especially suitable for treating water streams containing suspended solids in low concentrations (polishing).

1.6.4 *Rotating disk module*

In this process, discs equipped with two flat sheet membranes in both sides of each disc are rotating in feed to improve the membrane performance by producing shear stress on the membrane surface. In Japan in later 80's, the prototype systems equipped with 0.1 μm ceramic plate membranes were tested with anaerobic digester broth. The rotating disc module was encapsulated in a pressure vessel and permeate was obtained by pressure. Since the primary moving object was not waster, the energy cost of developing shear stress on the membrane surface was low. However, the benefit of the energy cost savings was offset by the capital cost increases created by the complexity of the rotating disc module.

1.7 Membrane material selection

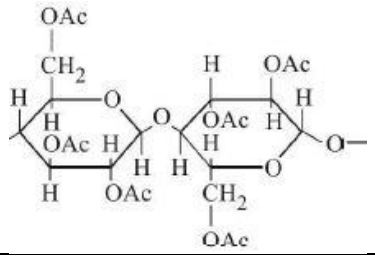
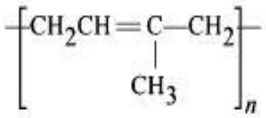
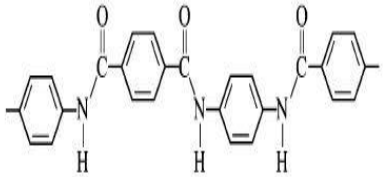
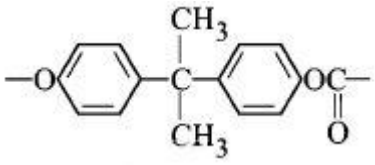
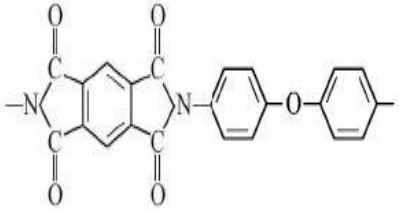
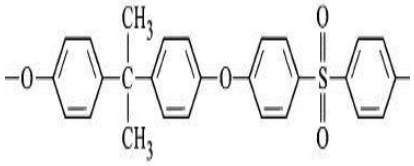
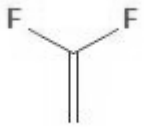
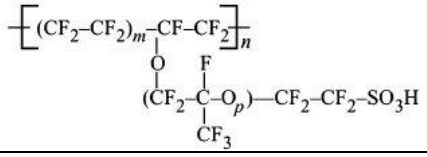
The majority of commercial membranes are made of a wide variety of organic polymers: cellulose and its derivatives (mainly cellulose acetate), polyolefins, polysulfones, polyamides, chlorine and fluorine substituted hydrocarbons, etc. Inorganic (ceramic) membranes based on

oxides of zirconium, titanium, silicon, and aluminum have been developed. They are produced by precipitation of the oxides from salts on a macroporous ceramic support, followed by sintering of the colloidal solid particles at high temperature to form a microporous inorganic film. The suitability of membranes for use in the process industry in general and in food processing in particular depends on a number of characteristics. The principal requisites are:

- Good permeability, so that the rate of filtration is not too slow to be effective pragmatically.
- High selectivity, which ensures the separation of the intended solute from the solution or an intended gas from a gas mixture.
- Chemical stability and compatibility, so that it can be used in a wide pH range or with any kinds of materials. The material should also be able to withstand chemical cleaning solutions.
- Mechanical strength, so that the membrane can withstand high operating transmembrane pressure and hours of application,
- Resistance to fouling and adsorption, these phenomena reduce the permeate flux and all over reduces the membrane performance.
- Amenability to casting of a thin film, so that the material can be cast as sheets and be used as membranes
- Suitability for fabrication of a module. So that the material can be made into hollow fiber and spiral wound modules.
- Bio-inertness, so that it can be used with enzymes and biologically active materials.
- Long service life.

Table 1.2 very commonly used material for membrane synthesis (Seader & Henley, 1998)

Polymers	Type	Representative unit	Glass transition temperature	Melting point (^{0}C)

Cellulose triacetate	crystalline			300
Polyisoprene	Rubbery		-70	
Aromatic polyamide	crystalline			275
Polycarbonate	Glassy		150	
Polyimide	Glassy		310-365	
Polysulfone	Glassy		190	
Polyvinylidene fluoride	Glassy		-35	160
PTFE (polytetrafluoroethylene)	Crystalline	$-CF_2-CF_2$		327
Nafion				

The Polysulfones possess very good chemical stability, resistance to chlorination, oxidation and good thermal stability as indicated by their glass transition temperature (T_g = 190^{o}c) [6]. Also, PSF has a very good solubility and tendency to co-dissolve with polymeric additives. This allows us to modify the characteristics of the membrane and makes PSF a desired support material for composite membrane preparation used in Ultrafiltration. However, due to the hydrophobic characteristic of PSF it is prone to fouling, pore blocking by molecules in the solution, which deteriorates permeate flux and decreases membrane reusability. Therefore, to increase membrane hydrophilicity is considered to be a suitable way to minimize membrane fouling. Several approaches to improve the hydrophilicity of PSF UF membrane have been tried, including surface coating, surface grafting, and blending hydrophilic additives, plasma treatment, redox initiated grafting [7-10]. Among these methods, blending hydrophilic additives have been widely studied since it is simple, relatively low-cost, and effective in improving membrane permeability and antifouling property. The polymer blends are of either miscible (homogenous) or immiscible (heterogeneous) type. **I**n most cases, the polymeric blends are heterogeneous for thermodynamic reasons [11]. This process is simple, efficient and inexpensive. Various polymeric blends have been used to synthesize membranes with better performances. Water-soluble polymers, such as poly(vinylpyrrolidone) (PVP) and poly(ethylene glycol) (PEG), are commonly used as polymer additives for the preparation of ultrafiltration membranes. The preparation is largely done by phase inversion method, which, may be due to their good solubility in water and organic solvent, low toxicity, high complexing ability, and good film-forming characteristics. In most of the cases, these water-soluble polymers increase membrane surface pore size and porosity due to their pore-forming effect [12, 13]. However, most water-soluble polymers are easily lost during membrane formation and usage and that diminishes its capability to increase hydrophilicity of the membrane.

From dairy wastewater the proteins like Serum albumin, lactoferrin are bigger in size thus, easier to separate using ultrafiltration by a membrane of suitable molecular weight cut-off (MWCO). Also, these proteins have pharmaceutical value, so, extracting these with less cost would be a necessary task. In my work the recovered proteins are mixed together and need to be separated afterwards which is beyond the scope of my work. Model/simulated dairy wastewater is used by other researchers for the experiment purposes [14]. A large part of milk protein is Casein and it is usually separated by isoelectric precipitation and the rest of

the protein is separated by membrane separation. The pH range acidic and neutral is taken here for experiments as the basic conditions may need further treatment and thus more cost can be associated with that. Fouling is a great concern while working with biomolecule separation and in case of PSF membranes, protein fouling is a grave concern as it decreases the permeate flux considerably.

1.8 Present work

In this work, flat-sheet type asymmetric ultrafiltration membranes have been prepared using base material homogeneous Polysulfone (PSF) solution in Dimethylacetamide (DMAc) solvent with Polyvinylpyrrolidone (PVP) as a polymer additive using phase inversion method. The casting solution was stirred with the help of magnetic stirrer for 12hours at room temperature and further left to settle for 12hours at room temperature. The solution was then cast on a clean glass plate with a casting knife maintaining a uniform thickness of 200 μm, in ambient atmosphere. The glass plate was immediately immersed into the cold-water bath. The casted films immediately changed to white color after the immersion in the water bath and separated out from the glass plate. The prepared membranes were characterized by Liquid-liquid dispersion Porosimetry (LLDP). The ultrafiltration performance in a wide pH range (4.7-11.5) was tested using bovine serum albumin (BSA) solution and reusability of the membrane was also tested by the same. The best performing membrane from above experiments were chosen for wastewater treatment application. Model dairy wastewater was treated using the prepared membrane and reduction in total protein percentage and carbohydrate percentage was investigated.

Chapter 2.

Literature Review

2. Literature review

To prepare a modified asymmetric flat-sheet polymer membrane for ultrafiltration purpose and the purpose of dairy wastewater treatment the choice of polymer, the process of synthesis, the choice of modifying agent (additive), the choice of membrane cleaning solution, the analytical methods for protein quantification was to be investigated. Previous work on these questions have been studied. Following are some of the relevant literature which were consulted for the present body of work.

2.1 Membrane synthesis and modification

- Flat sheet asymmetric polymeric membranes were prepared by **Sinha, M.K et al. [19]** from homogeneous solution of Polysulfone (PSF) by the phase inversion method using N-methyl-2-pyrrolidone (NMP) as solvents. Results showed that with increase in molecular weight of PEGME, the pore number as well as pore area in membranes increased. Membranes with PEGME of higher molecular weights have higher PWF and higher hydraulic permeability due to high porosity. With increase in molecular weight of PEGME from 550 to 5000, the PWF increased from 17.5 to 227.8 Lm−2h−1. Similarly, EWC increased from 59.7% for PEGME 550 to 70.8% for PEGME5000 membranes. Contact angle was also decreased from 71° for PEGME550 to 47° for PEGME5000.
- Well-dispersed polyaniline−poly(vinylpyrrolidone) (PANI−PVP) nanocomposite was synthesized by **Zhao et al. [20]** through dispersion polymerization and then used as a novel additive to prepare a polysulfone (PSf)/PANI−PVP nanocomposite membrane via immersion precipitation process. The addition of PANI−PVP nanocomposite increased membrane surface pore size, porosity, and hydrophilicity. Pure water fluxes of PSf/PANI−PVP nanocomposite membranes were 1.8−3.5 times that of PSf membrane with a slight change of bovine serum albumin (BSA) rejection.
- Integrally skinned ultrafiltration (UF) membranes for wastewater treatment were prepared by **Ahmad et al. [21]** the phase-inversion process with an immersion precipitation technique to investigate the effect of different formulations on UF performance. Three new polymer solutions were used, consisting of polysulfone (Psf), 1-methyl-2-pyrrolidone (NMP) and polyvinylpyrrolidone (PVP). Results showed that the flux of the membrane decreased from 70.77 to 32.82 L/m2h while the separation performance for

particle solutes increased from 10.31 to 33.89% at 2.5 bar with an increase in polymer concentration.

- Membranes were prepared by **Boom et al. [22]** from a casting solution of a water-soluble polymer, poly (vinyl pyrrolidone) (PVP), and a membrane forming polymer, poly (ether sulfone), m l-methyl-2-pyrrohdone (NMP) as solvent by immersing them in mixtures of water and NMP. It was found that the addition of PVP to the ternary system suppresses the formation of macrovoids m the sub-layer, while the ultrafiltration-type top-layer consists of a closely packed layer of nodules.

- Polyaniline (PANI) of high stability and good processibility was prepared by **Ghosh et al. [23]** in acidic aqueous dispersion/solution, using the support of a water soluble polymer poly(vinyl pyrrolidone) (PVP). The high degree of dispersion and near solubility and storage stability of the PANI prepared, are explained on the basis of the synchronized establishment of hydrogen bonding, between segments of PANI being formed during the polymerization of aniline and the PVP present in the solution.

- This study by **Chakraborty et al. [24]** investigates the effect of polyvinyl pyrrolidone (PVP) of different molecular weights on the structure and permeation properties of polysulfone (PSf) membranes. The membranes were prepared by phase inversion method using PSf in two solvents, viz. *N*-methyl-2-pyrrolidone (NMP) and dimethyl acetamide (DMAc) separately. Results show that the morphological parameters and flux performance of the membranes have a significant inter-relationship with the molecular weight of PVP. The membrane pore number and pore area are seen to increase with molecular weight of PVP. The maximum rejection found in this study is 76% with PSf/DMAc membrane with PVP 360,000 (at pH 9.3).

- Flat-sheet polyethersulfone (PES) membranes were prepared by **Jimenez et al. [31]** by wet phase inversion. The variables of interest were: the concentration of base polymer in the casting solution (dope solution), the solvent evaporation time, the addition of surface modifying macromolecules (SMMs), and the use of the additive polyvinylpyrrolidone (PVP). It was noticed that the average polyethylene glycol (PEG 35 ku (35 kDa)) separation by membranes with PVP was approximately 15% lower than the tightest membranes prepared without PVP. Membranes prepared with PVP had pure water

permeation rates (PWP) significantly higher than membranes prepared without the PVP additive.

2.2 Membrane characterization methods

- According to **Calvo et al. [25]** Liquid–liquid displacement porometry (LLDP), is proposed to estimate the molecular weight cut-off value of Ultrafiltration (UF) membranes. Several commercial UF membranes are analyzed by using LLDP and their pore size distributions have been used to estimate the molecular weight cut-off as should be obtained by dextran retention. Results compared reasonably with nominal cut-off values given by manufacturers. The method offers a fast and accurate way to assign cut-off values for UF membranes, without having to perform expensive and time-consuming solute retention tests, which bring results very often difficult to compare due to the difficulties in the standardization of such methods.

- Membranes from different commercial polymers (Trogamid® and Radel®) and a new (PAA-g-PEG550) copolymer, consisting of an aromatic polyamide modified with PEG, have been prepared with pore sizes from 0.4 μm to 8 nm by **Carretero et al. [25]** Their porosimetric features have been analyzed by liquid–liquid displacement porometry. In all cases narrower pores are obtained when the polymer concentration in the casting solution increases. Good accordance with image analysis pore sizes is noted. Good correlation is also detected when air–liquid porometry can be used. Permeability decreases always with increasing polymer concentration. Porosity increases when finger like structures are obtained (Trogamid® and PAA-g-PEG550); while, when granular structures are obtained (Radel®), porosity decreases when more polymer is used in the casting procedure.

- Liquid–liquid displacement Porosimetry (LLDP) has been used by **Enrique Antón et al. [30]** to characterize several UF membranes in a wide range of molecular weight cut-offs (MWCO). A new method to convert Porosimetric data into pore size distributions and related information has been developed based on assuming log-normal pore size distributions. The results of this are in good agreement with those from the customary data conversion algorithm (as derived by Grabar and Nikitine). The proposed method can

also be used when a reduced number of experimental data points is available, leading to a significant reduction of data acquisition time needed to complete a reliable analysis.

- **Calvo et al. [26]** in their another work has suggested for an estimation of molecular weight cut off of membranes with empirical equations and correlations. Considering infinite dilution conditions, the radius of a molecule was estimated by Stokes-Einstein equation and another correlation that connects diffusion coefficient at infinite dilution condition to the molecular weight of the molecules was used to estimate the molecular weight cut-off of the membranes.

- **Schultz et al. [27]** obtained data for the osmotic reflection coefficient (σ) for dextrans with weight-average molecular weights from 70 kDa to 500 kDa by using track-etched polycarbonate membranes with uniform cylindrical pores. The dextran sieving coefficients estimated from these results were substantially larger than those predicted by hydrodynamic models for spherical solutes in cylindrical pores. Then, they evaluated an equivalent spherical radius for the studied dextrans from their free solution diffusivities according to the Stokes-Einstein equation.

- **Reiss and Zydney [28]** proposed a relationship between the molecular weight of a protein and its Stokes-Einstein radius, derived for a wide range of proteins and given by a 1/3 power: $r = 0.88\ M_w^{1/3}$

- According to **Sinha, M.K et al. [19]** solution of bovine serum albumin (BSA) of molecular weight 68,000 Da was used to study the permeation performance of prepared membranes using a batch membrane cell of 350 mL capacity. Results showed that with increase in molecular weight of PEGME, the pore number as well as pore area in membranes increased. Membranes with PEGME of higher molecular weights have higher PWF and higher hydraulic permeability due to high porosity.

- In the works of almost all of the above scientists, field emission scanning electron microscope (FESEM) images has been used to examine the structure of pores or layers in the asymmetric membrane. These images directly provide the top layer visual information as well as cross sectional information of the membranes. A number of FESEM images were taken at different magnification for both top surface and cross section of the prepared membranes.

- Pore size distribution obtained from LLDP analysis was smaller than that of the FESEM method. It may be due to the fact that in FESEM analysis using ImageJ software, comparatively pores bigger than 10nm were considered on the membrane surface. So, it is possible that, this method may over-estimate the pore size by considering the wider pores on the surface which may not even continue till the end of the membrane surface. [19]

2.3 Ultrafiltration experiment

- A protein determination method which involves the binding of Coomassie Brilliant Blue G-250 to protein is described by **Bradford et al. [29]** The binding of the dye to protein causes a shift in the absorption maximum of the dye from 465 to 595 nm, and it is the increase in absorption at 595 nm which is monitored. This assay is very reproducible and rapid with the dye binding process virtually complete in approximately 2 min with good color stability for 1 hr.

- Ultrafiltration experiments were conducted by **Sinha, M.K et al. [19]** in the batch cell. To study the influence of molecular weight of PEGME on solute separation and permeate flux behavior of the prepared membranes. The protein, Bovine Serum Albumin (BSA), was dissolved in deionized water and the concentration was kept constant at 1000mgL−1 for all the experiments.

- To investigate the reusability characteristics of the membrane, the ultrafiltration experiment was conducted by first using pure water, then by 1000 ppm BSA solution. After the fouling by BSA solution, the membrane was cleaned by cleaning solution and again pure water was passed through it, then again, the BSA solution was used for ultrafiltration to see the steady state flux. [19].

- pH of the solution plays a vital role on the separation performance of the membrane. The ultrafiltration experiments were done through a wide pH range as suggested by several literatures. The experiments were done at pH~4.7, pH~11.3, pH~7 to see the behavior of the membranes in different conditions. The rejection was measured at different pressure point also to measure the role of the transmembrane pressure, on separation performance. Apart from transmembrane pressure, the rejection and flux characteristics of the membranes strongly depend on the structure of the membrane as well as the properties of

the feed solution. So, the prepared UF membranes were also characterized by estimating rejection and flux during permeation experiment using BSA solution.

- Among many colorimetric methods for carbohydrate analysis, the phenol-sulfuric acid method is the easiest and most reliable method. It has been used for measuring neutral sugars in oligosaccharides, proteoglycans, glycoproteins, and glycolipids. This method is used widely because of its sensitivity and simplicity. In its original form, it required 50-450 nmol of monosaccharides or equivalent for analysis and thus is inadequate for precious samples. [32]

- Promising results were obtained when BSA rejection ranged from 94.3% to 100%. The optimum membrane in this study was determined by PSF 17% (containing 17 wt% polymer concentration) which successfully exhibited 100% rejection with filtrate flux for about 23.86 $L/m^2.h$ at a pressure of 2 bar. This research also proved that polymer concentration would greatly affect the membrane performance and structural properties, consecutively enhancing the membranes ability for BSA separation. [33]

- Membrane fouling is often characterized in the laboratory by flux decline experiments, where an increase in transport resistance due to accumulation of foulants on and/or in a membrane is manifested as a decrease in permeate flux with filtration time at fixed trans membrane pressure. However, many industrial microfiltration and ultrafiltration applications operate at constant permeate flux, and there are few reports comparing these modes of operation. [41]

2.4 Membrane fouling & cleaning

- In the study by **Yongjun Sun et al. [40]** the fouling behavior of PES ultrafiltration (UF) membrane with different DOM fractions including bovine serum albumin (BSA), sodium alginate (SA) and humic acid (HA) was systematically investigated. The result showed that the fouling mechanism of HA was cake formation while that of BSA and SA was caused by both pore-blocking and cake formation due to the different particle size. Moreover, membrane fouling became more severe with the increase of feed concentration and TMP and it could be accurately described by the cake-complete model. The pore blocking resistance for SA was larger than that for BSA, whereas the cake resistance followed the sequence SA>BSA>HA. This observation offered insight into the

differences in fouling behavior of the various DOM components and was further used as guidance for practical application.

- From the works of **Wienk et al. [34]** it is found that Sodium hypochlorite solutions are used to treat membranes prepared from a polymeric blend containing poly(viny1 pyrrolidone) (PVP) to increase their water permeability. Sodium hypochlorite affects the membrane material in such a way that PVP is selectively removed from the membrane matrix. The mechanism of the reaction between hypochlorite and PVP is investigated by several chemical analysis techniques of the reaction products. Strong indications are found that the reaction involves chain scission of PVP according to a radical mechanism.

- For foulants containing proteinaceous components enzymatic cleaners play a vital role in scissioning specific points in the protein strands while detergent cleaners also interact with the protein strands at specific points but in addition rapidly solubilize any small loose protein fragments. Results of the works of **Munoz-Aguado et al. [35]** show that it is most effective to clean first with an enzyme and then with a detergent, or, if both are present in the same cleaner it must be formulated in such a way that the action of each component does not interfere with any others. The efficiency of detergent cleaners usually increases with concentration up to a point where the cleaner attacks the membrane itself.

- During chemical cleaning, membranes are soaked in a solution of strong acids and bases such as hydrogen chloride (HCl) or sodium hydroxide (NaOH), or disinfection agents such as hypochlorous acid (HOCl). As a result of the effective chemical cleaning, the initial flux is restored and the membrane deemed as amenable for further operation. The shadow side of the process is an alteration of the membrane surface, which under some forced cleaning conditions results in formation of holes in the membrane skin layer. As was found during the study by **Kuzmenko et al. [36]** higher dosages of cleaning agents result in complete restoration of the initial flux at the first step, but lead to more severe fouling, thus requiring faster clean-in-place operations in the long term.

- Sodium hypochlorite (NaOCl) is a widely used cleaning reagent for membrane separation processes to recover membrane permeability; however, the competitive interactions of different chlorine species with fouling layers have not been adequately elucidated. In this work, **Wang et al. [37]** investigated the pH-dependent diffusion of the active chlorine species and reactions involved in the consequent dissociation and/or destruction of the

fouling layers. The hypochlorite conductivity and dynamic diffusion tests showed that an *increase in pH* facilitated the uneven and fast diffusion of active chlorine via relaxing the matrix structure of the fouling layer. Under the synergetic effects of oxidation, hydrolysis and hydraulic shearing, the enhanced diffusion resulted in an uneven but massive removal of the foulants rather than a layer-by-layer dissociation, leading to a higher membrane cleaning efficiency.

❖ Most commonly used chemical agents or components entering in the formulation of detergents for the membrane cleaning/disinfection in dairy industries and drinking water production plants. [38]

Basic cleaning/ disinfection agent categories	**Interaction between foulant and cleaning agents**	**Examples**	**Advantages**	**Disadvantages**
Caustic Soda	Organic: Hydrolysis Inorganic: Solubilization/Chelation	NaOH (KOH, NH_4OH)	Modification of the charge of ionizable solutes favoring their solubilization, particularly for organic molecules Saponification of fat matters	No protein hydrolysis at T = 50^oC during less than 1 h at pH 11.5
Acidic	Organic: Hydrolysis/saponification Inorganic: Solubilization/ Chelation	HNO_3/ H_3PO_4 Citric acid	Dissolution of inorganic salts or oxide films. Solubilization of free minerals Good rinsibility. Citric acid is favored because its mildness compared to nitric acid.	Contribute to nitrate/ phosphorus amount in effluents.
Oxidizing	Organic: Oxidation Inorganic: Oxidation	NaOCl	Membrane swelling agent.	Deteriorations of membranes

	Microbial: Disinfection	H_2O_2 Peracetic acid Metabisulphite	Destruction of pathogenic microorganism. Compatible with nearly all membranes. Fact acting, good rinsability. Compatible with sensitive membranes - Not oxidizing	Incompatible with NF, RO membranes. Contribute to a more or less biodegradable effluent Care must still be taken to avoid corrosion. Time reaction is very long.
Enzymatic	Organic: Peptization Microbial: peptization	Lipases, proteases	Compatible with sensitive membranes. Enzymes are specific of a fouling type. Widely biodegradable and let effluents more digestible for the microorganisms. Reduction of waste water volumes.	Cleaning has to be performed in precise conditions: $40^oC < T < 50\ ^oC$ and $4 < pH < 10$

Table 2.1 Compiled from the works of D'Souza and Mawson, 2005; Zondervan and Roffel, 2007; Rabiller-Baudry et al., 2009; Lin et al., 2010.

- Four ultrafiltration (UF) membranes with molecular weight cut-offs (MWCOs) of 5, 15, 30 and 50 kDa, respectively, were fouled with 1% BSA aqueous solutions and cleaned with different saline solutions. The influence of MWCO, membrane material and operating conditions on the cleaning efficiency was investigated by **Corbatón-Báguena et al. [39]** Saline solutions were able to clean the 5, 15 and 30 kDa membranes, but not the 50 kDa membrane. NaCl, $NaNO_3$, NH_4Cl and KCl were the most effective salts. The

cleaning tests demonstrated that the higher the temperature of the saline solution was, the higher the cleaning efficiency was also.

- It is evident from the above literature that oxidizing agents like NaOCl and basic cleaning agents like NaOH are capable for cleaning the fouling caused by protein solutions. Thus, a mixture of these two can also be used in membrane cleaning for better performance, lesser cleaning time and complete pure water flux recovery.

2.5 Dairy wastewater treatment

- Dairies are obligated to utilize whey after cheese production. From an environmental protection point of view, the high content of lactose and proteins in post-production wastes, like whey, is harmful for the environment. From another point of view, whey is a source of very valuable, active proteins, particularly lactoferrin and serum albumin. Their modulatory potential is exhibited in their pure form and improves after partial, controlled hydrolysis. Unfortunately, the fractionation of this multicomponent medium is not an easy task. **Magdalena Lech et al. [5]** describes an integrated process of fractionation of whey proteins. After the first step of treatment based on membrane techniques, the concentrated, most valuable whey proteins were subjected to a few steps of chromatographic separation.

- A two-stage ultrafiltration and nanofiltration (UF/NF) process for the treatment of model dairy wastewater was investigated by **Jianquan Luo et al. [43]** to recycle nutrients and water from the wastewater. Ultracel PLGC and NF270 membranes were found to be the most suitable for this purpose. In the first stage, protein and lipid were concentrated by the Ultracel PLGC UF membrane and could be used for algae cultivation to produce biodiesel and biofuel, and the permeate from UF was concentrated by the NF270 membrane in the second stage to obtain lactose in retentate and reusable water in permeate, while the NF retentate could be recycled for anaerobic digestion to produce biogas.

- An integrated isoelectric precipitation (IP) – ultrafiltration (UF) – nanofiltration (NF) – lactic acid (LA) fermentation process was established by **Zhiwei Chen et al. [42]** for recovering water, proteins, cells and LA from model dairy wastewater (MDW). This process could solve the problems of sludge/retentate disposal and membrane fouling during membrane-based wastewater treatment. The IP process greatly retarded

concentration polarization and fouling of UF. However, PES membrane was still severely fouled by whey proteins.

- In the work of **Cheïma Fersi Bennani et al. [44]**, a real sample of dairy wastewater was treated using ultrafiltration (UF) and process efficiency and permeate quality were improved by operating under optimum conditions of transmembrane pressure (TMP) and volume reduction factor (VRF). More than 99% of retention rate were observed for turbidity and the BDO5, more than 80% for suspended matter, and 95% for proteins with an optimal TMP fixed at 2.5 bar. A recovery of 58% of the dairy effluent is possible after treatment by UF using the PES-5 membrane.

Chapter 3.

Aims & Objective

3.1 Objective of the study

The objective of this study is to synthesize a modified membrane which will done by varying compositions of the polymer matrix of the membrane. The best membrane from those variations will be selected to use for wastewater treatment application to see the performance of the membrane. The chosen base polymer for the membrane is Polysulfone and the additive is poly(vinylpyrrolidone) (PVP). The additive creates a more hydrophilic membrane which will perform better in water-based separation applications. Dairy wastewater was chosen to be used in wastewater application, mostly because the two-fold objective of its treatment. In one hand the protein, lipid, fat present in the wastewater stream can cause environmental pollution by feeding microorganisms and increasing the BOD of the water, so those organic matters are needed to be removed from the wastewater stream. In the other hand, most of these proteins present in the dairy wastewater stream has food or pharmaceutical value. Thus, extraction of these whey proteins is a necessary task to completely utilize the resources of the dairy industry.

From a rather theoretical perspective, the objective is to study the effect of the additive PVP in the membrane matrix added to Polysulfone as a pore forming agent in the solvent DMAc. Studies have been done to investigate the effects of PVP mixed in different molecular weights in the membrane matrix [23] but the effect of PVP mixed in different weight percentages haven't been done yet. In this study we have tried to measure the effects of PVP in different weight percentages. Also, from the result of modification of the membrane, experiments have been done to see the effectiveness of the membranes in wastewater treatment applications.

Another theoretical perspective would be the estimation of the molecular weight cut off of the manufactured membranes using empirical equations and theoretical approximations rather than using the classical method of determining a range for MWCO using standard molecules of wide molecular weight range which is time consuming and costly. Previous works by Calvo et al. [24] has been consulted for this purpose. Results of ultrafiltration experiments and the wastewater treatment application further suggests the validity of the empirical method of molecular weight cut-off determination.

From literature it can be seen that though there have been studies on effect of PVP additive in different molecular weights but there is no study on effects of addition of PVP on PSF membrane in DMAc solvent in different weight percentages. This work also includes the

membrane cleaning procedure and the application of prepared membrane which hasn't been done in other works.

3.2 Aims of the study

- Preparation of an Ultrafiltration membrane using Polysulfone (PSF) as the base material for dairy wastewater treatment.
- Modification the membrane with an additive to enhance its hydrophilicity, pure water flux, porosity, hydraulic permeability and other characteristics
- Preparation of membranes with different weight percentage of PVP additive to investigate the trend in enhancement of membrane characteristics and find an idea of optimum additive composition for a better membrane.
- Characterization of the prepared membrane with Porosimetric methods (Liquid-liquid displacement Porosimetry) and permeation tests.
- Testing for rejection performance of Bovine Serum Albumin of 68000 kDa, which is a constituent of dairy wastewater.
- Checking for fouling and permeate flux.
- Using chemical cleaning methods for permeate flux restoration.
- Checking reusability of the membrane by repeating above ultrafiltration test and comparing steady state flux results
- Preparation of model dairy wastewater and use it for wastewater treatment application by the selected best membrane
- To experiment in a wide pH range to find pH dependency of the membranes and the whole separation process.

Chapter 4.

Membrane synthesis & modification

4. Introduction

In chapter 1, section 7 it was shown that a large number of materials can be used as the basis for membrane preparation. A spectrum of preparation techniques exist which enable a membrane to be constructed from a given material. The kind of manufacturing technique employed depends mainly on the material used and on the needed membrane structure, which in turn is dependent on the specific separation process we're dealing with. Three basic types of membrane can be distinguished based on structure and separation principles: porous membranes (microfiltration, ultrafiltration) non porous membrane (gas separation, pervaporation, dialysis) carrier membranes.

Not all membranes and membrane structures are covered by the classification given in last paragraph. There is a distinct transition from one type to the other. Reverse osmosis membranes, for example, can be considered as being intermediate between porous and nonporous membranes. For the *porous membranes* the dimension of the pore mainly determines the separation characteristics, the type of membrane material being of crucial importance for chemical, thermal and mechanical stability but not for flux and rejection. On the other hand, for *nonporous membranes*, the intrinsic properties of the material are mainly responsible for the separation.

4.1 Preparation of synthetic membranes

Different synthetic materials can be used for preparing membranes. The aim is to modify the material by means of appropriate technique to obtain a membrane structure with a morphology suitable for specific separation purposes. The membrane material limits the preparation technique employed, the morphology obtained and the separation principle obtained.

A number of different techniques are available to prepare synthetic membranes, some of these methods can be used to prepare polymeric as well as inorganic membranes. A brief description of the important processes is given below.

4.1.1 *Sintering*

Sintering is a simple technique allowing porous membranes to be obtained from organic as well as from inorganic materials. The method involves compressing a powder consisting of particles of a given size and sintering at elevated temperatures. The required temperature

depends on the material used. During sintering the interfaces between the contacting particles disappears. A wide range of different materials can be used such as powders of polymers (polyethylene, polytetrafluoroethylene. polypropylene), metals (stainless steel, tungsten) ceramics (aluminum oxide, zirconium oxide), graphite (carbon) and glass (silicates). The pore size of the resulting membrane is determined by the particle size and particle size distribution of the powder. The narrower the particle size distribution the narrower the pore size distribution in the resulting membrane. This technique allows pore sizes of about 0.1 to 10 μm to be obtained, the lower limit being determined by the minimum particle size. Sintering is a very suitable technique for preparing membranes from *polytetrafluoroethylene* because this very chemically and thermally resistant polymer is *not soluble*. In fact, all the materials mentioned here as basic materials for the sintering process, have the common feature of outstanding chemical, thermal and mechanical stability, particularly the inorganic materials. Only microfiltration membranes can be prepared via sintering, however. The porosity of porous polymeric membranes is generally low, normally in the range of 10 to 20% or sometimes a little higher.

4.1.2 *Stretching*

In this method an extruded film or foil made from a partially crystalline polymeric material (polytetrafluoroethylene, polypropylene, polyethylene) is stretched perpendicular to the direction of the extrusion, so that the crystalline regions are located parallel to the extrusion direction. When a mechanical stress is applied small ruptures occur and a porous structure is obtained with pore sizes of about 0.1 um minimum to a maximum of about 3 μm maximum. Only (semi) crystalline polymeric materials can be used for this technique. The porosity of these membranes is much higher than that of the membranes obtained by Sintering, and values up to 90% can be obtained.

4.1.3 *Track etching*

In track etching, a dense polymer film is subjected to high-energy, charged particle radiation from a suitable source. On hitting the film, the charged particles break the polymer chains creating tracks. The film is then passed through an etching solution (an acidic or an alkaline solution) when the polymer dissolves along the tracks forming pores. In a track-etched membrane, the pores are nearly straight and have a narrow size distribution. This is the greatest advantage of such membranes. However, the etching process is quite expensive. The

open area of the membrane is low (about 5-10%) and the solvent flux also remains low. Track-etched polycarbonate membranes are more common [17].

4.1.4 *Phase inversion*

Phase inversion is a process whereby a polymer is transformed in a controlled manner from a liquid to a solid state. The process of solidification is very often initiated by the transition from one liquid state into two liquids (liquid-liquid demixing) [6]. At a certain stage during demixing. one of the liquid phases (the high polymer concentration phase) will solidify so that a solid matrix is formed. By controlling the initial stage of phase transition, the membrane morphology can be controlled, i.e. porous as well as nonporous membranes can be prepared. The concept of phase inversion covers a range of different techniques such as solvent evaporation, precipitation by controlled evaporation, thermal precipitation from the vapor phase and immersion precipitation. The majority of the phase inversion membranes are prepared by immersion precipitation.

- *Precipitation by solvent evaporation:* In this method, a polymer is dissolved in a solvent and then the polymer solution is cast on a glass plate, a porous or non-porous support. The solvent is allowed to evaporate in an inert atmosphere, in order to exclude water vapor, so that a dense homogeneous membrane is obtained.
- *Precipitation from vapor phase:* A cast film, consisting of a polymer and a solvent is placed in a vapor atmosphere where the vapor phase consists of a non-solvent saturated with the same solvent.
- *Precipitation by controlled evaporation:* In this case the polymer is dissolved in a mixture of solvent and non-solvent. Since the solvent is more volatile than non-solvent, the composition shifts during evaporation to a higher non-solvent and polymer content. This leads eventually to the polymer precipitation leading to the formation of the membrane.
- *Thermal precipitation:* A solution of polymer in a mixed or single solvent is cooled to enable phase separation to occur. Mostly used to prepare microfiltration membranes.
- *Immersion precipitation:* A polymer solution (polymer and solvent) is cast on a suitable support and immersed in a coagulation bath containing a non-solvent. Precipitation occurs because of the exchange of solvent and non-solvent. The membrane structure ultimately obtained results from a combination of mass transfer and phase separation.

4.2 Materials

Polysulfone (average molecular weight 30,000 Da) was purchased from Sigma-Aldrich Co. USA and was used as base polymer in the membrane casting solution. DMAc (99% purity) supplied by Central Drug House (CDH) Ltd. was used as solvent. Reagent grade PVP (average molecular weight 24,000Da) was used as the polymer additive in the casting solution. The ratio in which PSF, DMAc and PVP was mixed is y :84: x. x and y has been varied here. X varies in the range of 13-10% and Y varies in the range of 3-6%. Magnetic stirrer has been used to mix the compounds. Deionized water was used as the main non-solvent in the coagulation bath, it was from Millipore system (Millipore, France).

4.3 Methodology

The methodology of manufacturing a modified membrane includes two parts, the synthesis part and the membrane compaction part. We'll discuss in the following sections why compaction is a very important part in the manufacturing of a membrane.

4.3.1 *Membrane preparation methodology*

- Asymmetric flat sheet membranes were prepared by **phase inversion** method with PVP additive (molecular wt. 36000Da) in the range of 3-6% weight percentages in the casting solution.
- the solution was stirred in a magnetic stirrer for 12 hours and further degassed for 6 hours in room temperature.
- After that, the resulting solution was cast on a smooth glass plate with the casting knife maintaining a 200 μm thickness all through, in room temperature.
- Then the plate was completely immersed in non-solvent, which is cold bath of deionized water.
- Then, the casted solution immediately turned into white films and got separated from the glass surface.
- Prepared membrane was kept cut into the round shape of the membrane module and immersed in water overnight to wash out unnecessary residue.

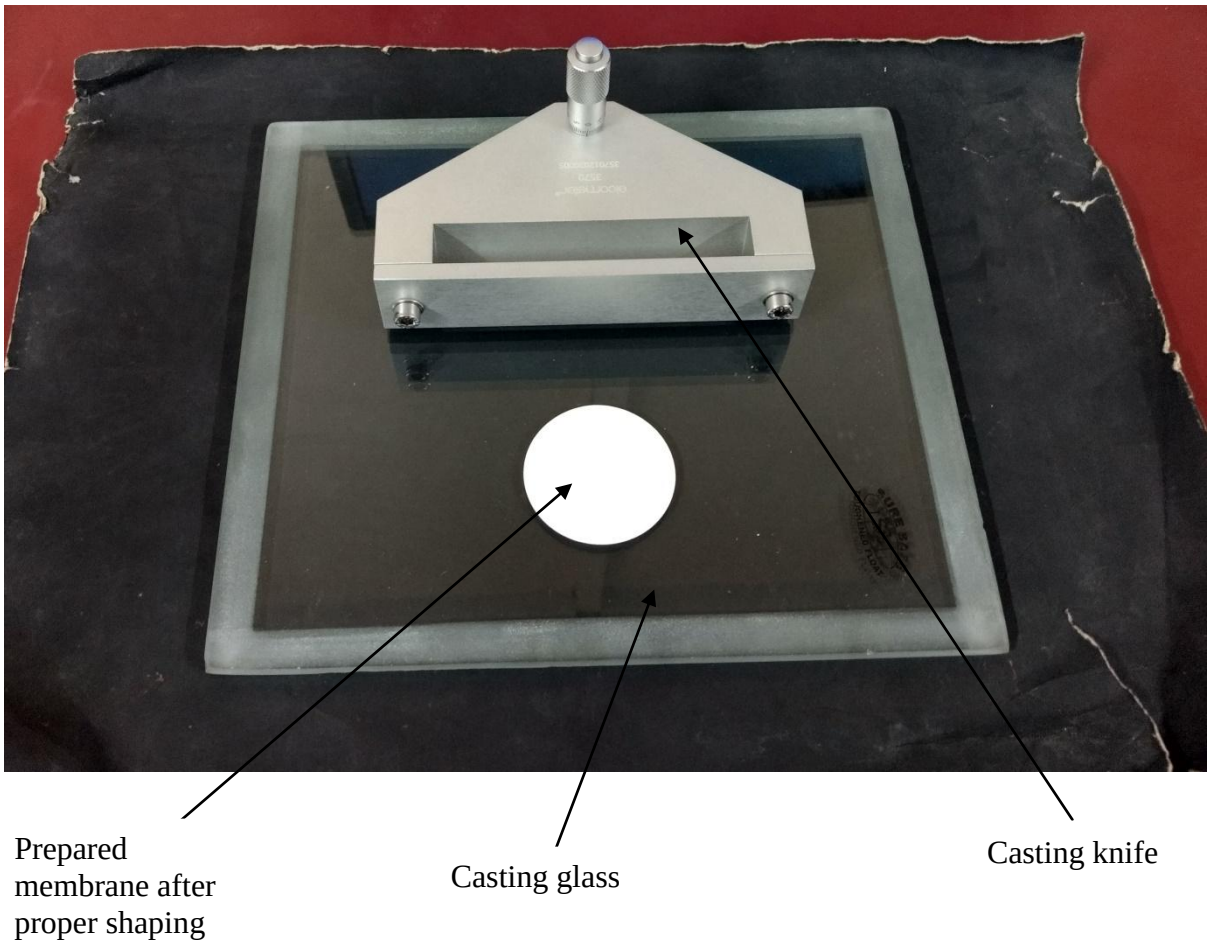


Fig 4.1: The setup for manufacturing a phase inversion membrane

4.3.2 *Membrane compaction*

Compaction is the mechanical deformation of a polymeric membrane matrix which occurs in pressure-driven membrane operations [6]. During these processes, the porous structure densifies and as a result the flux will decline. After relaxation (affected by reducing the pressure) the flux will generally not return to its original value since the deformation process is often irreversible. Compaction will especially occur in reverse Osmosis since the applied pressures are relatively high. However, in nanofiltration and ultrafiltration compaction may occur as well and the extent depends on the pressure employed and membrane morphology.

The goal of membrane compaction in the membrane synthesis step is to form the pores properly by irreversibly deforming the pores under pressure. The result of this step is to get steady flux when subjected to ultrafiltration experiments.

Chapter 5.

Membrane Characterization

5. Introduction

The membranes with different weight percentages of PVP were prepared in the last chapter. Now the task is to characterize the membrane properties. The membrane properties can be expressed as *Morphological properties* and *Permeation properties*. Important factor for the characterization of a porous membrane and its performance is the geometry of the pores and how they're distributed in the membrane surface. The structure related parameters were evaluated by microscopic observations and *liquid-liquid displacement Porosimetry* (LLDP) to get an idea about the membrane structure. The performance of each membrane was evaluated in terms of equilibrium water content, compaction factor, hydraulic resistance, porosity, pure water flux. The molecular cut-off was estimated by employing empirical method. A brief introduction to the various characterization processes is given in the following section.

5.1 Membrane characterization techniques

For any technique of membrane characterization one important but often not satisfactorily defined variable in the characterization of porous membranes, is the shape or the geometry of the pores. Several assumptions are made in this respect, in many of them the pores are assumed to be cylindrical and the Poiseuille's equation has been used to define the flow characteristics. In another description, flow is characterized by using Kozney-Carman equation, assuming the pores to be voids in closely packed spherical membrane molecules of same radius. These assumptions and corresponding geometries are extreme examples in most cases because such pores do not exist. However, to interpret the characterization results it is often essential to make assumptions about the pore geometry. In some techniques the dimension of pore entrance is determined rather than the pore size. These techniques often provide better information about permeation related characteristics.

Another important factor is pore size distribution in the membrane surface. In general, the pores in a membrane are not of same size, they exist as a distribution of sizes. It should be noted that this definition does not characterize the membrane nor the pores of the membrane, rather the size of particles or molecules retained by the membrane. The separation characteristics are determined by the large pores in the membrane.

Two different types of characterization methods for porous membranes can be distinguished from the above considerations:

1. Structure related parameters: pore size, pore size distribution, porosity etc.
2. Permeation related parameters: Molecular weight cut-off, rejection etc.

It is often very difficult to relate the structurer-related parameters directly to the permeation-related parameters because the pore size and shape is not very well defined. The configuration of the pores (cylindrical, packed shapes) used in a model description deviate dramatically from the results sometimes. The most prominent characterization methods for ultrafiltration membranes are:

- Gas adsorption-desorption
- Thermoporometry
- Permporometry
- Liquid displacement
- Fractional rejection measurements
- Transmission electron microscopy
- Scanning electron microscopy

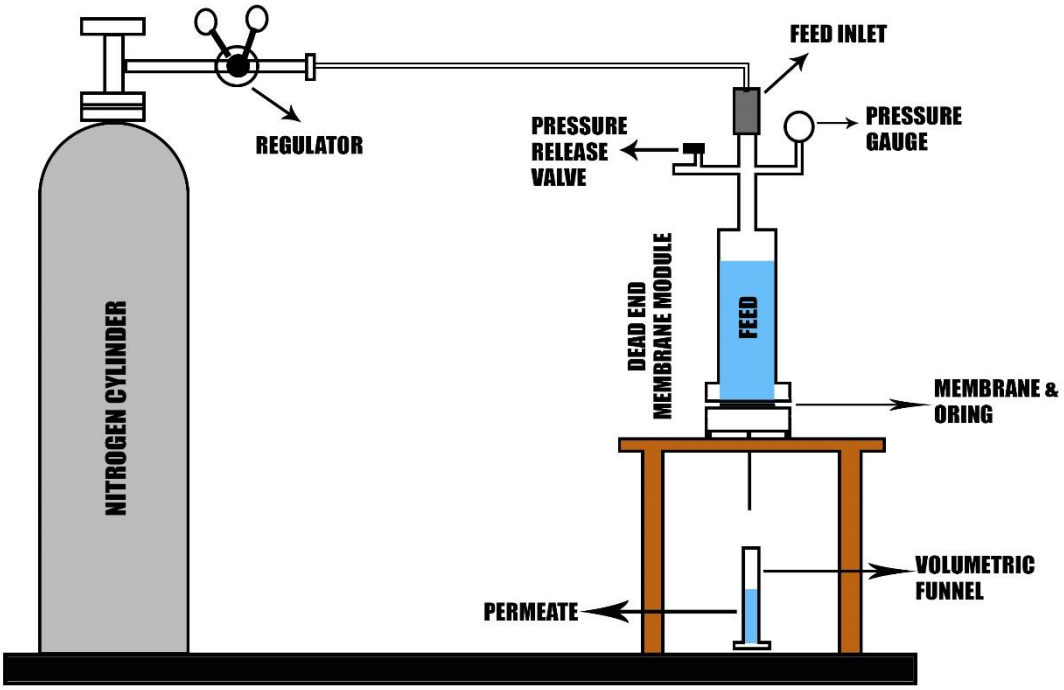


Fig. 5.1: Schematic of the LLDP and permeation experiment setup

5.2 Materials

Methanol, Isobutanol was used. Deionized water used was from Millipore system (Millipore, France). Magnetic stirrer. The batch experiment was performed in 300 ml stainless steel cylindrical permeation cell. At the bottom of the cell cavity the membrane was placed on top of a metallic porous support. The effective membrane diameter was 1.9×10^{-2} m and the effective area of the membrane was 11.34×10^{-4} m^2. The FESEM was done by Zeiss LSM510 Meta from Jadavpur University Dept. of Geological Science.

5.3 Methodology

Among the techniques mentioned, we have employed the liquid-liquid displacement porosimetry (LLDP) and Field emission scanning electron microscope images to determine the structure-related parameters of the prepared membranes and used an empirical method as described by Calvo et al. [21] to determine permeation-related parameter, molecular weight cut-off.

5.3.1 *Microscopic observation (FESEM)*

Field emission scanning electron microscopy (FESEM) provides topographical and elemental information at magnifications of 10x to 300,000x, with virtually unlimited depth of field. Compared with convention scanning electron microscopy (SEM), field emission SEM (FESEM) produces clearer, less electrostatically distorted images with spatial resolution down to 1-1/2 nanometers – three to six times better. A field-emission cathode in the electron gun of a scanning electron microscope provides narrower probing beams at low as well as high electron energy, resulting in both improved spatial resolution and minimized sample charging and damage. For applications that demand the highest magnification possible [49]

Microscopic observation was performed by field emission scanning electron microscope (FESEM, ZeissLSM510Meta, Jadavpur University Dept. of Geological Science) with an acceleration voltage of 10kV after the samples were coated with thin gold layer. The pore size on the membrane surface as well as skin layer thickness was measured with the help of image J software. These images directly provide the cross-sectional information of the membranes. A number of FESEM images were taken at different magnification for both top surface and cross section of the prepared membranes. Computerized analysis of FESEM [28]

image was extensively performed for this study. LLDP was also conducted to compare the morphology of different membranes.

5.3.2 *Liquid-liquid displacement porosimetry*

Cumulative Permeability, average pore size, pore number, pore area distribution data of the flat sheet membrane can be generated by using LLDP method. The liquid displacement method for determination of pore size was introduced by Behold and Erbe [44,45] and further developed by Munari [46]. For this method, two immiscible liquids are employed. One of these liquids is used to fill the pores of the membrane and another liquid is used to displace the pore filling liquid. This can be achieved when certain pressure is employed as given by the Laplace equation $r_p = \frac{2\gamma}{\Delta P}\cos\theta$ where γ is the surface tension between the two liquids and by a proper choice of liquids, a low value of can γ be obtained, such that the pressure to displace the fluid doesn't become too much for the mechanical strength of the membrane [6]. Displacement will start at the largest pores resulting in a flux that can be described by Hagen-Poiseuille's equation. The flow can be measured with mass or volumetric flow measurement tools. By increasing the transmembrane pressure, the liquid inside smaller pores will be displaced and this will enhance the flux of the membrane. In this way we can find a relationship between the pore radius and the flux at a certain pressure. From this, we can determine the pore size distribution.

In summary, liquid displacement is another method to determine the pore size distribution in microporous and mesoporous materials. The advantage of this method is that only active pores are characterized. A drawback may be the occurrence of swelling due to the stagnant liquid that changes the pore sizes. Moreover, the setup is rather complex and a pressure build-up may occur which interferes with the measurements.

5.3.2.1 Procedure

Here water-isobutanol-methanol (25:15:7, v/v) was taken with surface tension of 0.35 mN/m and dynamic viscosity of 3.4 mPa-s [19]. The mixture was prepared by mixing deionized water and the alcohols stirred in a magnetic stirrer for 6 h and then letting it settle in a separating funnel overnight. After the separation, water rich phase was used as the wetting liquid and the alcohol rich phase was used as the displacing liquid. Displacement will start at the largest pores. The pressure was varied from 7.5 – 45 psi, taking 15-16 intermediate

pressure points and corresponding steady state flux values. The flux was measured by volumetric funnel and mass flux measurement.

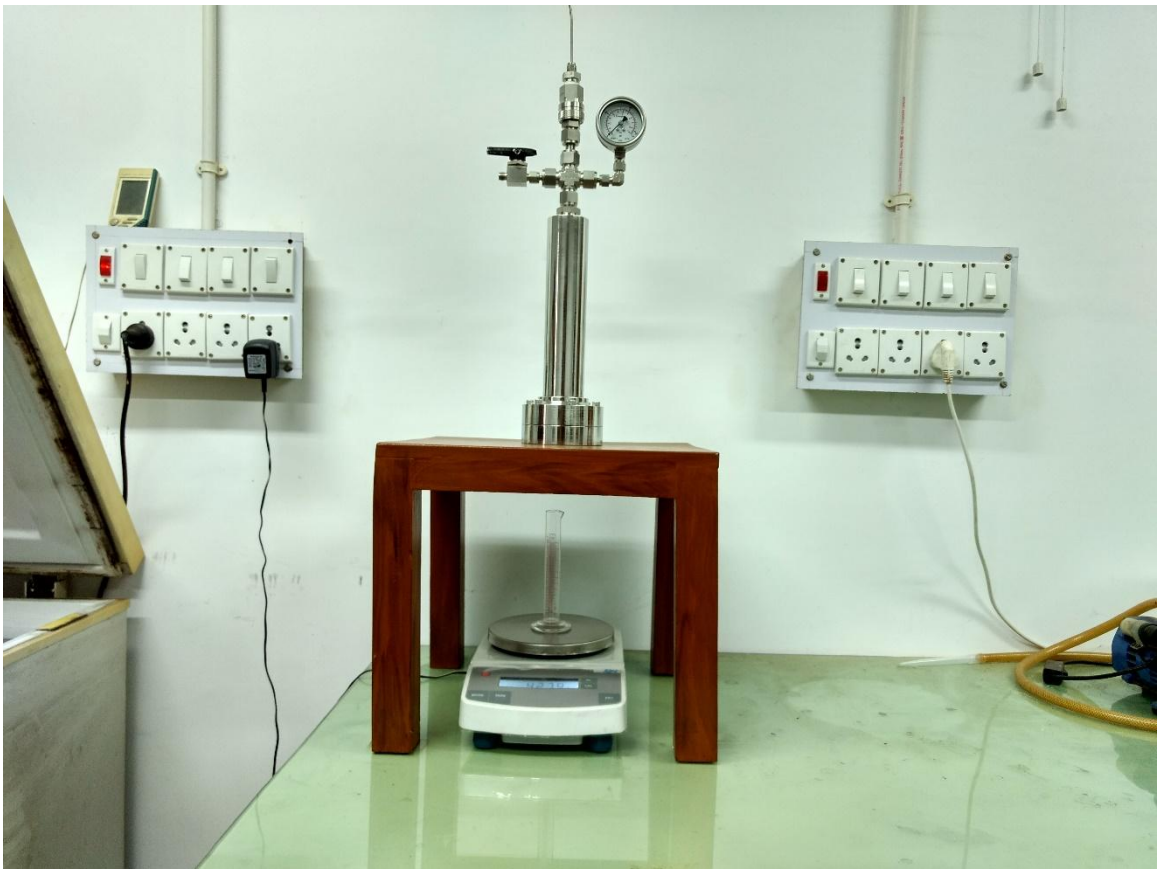


Fig. 5.2: Picture of the setup for LLDP and permeation experiments

5.3.2.2 Theoretical model

By changing the transmembrane pressure, we will get a data set of flux vs pressure which will be used to determine the pore size distribution [47]. The radius (r) was calculated by Cantor's equation:

$$r = \frac{2\sigma}{P}$$

(1)

Where, P is the transmembrane pressure and σ is the interfacial tension between the two liquids. The total hydraulic permeability coefficient (L_n) was obtained by

$$L_n = \sum L_{i,k} = \sum \frac{J_{i,k}}{P_{i,k}}$$

(2)

Where, $J_{i,k}$ is flux at pressure $P_{i,k}$ and $L_{i,k}$ is partial permeability coefficient of the pores with radius r_i and r_k evaluated at $P_{i,k}$, which corresponds to a mean radius $r_{i,k}$.

$$r_{i,k} = \frac{r_i + r_k}{2}$$

(3)

Combining Eqs. (1) and (2), flux versus pressure data gives the permeability versus pore radius curve. Again, the pore number versus pore radius and pore area versus pore radius curves can be obtained using the following equations

$$N_{i,k} = \frac{d\eta P_{i,k}^3 J_{i,k}}{2\pi\sigma^4}$$

(4)

$$A_{i,k} = \pi r_{i,k}^2 N_{i,k}$$

(5)

Where $N_{i,k}$ is the pore density which is given by the number of pores having radius between r_i and r_k per unit membrane surface area; d is the pore length which can be taken as approximately equal to the skin layer thickness and η is the viscosity of alcohol rich phase. $A_{i,k}$ is the area of pores with radius between r_i and r_k. These two equations are derived from the Hagen-Poiseuille's equation of flow assuming laminar conditions and cylindrical pore shape. Thickness of the skin layer was considered as 0.1μm as an average because it is not uniform all along the surface. Total area A_t and total number of pores per unit area N_t was calculated by,

$$A_t = \sum A_{i,k}$$

(6)

$$N_t = \sum N_{i,k}$$

(7)

The mean pore radius r_m was determined by [47]

$$r_m = \frac{\sum N_{i,k} r_{i,k}}{\sum N_{i,k}}$$

(8)

This method has its limitations with assumption of cylindrical pore structure and averaging the skin layer thickness. For this deviation we may get error with the absolute value of A_t and

N_t. However, when comparing membranes with the same method, this information becomes pertinent.

5.3.3 *Permeation experiments*

Permeation-related characteristics were determined after the LLDP was performed. In a way, LLDP helps to develop all the active pores of the membrane with gradually changing the pressure, opening up and permanently deforming the pores to provide a steady permeate flux in later experiments or applications. Now, the compaction factor, pure water flux (PWF), hydraulic permeability, equilibrium water content, porosity and molecular weight cut-off will be determined by permeation experiments and with the help of previously obtained LLDP data.

5.3.3.1 Compaction factor

Compaction of the membranes was done using deionized water for 4 hours at a transmembrane pressure 300 kPa which is higher than the maximum operating pressure used in the experiments. The steady permeation flux was taken after 30 min interval. Compaction factor (CF) is defined as the ratio of initial pure water flux to the steady state pure water flux.

$$CF = \frac{PWF_{initial}}{PWF_{ss}} \tag{9}$$

We get a steady state flux after the compaction of the membrane. As the working pressure used in this experiment is higher than the working pressure in all other experiments, any further deformation of the pores cannot happen and we get a membrane with steady flux.

5.3.3.2 Pure water flux (PWF) and hydraulic permeability (P_m)

Hydraulic permeability measurements provide information on the diffusive or convective transport of components through a membrane under a hydrostatic pressure driving force [48]. Measure of PWF and hydraulic permeability is very important to check for defects in a membrane and its hydrophilic properties. If there are pinholes or fractures in the membrane, the PWF vs pressure graph won't remain linear. On the other hand, with higher hydraulic permeability we can infer a higher hydrophilicity of the membrane.

The value of pure water flux (PWF) was determined by passing deionized water through the compacted membrane in the batch cell module. The operating transmembrane pressure was varied up to 300 kPa and steady states values of the water flux were measured at

those pressure points with the help of volumetric funnel. The working equation to measure PWF was:

$$J_w = \frac{Q}{A\Delta t}$$

(10)

Where, J_w is the pure water flux in L/m^2-h, Q is the volume of water coming through the permeate side, in Liter, A is the effective filtration area of the compacted membrane and Δt is the permeation time in hour. The slope of the straight-line plot, i.e, hydraulic permeability was derived from J_w vs Pressure data. The working equation to calculate P_m (L/m^2-h-kPa) was as follows:

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

(11)

From these values we would be able to compare the performance of the manufactured membranes, change in their hydrophilic nature and the flux they'll be providing.

5.3.3.3 Equilibrium water content (EWC), porosity and hydrophilicity

The porosity of a membrane is one of the most important characteristics. EWC is directly related to the porosity of membrane. It also indicates the hydrophilicity or hydrophobicity of the membranes. EWC at room temperature was calculated as

$$EWC\% = \frac{W_w - W_d}{W_w} \times 100$$

(12)

Porosity of the membrane is defined as [23]

$$Porosity = \frac{W_w - W_d}{\rho \times V}$$

(13)

Where, weight of the membrane in wet and dry condition is respectively W_w and W_d. Volume of the membrane is V and ρ is density of water at room temperature. The wet membranes were dried in a vacuum oven at a temperature 60^{o}C for approximately 24 h. The weights of wet and dry membranes were measured in an electronic balance. Average thickness found in FESEM images was taken for calculation of the volume of the membrane.

5.3.3.4 Molecular weight cut-off determination

Different ways to correlate the pore size of a membrane with the molecular weight of molecules that can pass through it can be found in the literature. In principle, these approaches are based on empirical relationships between the size of a particular molecule and its molecular weight.

A graphical determination of the pore size such that 90% of the pores are smaller than it and only 10% of the total pores are bigger should define what will be used to estimate the molecular weight cut-off for the membrane. In effect, it can be assumed that if this membrane is used to filter similar spherical molecules, the molecules with sizes up to that corresponding to the 90% of the pores would be retained by 90% of the pores only passing through the remaining 10% pores which are bigger than the 90% pore size [21]. So, it can be taken that, this value is a logical indication of the cut-off pore radius for that a membrane. The only remaining and not easy step is to convert the obtained value from pore size terms to molecular weight units in conditions that could be valid or at least useful for non-actually spherical molecules.

For this purpose, various equations are available in literature. In this work, we equated the pore radius with the Stokes-Einstein radius, as it is suggested by the study of Schulz et al. [27] the equation is:

$$r_S = \frac{k_B T}{6\pi\eta D_\infty}$$

(14)

Here D_∞ is the diffusion coefficient of dextran at infinite dilution in water, K_B is the Boltzmann's constant, T is the absolute temperature, η is the water viscosity. The diffusion coefficient of dextrans at infinite dilution in water was expressed as a function of molecular weight of dextran (M) by Chen et al. [14]:

$$\log D_\infty = -4.1154 - 0.47752 \log(M)$$

(15)

Equations (14) and (15) can be used to get the MWCO corresponding to a given cut-off pore size.

5.4 Results and discussion

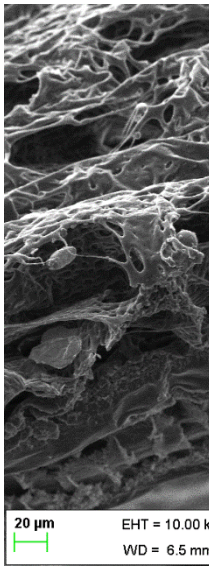
The aforementioned experiments were done and the data has been sorted properly to come to several inferences about the effect of modifying additive PVP on Polysulfone membrane's

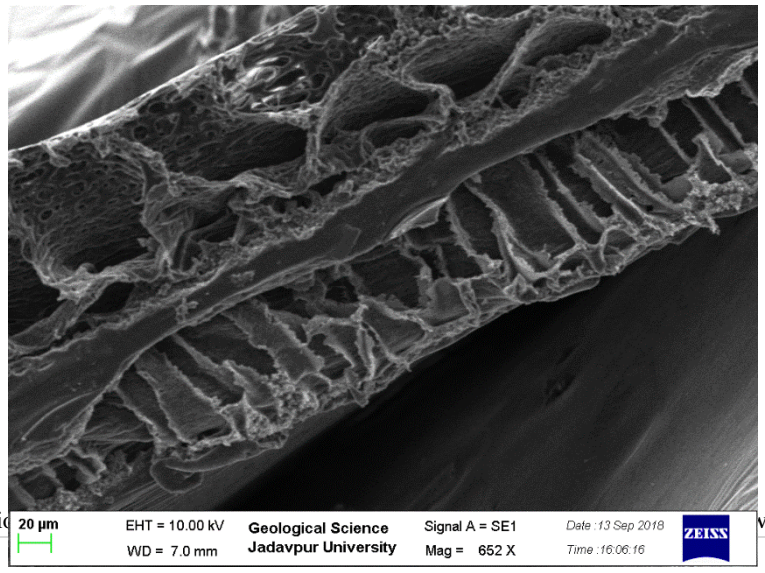
hydrophilicity, structure related characteristics and permeation related characteristics. We'll also see if the membranes are microfiltration or ultrafiltration membrane, according to their pore size and molecular weight cut-off.

5.4.1 *Structure related parameters*

PSF membranes with PVP additive were prepared by phase inversion method using different weight percentages of PVP. The morphology of the prepared membranes was studied by high resolution field emission scanning electron microscope (FESEM). Quantitative parameters like pore size distribution, pore number, pore area, pore density, MWCO were calculated by the liquid-liquid porosimetry method

5.4.1.1 Microscopic observation





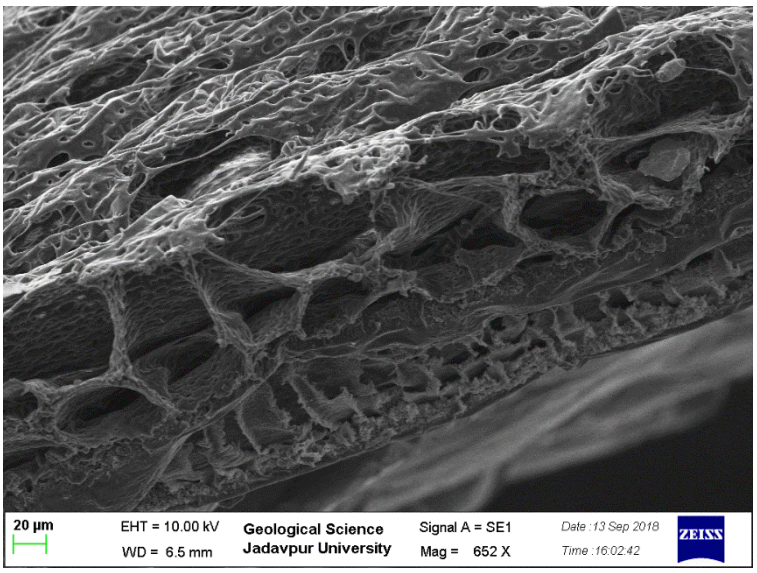


Fig. 5.3 FESEM images of 3 membranes prepared with different wt.% of PVP

Fig. 5.3 shows the FESEM images of cross-sectional view of various PSF/PVP blend membranes prepared in this study. From the image it can be observed that membranes we prepared had asymmetric structure. General structure was very similar for all three membranes consisting of a top dense skin layer and a porous sub-layer. The porous sub-layer consists of finger like structure. Similar observation was also found by Chakrabarty et al. [12] for the system of PSF as polymer using NMP and DMAc as solvent, separately with PVP as additive, varying the molecular weight of PVP. Due to high affinity of PVP towards the non-solvent water, it gets dissolved in the water and gets out of the polymer matrix creating finger like structures. That's why PVP is considered here as the pore forming reagent. There was no noticeable morphological variation between the membranes with different weight percentage of PVP in the blend membranes, as weight percentages are not that much different.

From the pictures, and using software, the thickness of the skin layer was considered 0.1 µm as an average of the thicknesses taken at different points of the FESEM image.

5.4.1.2 Liquid-liquid displacement porosimetry data

The pore size, membrane permeability, pore number and pore area for prepared membranes were determined by Equations. (1), (2), (4) and (5), respectively. The pore size distribution of the membranes is shown in Fig. 5.4 For PSF 3 (high PVP), 30% of the pores were in the size of around 2.26 nm. For PSF 2 (medium PVP), 28% and PSF 1 (low PVP) 27% of pores were of that size.

Membrane	**L_n (m/s-Pa) × 10^{10}**	**r_m (nm)**	**$N_t \times 10^{-14}$**	**A_t (m^2)**	**MWCO (Da)**
PSF 1	4.33	2.38	5.34	.11	15033
PSF 2	4.41	2.30	5.71	.114	14763
PSF 3	4.57	2.28	6.19	.119	14461

Table 5.1: Morphological parameters of all membranes obtained from LLDP.

Table 1 reports the results of the LLDP method. It can be inferred that,

- with the increase in PVP percentage in the membrane, the total number of pores are increasing from 5.34×1014 to 5.84×1014 resulting in more porous membranes.
- There's also a marginal decrease in mean pore size from 2.38 nm to 2.28 nm with the increase in percentage of PVP added.
- The total hydraulic permeability is seen to be increasing with the higher amount of PVP added. This can be explained by Hagen-Poiseuille's equation which states that transport through cylindrical pores is directly proportional to the fourth power if radius (i.e., $Ln \propto r^4$). Similar results were observed by M.K. Sinha et al. [19] for PSF membranes using polyethylene glycol methyl ether (PEGME) additive.
- Since the total number of pores and total permeability is seen to be increasing, it can be inferred that addition of PVP in higher percentage increases the porosity of the membrane.

The complete LLDP data and corresponding calculations are shown in following tables 5.2, 5.3 and 5.4.

Table 5.2 LLDP data for Memb

Cumulative Permeability	Cumulative Pore Number	
4.330573E-10	100	8.008436E+03 Radius Corresponding to 90% Cumulative Pore Number (from graph3) R_s 3.0
4.101126E-10	94.70170391	99.98771412 1.896269E+04
3.871925E-10	89.4090666	99.94892613 3.827077E+04 Boltzmann's Constant (K_B) 1.3
3.635085E-10	83.94004677	99.85107301 8.073400E+04 Temparature(T)
3.396845E-10	78.43870243	99.58684801 1.167709E+05 water Viscocity (η)
3.133492E-10	72.35745237	99.16885387 1.856228E+05
2.853040E-10	65.8813517	98.40947466 4.020057E+05
2.542062E-10	58.70035896	96.3537277 7.269469E+05 the diffusion coefficient of the dextran at infinite dilution in water (D) 7.7
2.216633E-10	51.18566685	91.89283944 9.979852E+05 log(D) -
1.865241E-10	43.0714556	85.25839001 1.296111E+06 log (molecular weight)
1.499851E-10	34.63402158	75.97925056 1.591456E+06
1.135082E-10	26.21089712	63.77184359 1.968997E+06
7.632191E-11	17.62397588	47.6615825 2.374312E+06 Molecular Weight Cut-Off (Da)
3.893766E-11	8.991342976	27.02089647 2.935552E+06

Table 5.3 LLDP data for Memb

Cumulative Permeability	Cumulative Pore Number			
4.413575E-10	100	8.033984E+03	Radius Corresponding to 90% Cumulative Pore Number (from graph3) R_c	3.06355417E-09 meter
4.183397E-10	94.78476004	1.915027E+04		
3.951928E-10	89.54028497	5.228041E+04	Boltzmann's Constant (K_B)	1.38064852E-23 $m^2 kg/s^2.K$
3.721639E-10	84.32255079	6.576580E+04	Temparature (T)	298 k
3.486110E-10	78.98608893	1.881090E+05	water Viscocity (η)	0.00091 Pa.s
3.201902E-10	72.54666975	2.761215E+05		
2.908900E-10	65.90801981	4.120251E+05		
2.590171E-10	58.68646414	7.324961E+05	the diffusion coefficient of the dextran at infinite dilution in water (D)	7.82945111E-11 m2/s
2.262258E-10	51.25680933	1.020840E+06	log D	-6.106268684
1.902819E-10	43.11286773	1.322562E+06	log (molecular weight)	4.169183874
1.529973E-10	34.66515528	1.608661E+06		
1.161260E-10	26.31108922	1.991899E+06		
7.850717E-11	17.78765841	2.330613E+06	Molecular Weight Cut-Off (Da)	14763.31459
4.181098E-11	9.473267092	3.152174E+06		

Table 5.4 LLDP data for Membra

Cumulative Permeability	Cumulative Pore Number
4.579023E-10	100
94.17140829	99.98683835
88.4855708	99.94625985
83.02270984	99.85107629
77.80235263	99.66246533
72.41975495	99.30218067
66.12899297	98.5838492
59.02821583	96.60429419
51.78308611	92.41604183
43.82216555	86.07736819
35.63727391	77.31166485
27.42206377	65.71734156
18.90721125	50.16059585
10.26054988	30.02771937

Radius Corresponding to 90% Cumulative Pore Number (from graph3) R_s	3.033478788E-09	meter
Boltzmann's Constant (K_B)	1.380662652E-23	$m^2 kg/s^2.K$
Temparature (T)	298	k
water Viscocity (η)	0.00091	Pa.s
the diffusion coefficient of the dextran at infinite dilution in water (D)	7.907156655E-11	m2/s
log D	-6.101979657	
log (molecular weight)	4.160201996	
Molecular Weight Cut-Off (Da)	14461.12219	

Fig. 5.4 Percentage pore (%) vs Pore size (nm) – Pore size distribution

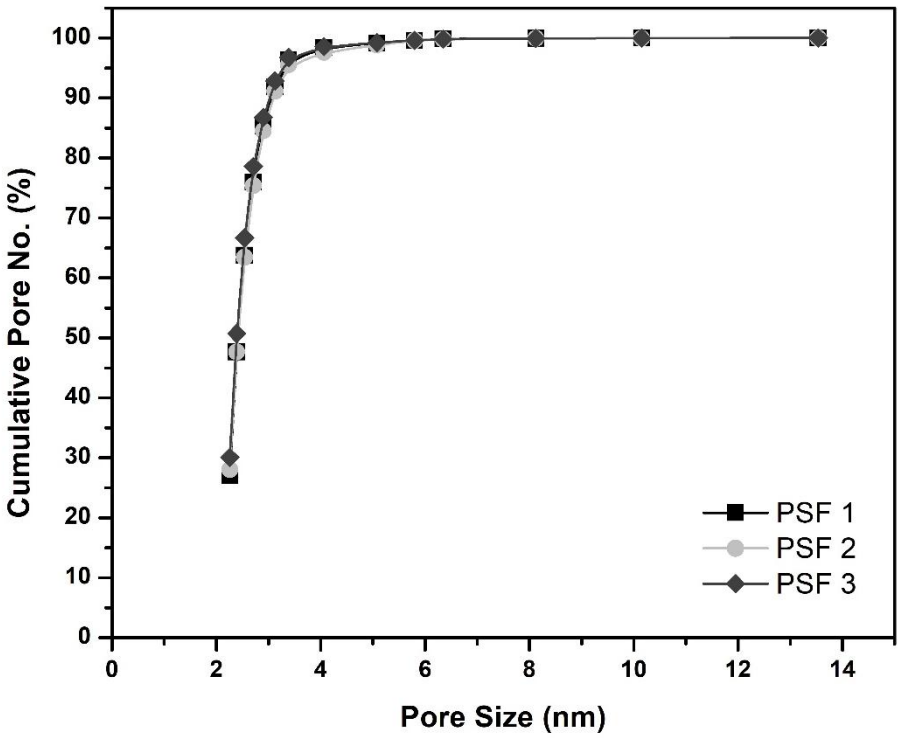


Fig. 5.5 Cumulative Pore Number (%) vs Pore size (nm)

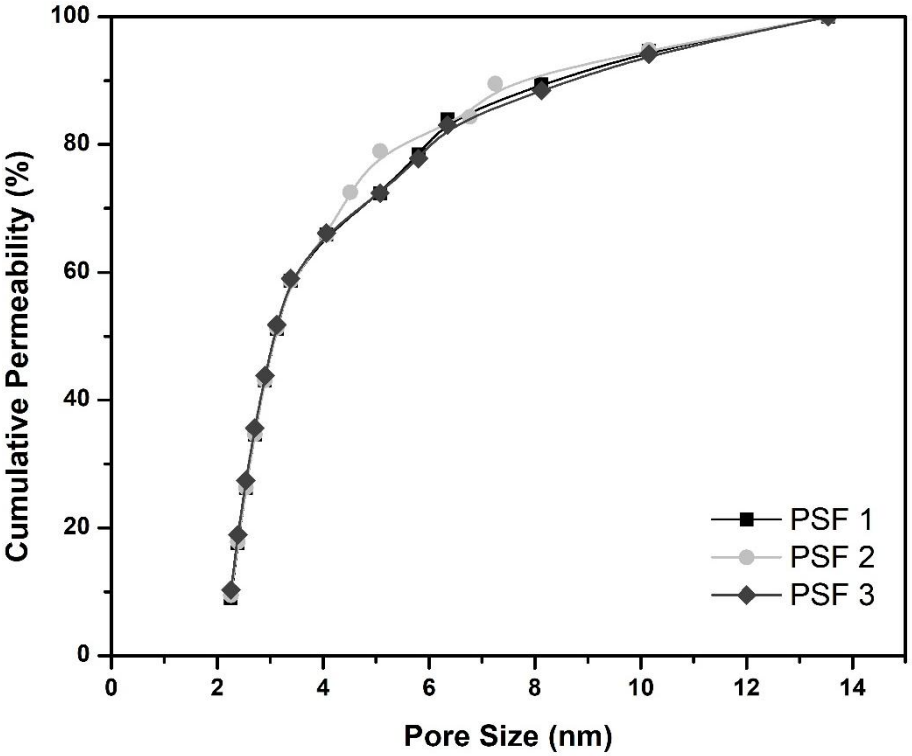


Fig. 5.6 Cumulative Permeability (%) vs Pore size (nm)

Membrane cumulative permeability and cumulative pore number were plotted against pore size (radius) and shown in Figs. 5.5 and 5.6 respectively. It can be inferred from both the images that

- majority of the pores (90% pores) of all three membranes are in the range of 2-3.5 nm.
- From this observation we can say that the membranes are applicable for UF purpose.
- It is difficult to get the exact fraction of the larger pores (>5 nm) as well as smaller pores (2-3.5 nm) by the LLDP method. But we can say that the majority (90%) of pores, i.e., pores having 2-3.5 nm radius contribute around 60% to the overall membrane permeability.
- We can see from here that the larger pores actually constitute the overall membrane performance by increasing the permeability.

5.4.1.3 Molecular weight cut-off determination

By the method described in section 5.3.3.4, LLDP offers a swift and reasonable estimate of the molecular weight cut-off of UF membranes in Fig. 5.7

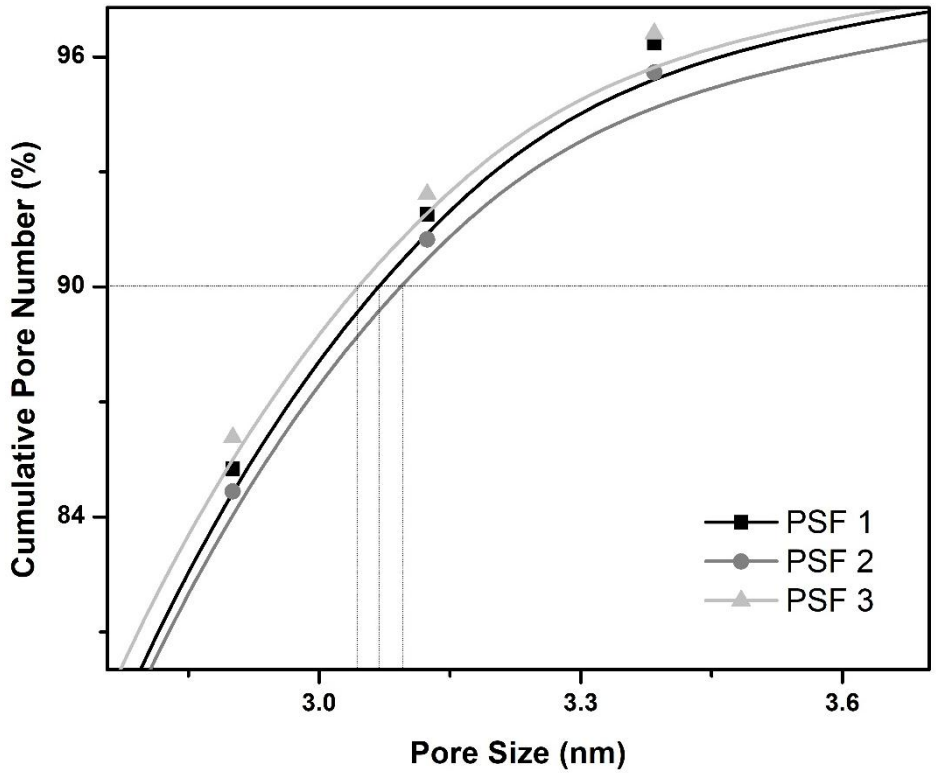


Fig. 5.7 Magnified portion of Figure 5.5 to determine pore radius corresponding to 90% cumulative pore number (%)

We can see a magnified portion of the cumulative pore number vs pore size (nm) (Fig. 5.5) graph obtained from the LLDP data. A line corresponding to the 90% cumulative pore number is drawn. From the x-coordinate intercept we get the pore radius which is larger than 90% of the total pores present. From this radius, using Equations. (14) and (15), we estimated the MWCO of PSF1, PSF2, PSF3 to be, 15033 Da, 14763 Da, 14461 Da respectively. This estimation is based on pseudo-empirical molecular-weight versus size correlations for dextrans. Similar correlations can be found for PEGs or other similar molecules commonly used as traces. But those correlations give only slightly difference cut-off values. The conventional method of cut-off determination deals with permeation of molecules covering a range of molecular weight. This process is costly, time consuming and only gives a range of MWCO. In comparison, this correlation gives a cost and time effective approximation of MWCO as described in the works of Calvo et al. [21].

5.4.2 *Permeation related characteristics*

PSF/PVP blended membranes were experimented through permeation behavior to observe the effect of PVP as an additive in different weight percentages. The membranes were

characterized in terms of compaction factor (CF), pure water flux (PWF) and hydraulic permeability.

5.4.2.1 Effect of weight percentage of PVP on CF

Compaction factor is an indicator of the intrinsic structure of the membrane. It says about the nature of the membrane sub-layer, presence of macrovoids. The compaction of membrane causes permanent deformation of pores. This process prepares the membranes for application and if a fracture is present, it can be detected by this process. The flux profiles during compaction of all the membranes are shown in Fig. 5.8

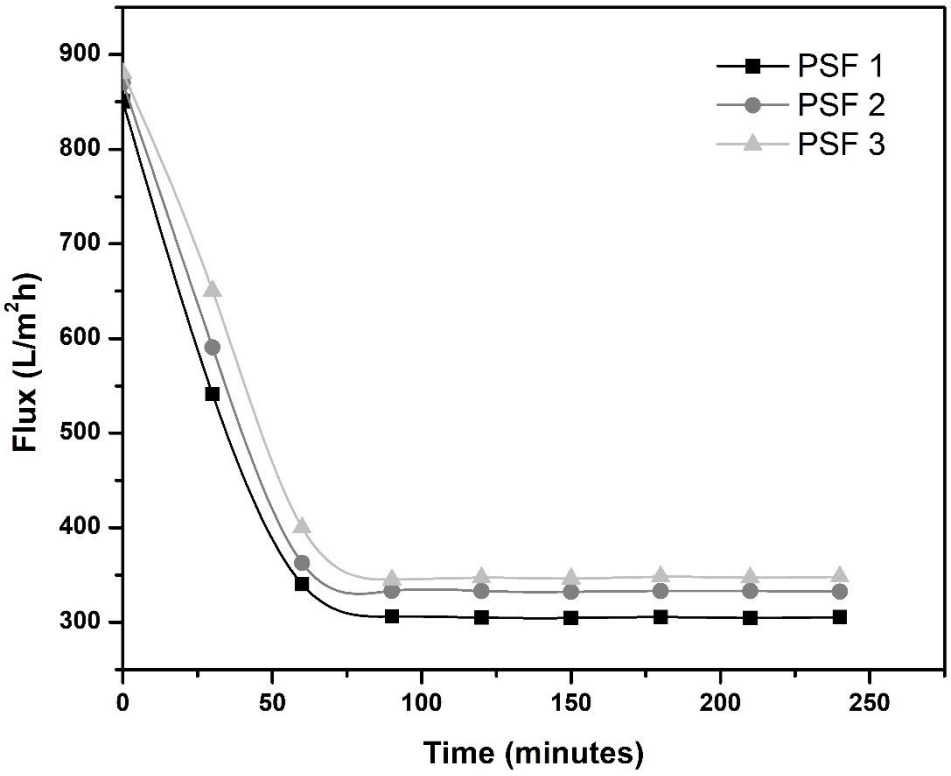


Fig. 5.8 Flux profile during compaction

- We can see the PWF is very high at the start and decreases sharply until it reaches a steady state after almost 70-80 minutes.

Table 5.5 Compaction profile time vs flux data

TIME		FLUX (l/m^2-h)		
In seconds				
		PSF1	PSF2	PSF3

0		850.465	870.4653	880.4567
30		541.1256	590.4526	650.4775
60		340.146236	362.6264	400.1446
90		316.16565	333.1646	345.1643
120		314.88366	332.906	342.1221
150		314.5911	332.1055	342.1221
180		315.561397	332.906	342.1221
210		314.47516	332.906	344.1546
240		305.591	332.4791	348.1221
CF		2.78301717	2.618105	2.52916

- From the figure 5. It is also found that the steady state flux increases from 305.6 L/m^2h to 348 L/m^2h with the increase in PVP percentage.
- We can also see that the compaction profiles of the three membranes are similar as the descent of flux is similar. It can be concluded that the structure of the sub-layer for all the three membranes made with different weight percentage of PVP are similar with just difference porosity and pore size.
- Due to increase in number of pores we get the increase flux in case of higher PVP membranes as discussed in section 5.4.1.
- It is seen that the increase in flux from low PVP membrane to medium PVP membrane is from 305.6 L/m^2h to 332.5 L/m^2h, whereas the increment is lesser from medium PVP to high PVP membrane, i.e., from 332.5 L/m^2h to 348 L/m^2h.
- From studies of Boom et al. [22] it can be said that with higher amount of polymer additive in the lean phase, the delay of demixing will become lower giving the two polymer phases (one consists of the membrane forming polymer PSF, solvent DMAc and nonsolvent water and the other consists of the polymeric additive PVP, solvent DMAc and nonsolvent water) lesser time to have diffusional exchange. This decrease in diffusional exchange will decrease the amount of PVP in the polymer mix which will later get demixed in water to create voids or pores. Thus, with increase in PVP percentage the flux increment will be less.

5.4.2.2 Effect of weight percentage of PVP on PWF and hydraulic permeability

The PWF profile is shown in Fig. 5.9 for membranes with different weight percentage of PVP. The experiment was carried out by taking steady state PWF values at different transmembrane pressure from 0 to 240 kPa. It can be seen that

- with increasing transmembrane pressure, the PWF is increasing almost linearly. As effective driving force increased, the water permeation increased.
- The PWF has also increased with increased weight percentage of PVP. This is in agreeance with the findings of compaction study.
- Hydraulic permeability was measured from the slope of the PWF vs transmembrane pressure plot as defined in Equation (11).

The Pressure vs Pure water flux data is given in the following Table 5.5, 5.6, 5.7.

Table 5.6: Values of characterization parameters of prepared membranes

Membrane	**CF**	**P_m**	**EWC (%)**	**Porosity**
PSF 1	2.78	1.33	81.4	1.9
PSF 2	2.61	1.39	83.6	2.42
PSF 3	2.52	1.46	85.2	2.83

- From Table 2, it can be seen that the hydraulic permeability (P_m) increases with increase in weight percentage of PVP added it increases from 1.33 to 1.46 (L/m2h-kPa).
- We can infer from the PWF profile that the membrane with high PVP gives the highest pure water flux and hydraulic permeability.
- The result indicates that with more PVP percentage, number of pores increases which in turn increases the PWF and hydraulic permeability.

Table 5.7 PWF data for Membrane - I

Pressure in psi	Pressure in kPa	Flux in l/m^2h
5	34.4738	65.7018
10	68.9476	105.62614
15	103.4214	148.94081
20	137.8952	185.09084
25	172.369	227.7169
30	206.8428	272.99509
35	241.3166	314.59095

Table 5.8 PWF data for Membrane - II

Pressure in psi	Pressure in kPa	Flux in l/m^2h
5	34.4738	69.61942
10	68.9476	110.66883
15	103.4214	158.03043
20	137.8952	194.6568
25	172.369	244.33736
30	206.8428	288.5761
35	241.3166	332.90601

Pressure in psi	Pressure in kPa	Flux in l/m^2h
5	34.4738	72.47841
10	68.9476	114.01277
15	103.4214	164.59375

Table 5.9 PWF data for Membrane - III

20	137.8952	199.31062
25	172.369	251.63437
30	206.8428	298.75583
35	241.3166	342.12206

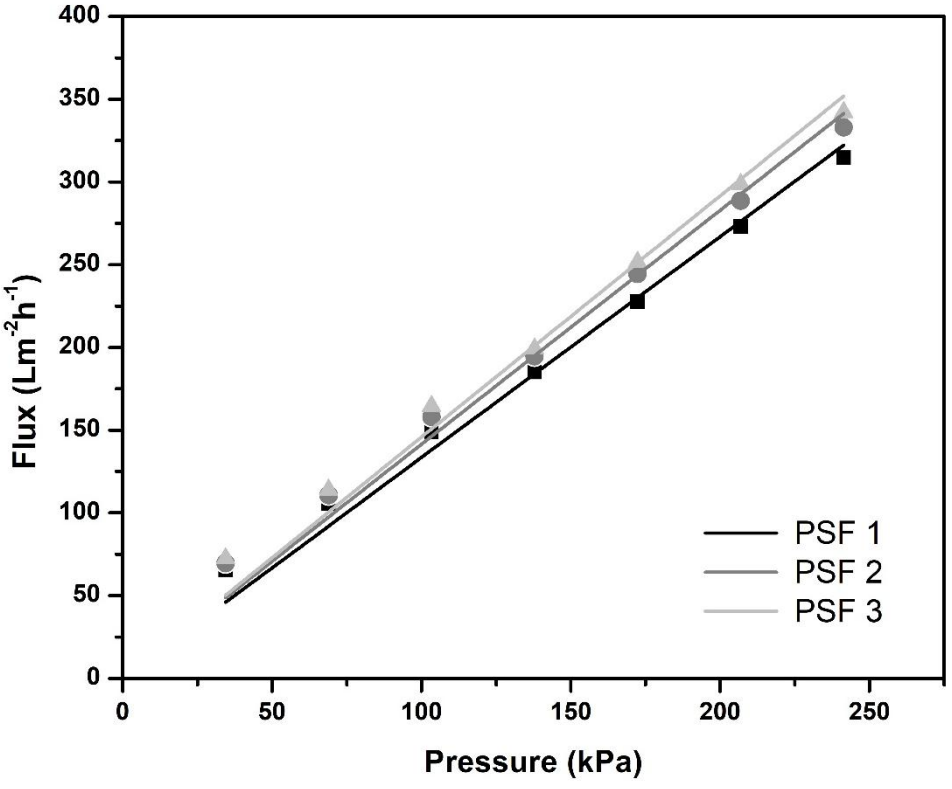


Fig. 5.9 Pure water flux profile of three membranes

In this plot too we can see that the increase in PWF for PSF 2 (medium PVP) to PSF 3 (high PVP) is lesser than the increase from PSF 1 (low PVP) to PSF 2 (medium PVP). This is due to the increase in PVP percentage decreasing the diffusional exchange between two phases as discussed in the previous section.

5.4.2.3 Effect of PVP percentage on equilibrium water content

Equilibrium water content of the prepared membranes was determined using Eq. (12) and shown in Table 5.8. It can be seen from the table that EWC increases with increasing PVP percentage in the membrane matrix. The value of EWC increases as 81.4%, 83.6%, and 85.2% for low, medium and high PVP membranes respectively. The equilibrium water content in a membrane is due to the capillary action of the pores and cavities present in the surface and the sublayer of the membrane. So, the increase in EWC with increasing PVP percentage confirms the increase in the number of pores. The EWC values are in accordance with the increasing PWF values as well proving the increase in number of pores with increasing PVP percentage.

5.4.2.4 Effect of PVP percentage on porosity and hydrophilicity

Porosity and hydrophilicity of the membrane are important parameters in membrane permeation and separation processes and it is closely related to PWF and morphology of the membrane. Porosity of the membranes was measured using Eq. (13). It can be found from Table 5.8 that porosity increases with the increase of PVP percentage. The Porosity PSF-1, PSF-2, PSF-3 is 1.9, 2.42 and 2.83 respectively.

The findings are uniform with the PWF and LLDP results. The variation of porosity can be explained on the basis of thermodynamic and kinetic consideration. Addition of an additive into the casting solution has two effects. Firstly, it causes thermodynamic enhancement of the phase separation by reducing the miscibility of the casting solution with nonsolvent; this results in the instantaneous demixing [6, 50]. Secondly, it causes kinetic hindrance against phase separation by increasing the viscosity of the solution; thus resulting in delayed demixing. When the PVP percentage is higher, more dimixing of PVP from solvant DMAc to non-solvant water occurs. This increases the porosity of the membrane.

Hydrophilicity of the membranes can be said to be increasing with increase in the PVP percentage considering all the above results.

5.5 Conclusion

From the above experiments and subsequent data, discussions, it is clear that the High PVP membrane has lower compaction factor, high porosity, lower molecular weight cut-off, higher pure water flux and higher hydrophilicity due to higher equilibrium water content. Thus, for any wastewater based application, this membrane will be best suited. That's why in further applications or experiments, in cases where the experiment is needed to be performed for only one membrane, the best membrane is chosen for that purpose from the findings of this chapter.

Chapter 6.

Ultrafiltration Experiments & Membrane Cleaning

.

6. Introduction

Ultrafiltration (**UF**) is a variety of membrane filtration in which forces like pressure or concentration gradients lead to a separation through a semipermeable membrane. Suspended solids and solutes of high molecular weight are retained in the so-called retentate, while water and low molecular weight solutes pass through the membrane in the permeate(filtrate). This separation process is used in industry and research for purifying and concentrating macromolecular (10^3 - 10^6 Da) solutions, especially protein solutions. [51] UF is used extensively in the dairy industry; particularly in the processing of cheese whey to obtain whey protein concentrate (WPC) and lactose-rich permeate. In a single stage, a UF process is able to concentrate the whey 10–30 times the feed.

In this section we'll examine the ultrafiltration performance of the prepared membranes. So far, we have investigated the morphological and permeation-based characteristics of the membrane. Now we'll use BSA solution to check the permeate flux, rejection and reproducibility characteristics of the prepared membranes. Because BSA is a small, stable, moderately non-reactive protein, it is used for all the standard ultrafiltration experiments. Another factor we'll investigate is the membrane performance in different pH values, as Polysulfone and protein molecules undergo electrostatic interactions in certain pH values.

Another important aspect we'll discuss in this chapter is the membrane fouling and the cleaning technique that is employed here. PSF blend membranes are susceptible to protein fouling and this has to be dealt with to reuse the membrane.

6.1 Materials

Ultrafiltration experiments were performed in the dead-end filtration module illustrated in the preceding section. Deionized water was used as the main non-solvent in the coagulation bath, it was from Millipore system (Millipore, France). Bovine serum albumin (BSA) with molecular weight of 68,000 Da was supplied by CDH Ltd. India. Varian UV-vis Spectrophotometer was used to analyze BSA concentration in the solution. Sodium hypochlorite and sodium hydroxide was used as a mixture, to clean the BSA fouled membranes.

6.2 Methodology

The experimental methodology for this chapter includes three sections, analytical estimation of BSA concentration, the procedure and theory behind ultrafiltration experiments and the membrane cleaning methodology.

6.2.1 *Analytical estimation of BSA concentration*

There are several ways of estimating the protein concentration such as amino acid analysis following acid hydrolysis of the protein; analyzing the changes in the spectral properties of certain dyes in the presence of proteins; and spectrophotometric estimation of the proteins in near or far UV region. UV spectroscopic quantitation holds good for the pure proteins. If a

protein is pure, UV spectroscopic quantitation is the method of choice because it is easy and less time consuming to perform; furthermore, the protein sample can be recovered back. From literature it can be found that the BSA gives a peak in the UV spectrum at the wavelength of 278 nm. Now the procedure will be first making the standard curve for BSA estimation.

- Prepare a BSA solution of 1000 ppm and dilute it into 1, 10, 100 ppm solutions.
- Deionized water is used as blank here.
- Optical density at each dilution was taken from the UV-vis spectrophotometer taking the peak at the wavelength of 278 nm
- A straight line was drawn through the absorbance values vs the concentrations to get a relationship between those.
- Now, for any solution with an unknown concentration can be fed to the spectrophotometer and according to its absorbance value we can find the concentration of that unknown sample.

6.2.2 *Ultrafiltration experiment*

Ultrafiltration experiments were performed in the dead-end filtration module illustrated in the preceding section. The experiments were done to analyze the permeate flux recovery, solute separation, i.e., rejection behavior of the prepared membranes. The feed solution for permeation experiment was made by dissolving the protein, BSA in deionized water. The concentration was kept constant at 1000 ppm for all of the experiments. The pH of the protein solution determines the kind of interaction between the membrane surface and the protein [52]. The pH of the BSA solution was taken at approximately 4.7 (i.e., isoelectric point), 7 (i.e., neutral condition) and 11.3 (i.e., basic condition). Each membrane was operated at a fixed pressure of 206.843 kPa (30 psi). After a run time of 60 minutes the steady state pure water flux was measured (J_{w1}). After that the module was emptied and the 1000 ppm BSA solution was fed. The steady state permeate flux was recorded after almost 4 hours of operation (J_p). The BSA rejection performance was calculated by the following equation:

$$R\ (\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \qquad (16)$$

Where, C_p and C_f are the concentrations of permeate and the feed in ppm, respectively. After 4 hours of ultrafiltration, the membranes were cleaned using the solution of NaOH and NaOCl. The steady state pure water flux was measured again after the cleaning (J_{w2}). BSA

concentration in the permeate was measured using a UV-vis spectrophotometer at wavelength of 278 nm. The percentage flux recovery was calculated by:

$$Recovery = \left(1 - \frac{J_{w2}}{J_{w1}}\right) \times 100 \quad (17)$$

6.2.3 *Membrane cleaning procedure*

One of the main barriers in application of the UF membrane process for direct water treatment is the effect of irreversible fouling. Membrane fouling is referred to as the decline of flux of a membrane filter caused by the accumulation of certain constituents in the feed water on the surface of the membrane or within the membrane. matrix. According to origin of the foulant, the membrane fouling is sub-divided into (a) inorganic fouling/scaling, (b) organic molecule adsorption (organic fouling), (c) particulate deposition (colloidal fouling), and (d) microbial adhesion and growth (biofouling). [36]. To minimize flux decline due to organic fouling, chemicals are used to break the bonds between the foulants and the membrane surface by either enhancing electrostatic repulsion by a drastic change in the pH values, or by oxidizing the organic compounds into more hydrophilic residuals. The drastic change in the pH is usually achieved with the addition of caustic soda, elevating pH values to 12-13. This causes sufficient deprotonation of carboxylic and phenolic functional groups, thus increasing a negative charge of foulants. For some limited cases such as polysaccharides and proteins, the introduction of NaOH might initiate the hydrolysis by addition of extensive charge on few sites within the macromolecule, resulting in strong electrostatic repulsion between the molecule's patches. Generally, however, to hydrolyze the foulants an introduction of strong oxidants such as free chlorine and hydrogen peroxide is necessary to oxidize the organic compounds with ketones, aldehydes and carboxylic acids as compound residuals. [36]

The reaction of PVP and sodium hypochlorite at pH 11.5 was studied earlier by Roesink et al. [53] Two possible explanations were given for the selective removal of PVP from the membrane:

1. Reaction of PVP with sodium hypochlorite causes chain scission of the polymer. This was confirmed by viscosity measurements. Since the molecular weight of PVP is decreased it can be washed out of the membrane matrix more easily.

2. Reaction of PVP with sodium hypochlorite causes ring opening of the pyrrolidone ring of the PVP molecule. The reaction is considered as an oxidation of PVP in alkaline

solution. According to Roesink [52] the change of the chemical structure of PVP diminishes the interaction of this polymer with base polymer and removal of PVP by washing the membrane is facilitated.

From the above considerations and the literature study discussed in section 2.4, we can conclude that a combination of NaOCl and NaOH may act as a good option for an optimum chemical cleaning agent for our ultrafiltration experiments and further dairy wastewater trials involving protein separation. In this work a mixture of 0.35N NaOCl and 0.2N NaOH has been used as the chemical cleaning agent. The cleaning procedure is:

- After the membrane is fouled after the ultrafiltration experiments, the module was cleaned with Isopropyl alcohol to denature the proteins that may be present in the module.
- After that the fouled membrane is kept submerged in a solution of NaOCl and NaOH overnight.
- The next day that solution is passed through the membrane at 30 psi operating pressure for 1 hour.
- When it is done, deionized water is passed through the membrane for 30 minutes.
- This experiment was done for three combinations of cleaning solutions – 0.1N NaOCl + 0.2N NaOH (C1), 0.35N NaOCl + 0.1N NaOH (C2) and 0.35N NaOCl + 0.2N NaOH (C3)

After the cleaning procedure was completed the membranes were kept drowned in deionized water again and reused. There are reasons to believe that the chemical cleaning washes off PVP from the membrane pores, but that hardly affects the positive effects of PVP on the membrane characteristics, like hydrophilicity of the membrane [54].

6.3 Results and discussion

The ultrafiltration experiment was conducted for three different membranes at three different pH values for each, and the reusability study was done to measure the amount of flux recovery after the chemical cleaning.

After determining the morphological and permeation characteristics of the membranes, the rejection and flux characteristics of three membranes were studied. These characteristics depend on the molecular structure of the membrane and the property of feed

solution. In this work, the rejection and flux during permeation were studied using BSA solution. The reusability of the membranes was investigated by the amount of pure water flux recovery after the first run of BSA permeation. After the first permeation run, the membranes were cleaned using a mixture of NaOH and NaOCl solution.

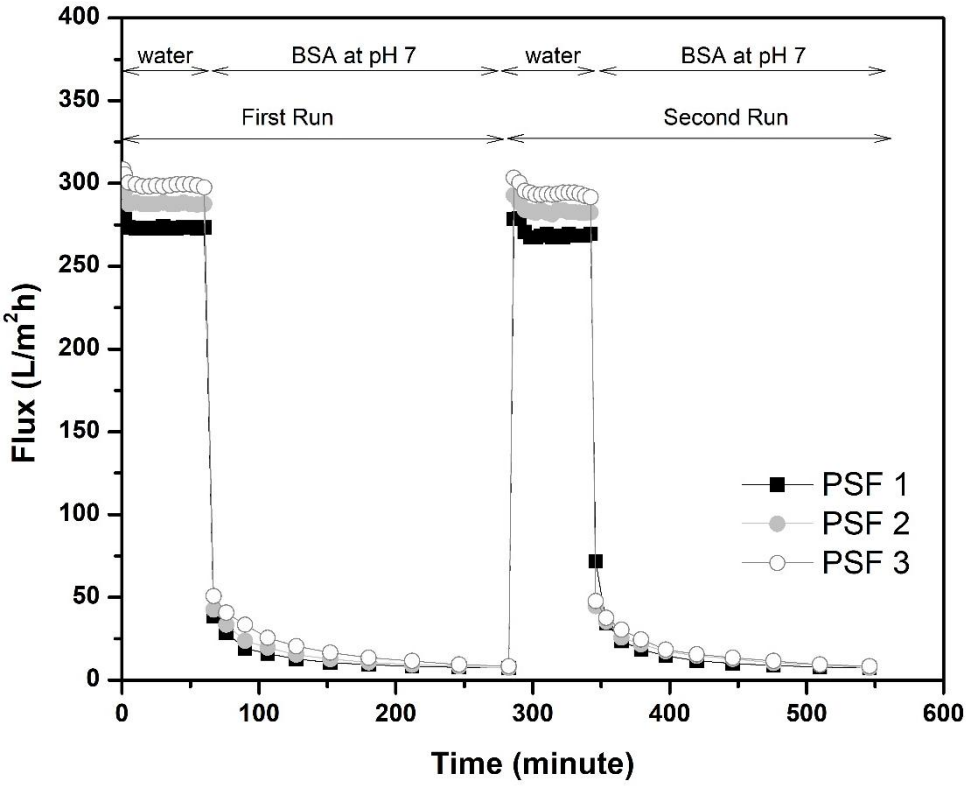


Fig. 6.1 Time dependent flux of membrane during ultrafiltration

It can be seen from Fig. 6.1 that the pure water flux (J_{w1}) before UF of the BSA solution is almost same after the permeation of BSA. From this, we can say that with the chemical cleaning prepared membranes can be reused with a slight difference in permeate flux value. The steady state flux of BSA permeate (J_p) was obtained in the final run of BSA ultrafiltration.

time		Flux (l/m2h)						
minutes		PSF-1		PSF-2		PSF-2		
1		284.0462954		301.04158		308.4166		Pure
2		279.8139201		297.164552		305.4968		

5		273.4653573		292.5616		300.4688	
10		272.9363104		293.45615		299.4568	
15		272.9363104		292.55361		298.1645	
20		272.9363104		292.55361		298.1645	
25		272.9363104		292.55361		298.7865	
30		273.9944042		293.41655		298.1645	
35		272.9363104		292.5652		298.7865	
40		272.9363104		292.55361		299.4568	
45		273.4653573		293.46482		299.4568	
50		273.4653573		292.4556		299.4568	
55		272.9363104		292.16485		298.7558	
60		273.4653573		292.576097		297.6485	
66.88333		38.42955706		42.6635785		50.74539	BSA - 1
76.13333		28.59712985		33.3852597		40.66556	
89.9		19.21477853		23.7195405		33.45587	
106.3833		16.04793435		19.5943297		25.56267	
127.2167		12.69712565		15.3792704		20.46957	
152.2333		10.57388879		12.6971257		16.56565	
180.25		9.447266112		10.7968756		13.54586	
212.0167		8.33582304		9.37472361		11.65644	
246.2		7.738374972		8.27066549		9.464661	
282.45		7.297198652		7.3820498		8.454855	
286.25		278.445738		292.915709		303.4166	Pure Water
290.1167		278.6449494		288.479578		300.4968	
294.1		270.6302438		283.945322		295.4688	
298.1333		267.3373069		283.089295		294.4568	

302.1667		267.3373069		282.334157		293.1645	
306.1833		268.4258434		283.860466		293.1645	
310.1833		269.5234511		282.334157		293.7865	
314.2167		267.3373069		281.411067		293.1645	
318.2333		268.4258434		283.860466		293.7865	
322.2667		267.3373069		283.860466		294.4568	
326.2667		269.5234511		282.660291		294.4568	
330.2833		268.4258434		282.582779		294.4568	
334.3		268.4258434		282.456521		293.7558	
338.3167		268.4258434		282.145553		292.4857	
342.3167		269.5234511		282.485645		291.6566	
346		71.81632157		44.6635785		47.74539	BSA - 2
353.65		34.5782289		35.3852597		37.66556	
364.8667		23.58307142		25.7195405		30.45587	
379.15		18.5197282		21.5943297		24.56267	
397.1334		14.70936707		17.3792704		18.46957	
419.7834		11.67873956		14.6971257		15.56565	
446.1		10.05155609		12.7968756		13.54586	
475.9		8.876625877		10.3747236		11.65644	
509.7		7.826137607		9.27066549		9.464661	
545.95		7.297198652		7.3820498		8.454855	

Table 6.1 above is showing the corresponding data for the reusability graph in Fig. 6.1.

6.3.1 *Reusability of the membranes*

We can infer from the above data and graph that,

- The flux recovery using Equation (17) is found to be over 90% for all of the three membranes. The use of chemical cleaning agent recovers the permeate flux totally.

- We can see, the amount of flux recovery in case of high PVP membrane (PSF 3) is comparatively higher. It is because NaOCl in the cleaning solution reacts with PVP in the membrane matrix causing chain scission and pyrrolidone ring opening as discussed in section 6.2.3.
- In addition to the clearing of pore blockage due to permeation of protein molecules this reaction increases the permeate flux after the cleaning even more. Thus, we can see a 101% recovery in case of high PVP membrane (PSF 3), where this reaction happens more and a 94% recovery in case of low PVP membrane (PSF 1) where this reaction is relatively less.
- However, this reaction doesn't affect the positive influence of PVP (like hydrophilicity) on membrane properties. So, we can say based on the flux recovery, prepared membranes can be reused making the effective life-span of the membranes longer.

6.3.2 *Effect of pH of BSA*

The nature of interaction between BSA molecules and the membrane surface is dependent on the pH of the BSA solution. We can see from Fig. 9 that the permeate flux is highest (12.42 l/m^2h at 35 psi) at basic conditions (pH~11.3) and lowest at isoelectric point of BSA (pH~4.7). The rejection is highest (90.87%) at basic condition and high operating pressure (35kPa). Rejection is lowest (69.98%) at isoelectric condition and low operating pressure (20kPa). From the study of Kuzmenko et al. [36] it is seen that BSA molecules have mild negative charge at around ph~7 and highly negative charge at around pH~11.3. At pH~4.7, i.e., isoelectric condition there is no electrostatic interaction between BSA molecules and the membrane surface. The filtration happens by simple sieving mechanism with gradual fouling of membrane and pore blocking. As the pressure is increased, more fouling creates a denser cake layer which acts as a sieve, providing slightly higher rejection with increase in pressure. At pH~7, there is mild repulsive interaction between the membrane surface and the BSA molecules. This repulsion decreases the pore blocking but due to dead end filtration but the phenomenon of cake layer formation stays the same, providing a sieving layer.

Table 6.2 Rejection and Flux values at diff

pressure (psi)	volm (L)	time (h)	area (m2)	flux (L/M2. Hr)	cf (ppm)	cp (ppm)	R (%)
pH = 4.7 (isoelectric point)							
20	0.005	0.485	0.001134115	9.09015296	1000	300.2	69.98
25	0.005	0.548	0.001134115	8.045117127	1000	236.6	76.34
30	0.005	0.67	0.001134115	6.580185351	1000	214.4	78.56
35	0.005	0.844	0.001134115	5.223606855	1000	204.6	79.54
pH = 11.3							
20	0.005	0.355	0.001134115	12.41894137	1000	91.3	90.87
25	0.005	0.427	0.001134115	10.324881	1000	111.9	88.81
30	0.005	0.545	0.001134115	8.089402175	1000	122.8	87.72
35	0.005	0.588	0.001134115	7.497830247	1000	134.8	86.52
pH = 7							
20	0.005	0.404	0.001134115	10.91268363	1000	189	81.1
25	0.005	0.487	0.001134115	9.052821736	1000	178.8	82.12
30	0.005	0.607	0.001134115	7.263137043	1000	159.7	84.03
35	0.005	0.689	0.001134115	6.398728861	1000	151.4	84.86

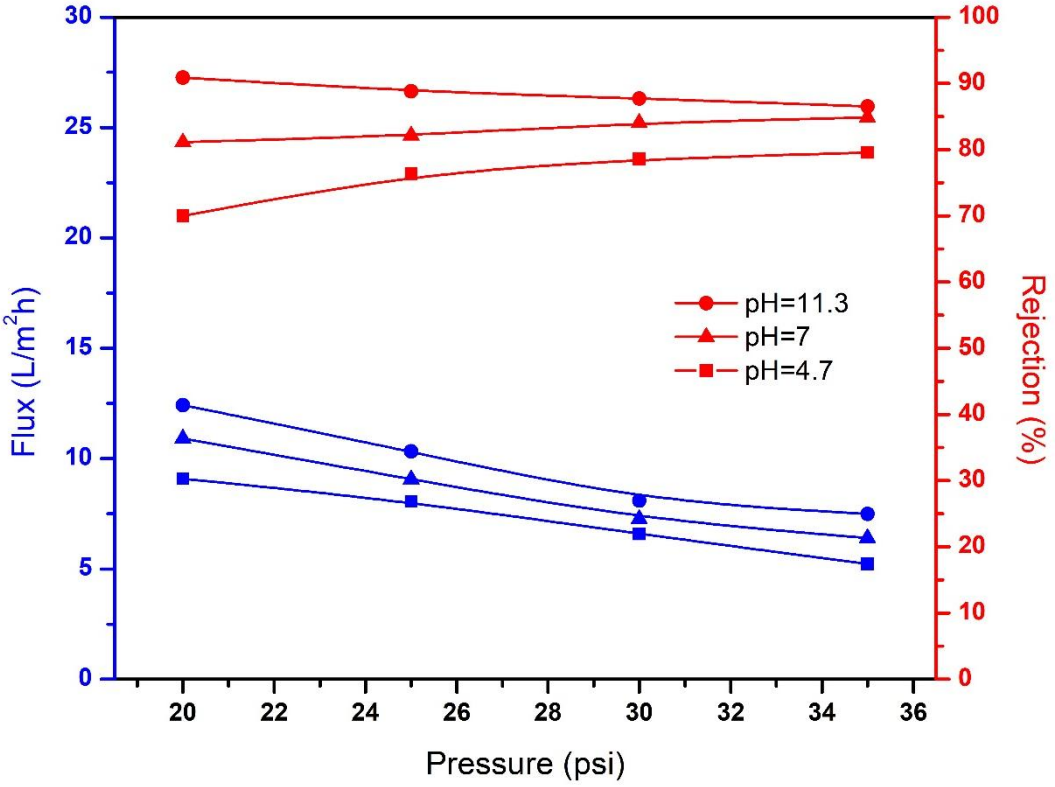


Fig. 6.2 Effect of pH on Rejection and Flux

This repulsive force also stops molecules from passing the membrane, providing higher rejection than isoelectric condition. As the repulsive force is mild, the increase in rejection is less and the trend remains almost linear. At pH~11.3, the repulsive force becomes higher as both the membrane surface and BSA molecules become highly negative charged. This repulsive force provides more resistance to the flow of BSA molecules, increasing the rejection. As pressure increases, more molecules are forced against the repulsive force to flow towards permeate side, decreasing the rejection. For the strong repulsive interaction and less pore blocking, the permeate flux at basic condition is highest. The flux declines with pressure in all cases.

6.3.3 *Membrane Cleaning*

As a result of this above study, it was concluded that of flux recovery greatly depend upon the cleaning procedure used. Effective oxidation with free chlorine resulted in complete restoration of the initial flux but caused a faster fouling than the incomplete removal of the protein followed by the same degree of fouling each consecutive time. /the probable cause of this phenomenon is the alteration in chemistry of the membrane surface other than

hydrophilicity and surface charge. The other possible explanation of the observed phenomena lies in the complexity of the protein molecules. The nature of interactions between BSA in solution and the membrane surface differs from the interactions of the adsorbed protein and the membrane surface. While in the former case the interactions are mainly electrostatic, in the latter case the bonds are probably covalent since the sharp increase in pH values had no effect on protein removal.

Another interesting result is that in case of higher PVP membrane the flux recovery was above 100%. The probable reason behind this is, due to washing of PVP from the pores of the membrane by hypochlorite oxidation, the pores get slightly bigger in the dimension, that's why they can pass more permeate than the virgin membrane.

The cleaning solution we finally used was mixture of 0.35N NaOCl and 0.2N, the results of flux recovery in other combinations are given below:

PWF before cleaning (l/m2h)		**PWF after fouling (l/m2h)**	**PWF After Cleaning (l/m2h)**			**Recovery (%)**		
			C1	C2	C3	C1	C2	C3
PSF 1	272.489	150.438	220.45	245.13	258.36	80.904	89.961	94.812
PSF 2	289.556	173.737	238.43	269.44	286.79	82.344	93.055	99.044
PSF 3	297.648	188.212	242.98	282.46	302.46	81.635	94.9004	101.619

Table 6.3 Flux recovery for different cleaning solutions

From this data we can see that from C1 to C2, the flux recovery increases more than it has from C2 to C3, so we can conclude that hypochlorite is a necessary factor for the cleaning of PSF/PVP membranes fouled by BSA. Now, the increment from C2 to C3 suggests that NaOH is also important for the efficient cleaning of the membrane. Thus, we can arrive to the conclusion that C3 is the best combination chemical cleaning agent.

Chapter 7.

Dairy Wastewater Treatment

7. Introduction

We have prepared three modified membranes, characterized them to find their morphological and permeability-based properties and then the ultrafiltration performance of the membranes. From those findings it can be concluded that the membrane with high PVP percentage perform better and the fouling is less in the neutral to basic pH range. Now, it is needed to use this membrane for a wastewater treatment application. The wastewater we have chosen is dairy wastewater. In section 1.3 we discussed about the dairy wastewater, its components and the targeted solute, i.e., as we can see from Table 1.1, the proteins with molecular weight greater than 14kDa should be rejected by the membrane we prepared. In this work, the standard protein chosen for ultrafiltration experiments is Bovine serum albumin (BSA, 68kDa) and we have seen almost 90% rejection in the ultrafiltration experiment in neutral to basic pH range. But, in case of the dairy wastewater, it contains a mixture of proteins and carbohydrate, that's why we have to measure the decline in total protein concentration and carbohydrate concentration rather than a single protein, which will be complicated to quantify. The point of this experiment is, by measuring the rejection of total protein and carbohydrate, we can examine the performance of the membrane in real conditions.

7.1 Materials

Bradford reagent from Himedia was used for the quantification of the total protein. Phenol, Sulphuric acid was used for assay, Skim milk powder made by Amul was used for making model dairy wastewater. The dead-end filtration module as discussed in previous chapters was used for ultrafiltration purpose. NaOCl and NaOH was used as cleaning agents. 0.1N Hydrochloric acid was used for isoelectric precipitation of the centrifuged model dairy wastewater. Centrifuge was used.

7.2 Methodology

The methodologies used for experiments in this chapter are protein quantification by Bradford protein assay method, total carbohydrate quantification by the Phenol-Sulphuric acid assay method and the ultrafiltration experiment methodology employed.

7.2.1 *Bradford assay method*

For estimating the total protein in a complex protein mixture, one can use dyes that exhibit changes in their spectral properties on binding to the proteins. Bradford is a dye-based assay for protein concentration estimation. The principle behind Bradford assay is the binding of the Coomassie Blue G250 dye (Figure 7.1) to proteins.

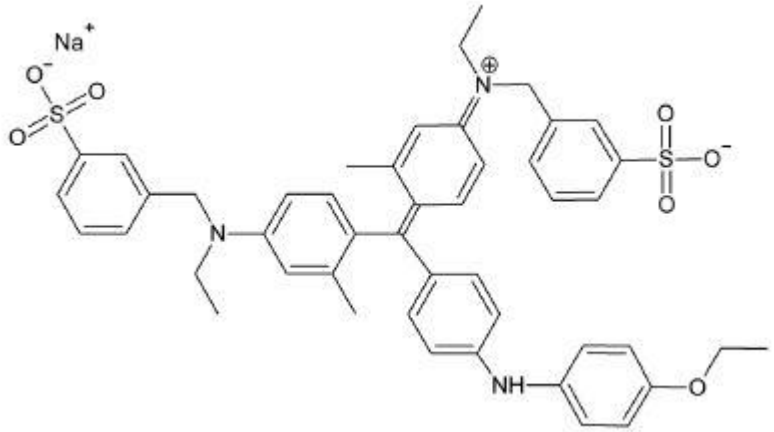


Fig 7.1 Structure of Coomassie Blue G250 dye

Free Coomassie Blue G250 can exist in four different ionization states with pK_{a1}, pK_{a2}, and pK_{a3} of 1.15, 1.82, and 12.4. At pH 0, both the sulfate groups are negatively charged and all three nitrogen are positively charged giving the dye +1 net charge (the red form of the dye). Around pH 1.5, the neutral green form of the dye predominates. At neutral pH, the dye has a net charge of +1 (the blue form of the dye). The red, green, and blue forms of the dye absorb visible radiation with absorption maxima at 470, 650, and 590 nm, respectively. It is the *anionic form* of the dye that binds to the protein. Binding of the blue form of Coomassie Blue G250 with proteins causes red-shift in its absorption spectrum; the absorption maximum shifts from 590 to 620 nm [29]. It, therefore, looks sensible to record the absorption at 620 nm. The absorbance, however, is recorded at 595 nm to avoid any contribution from the green form of the dye. The dye binds more readily to the cationic residues, lysine and arginine. This means that the response of the assay would depend on the amino acid composition of protein, the major drawback of the assay. The original assay developed by Bradford shows such variation between different proteins. Several modifications have been introduced into the assay to overcome this drawback; the modified assays, however, are more susceptible to interference by other chemicals than the original assay. The original Bradford assay, therefore, remains the most convenient and widely used method.

In this experiment, we shall be using the standard Bradford assay which is suitable for measuring the protein amount ranging from 10 – 100 μg, a microassay suitable for the protein ranging from 1 – 10 μg is also briefly discussed. BSA is used here as the protein standard.

Preparation of protein standard: BSA; the standard solution is prepared as follows:

- Weigh accurately 5*mg* BSA.
- Dissolve it in 5 *ml* distilled water; this gives a protein stock solution of 1 *mg/ml* concentration.
- Store the protein standard at –5 °C.

Procedure of standard Bradford assay: For the Bradford micro assay the Bradford Reagent is used undiluted.

- The reagent was mixed gently by inverting the bottle several times.
- To create a calibration-curve the reference protein was diluted as follows: 1, 5, 10, 25, 50, 100 ppm.
- The assay is performed as triplicate determination. The calibration curve should be created new for each series of tests.
- 5 ml of protein reagent was added to the test tubes of dilutions and the contents mixed either by inversion or vortexing
- The mixtures were incubated for 10 to 15 minutes in dark to let the dye bind to the proteins. And then, the absorbance at 595 nm was measured.
- A glass cuvette instead of a quartz one was used for the purpose because the dye binds with silica in it and sticks to it.
- The absorbance was plotted against the concentrations of the corresponding dilutions and the standard curve was drawn.

For microassay, the starting solution was made to be of 100 $\mu g/ml$ concentration. Dilutions were made as usual. 1 ml Bradford reagent was used in each dilution and we follow the same procedure as discussed above. An important point is that the assay standard curve may not be linear it may show a curvature at higher concentration points. The standard curve is nonlinear because of problems introduced by depletion of the amount of free dye [56].

7.2.2 *Phenol-Sulphuric acid assay (Dubois assay) method*

The phenol-sulfuric acid method is a simple and rapid colorimetric method to determine total carbohydrates in a sample. The method detects virtually all classes of carbohydrates, including mono-, di-, oligo-, and polysaccharides. Although the method detects almost all carbohydrates, the absorptivity of the different carbohydrates varies. Thus, unless a sample is known to contain only one carbohydrate, the results must be expressed arbitrarily in terms of one carbohydrate.

In this method, the concentrated sulfuric acid breaks down any polysaccharides, oligosaccharides, and disaccharides to monosaccharides. Pentoses (5-carbon compounds) are then dehydrated to furfural, and hexoses (6-carbon compounds) to hydroxymethyl furfural. These compounds then react with phenol to produce a yellow-gold color. For products that are very high in xylose (a pentose), such as wheat bran or corn bran, xylose should be used to construct the standard curve for the assay, and measure the absorption at 480 nm. For products that are high in hexose sugars, glucose is commonly used to create the standard curve, and the absorption is measured at 490 nm. The color for this reaction is stable for several hours, and the accuracy of the method is within ±2% under proper conditions. [55]

Materials needed: Phenol 5%: Redistilled (reagent grade) phenol (50g) dissolved in water and diluted to one liter. Sulphuric acid 96% reagent grade. Stock – 100mg in 100mL of water. Working standard – 10mL of stock diluted to 100mL with distilled water.

Procedure: the procedure is as follows

- Two milliliters of sugar solution containing carbohydrate is pipetted into a test tube, and 0.05 ml. of 80% phenol is added.
- Then **5** ml. of concentrated sulfuric acid is added rapidly, the stream of acid being directed against the liquid surface rather than against the side of the test tube in order to obtain good mixing.
- The tubes are allowed to stand 10 minutes, then they are shaken and placed for 10 to 20 minutes in a water bath at **25^o** to **30^o** C. before readings are taken.
- The absorbance of the characteristic yellow-orange color is measured at 490 nm.
- Dilutions were made accordingly and the absorbances were measured.
- Absorbance was plotted against the concentration values to get the standard curve.

7.2.3 *Model dairy wastewater (MDW)*

To check the performance of the membrane in real waste water treatment conditions, a solution of model dairy waste water (MDW) was prepared by

- mixing commercial skimmed milk powder in 3 g/l concentration with deionized water [14].
- The prepared MDW was centrifuged at 8500 rpm at 25^{o}c for 10 minutes to remove suspended particles.
- Then the solution was filtered using Whitman filter papers.
- 1 M hydrochloric acid solution was used to adjust the pH of the solution to 4.8, which is the isoelectric point of Casein.
- At pH~4.8, Casein gets precipitated, this is called *Isoelectric precipitation*.
- Then it was again centrifuged at 9000 rpm, 25^{o}c for 10 minutes. The resulting solution was filtered using Whitman papers and Casein was removed.
- The supernatant fluid was used for ultrafiltration experiment at pH~4.8 and pH~7. The proteins present in supernatant fluid is given in the table 1.1.

7.2.4 *Wastewater ultrafiltration*

The PSF-3 membrane was used for ultrafiltration as it was seen to provide highest permeate flux and lowest MWCO.

- The experiment was carried out in the same dead-end filtration module as mentioned before.
- The characterization of total protein percentage in the solution was done by Bradford method. The characterization of total carbohydrate percentage was done by phenol-Sulphuric acid assay.
- The concentration of total protein in the feed solution was found to be 112.5 ppm while lactose concentration was found to be 1400 ppm.
- Ultrafiltration was done by varying the pressure and continuing the process until steady state flux was reached. Rejection was measured at each pressure point using equation (16).

7.3 Results and discussion

Wastewater treatment application yielded almost similar results as that of the ultrafiltration experiments done in the previous chapter in a more standardized circumstance. However, in some aspects the results are different and pose some questions that will be discussed in the following sections.

7.3.1 *Bradford method standard curve*

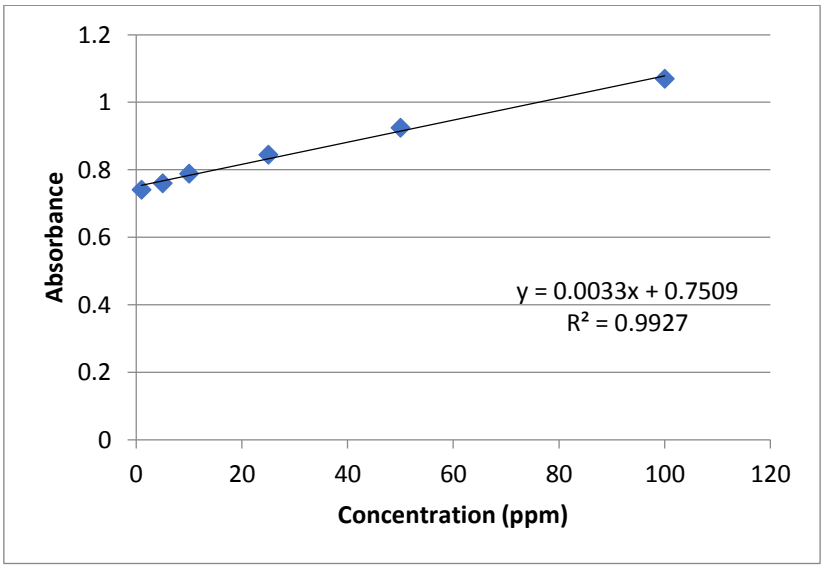


Fig. 7.2 Standard curve for Bradford assay method

This is the standard curve for Bradford assay. In experimental results it has been seen that, it is needed to re-do the standard curve experiment to experiment, because absorbance values change and give rise to a different standard curve in each experiment.

From the equation of the curve, where 'y' denotes the absorbance value corresponding to the concentration, we get the value of 'x', i.e., the concentration of the unknown sample. So, from here we get,

Concentration = (Absorbance – 0.7509) / 0.0033

From this equation we find the concentration of the model dairy wastewater and the permeates in different pressure values.

7.3.2 *Phenol-sulphuric acid assay standard curve*

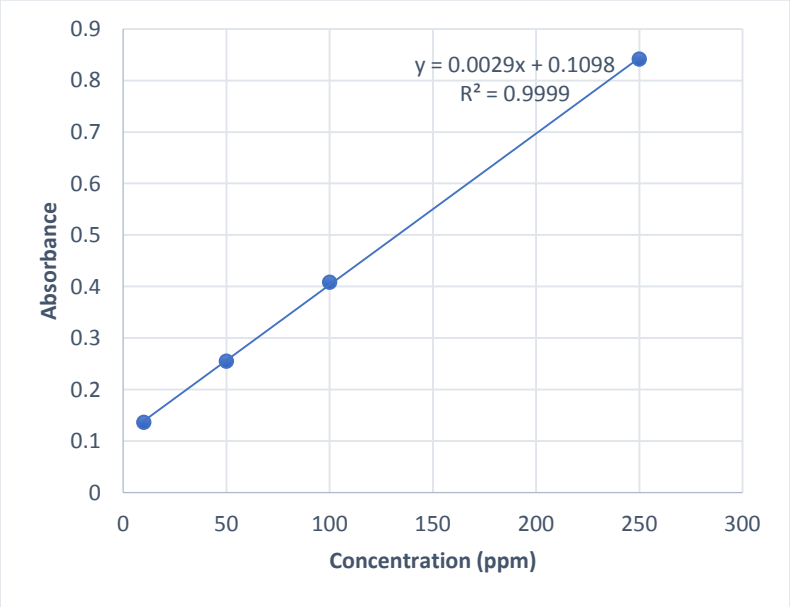


Fig. 7.3 Standard curve for phenol-sulphuric acid assay

From the standard curve we get the relationship between absorbance and concentration (ppm) of a solution containing carbohydrate. Here we get the equation:

Concentration = (Absorbance – 0.1098) / 0.0029

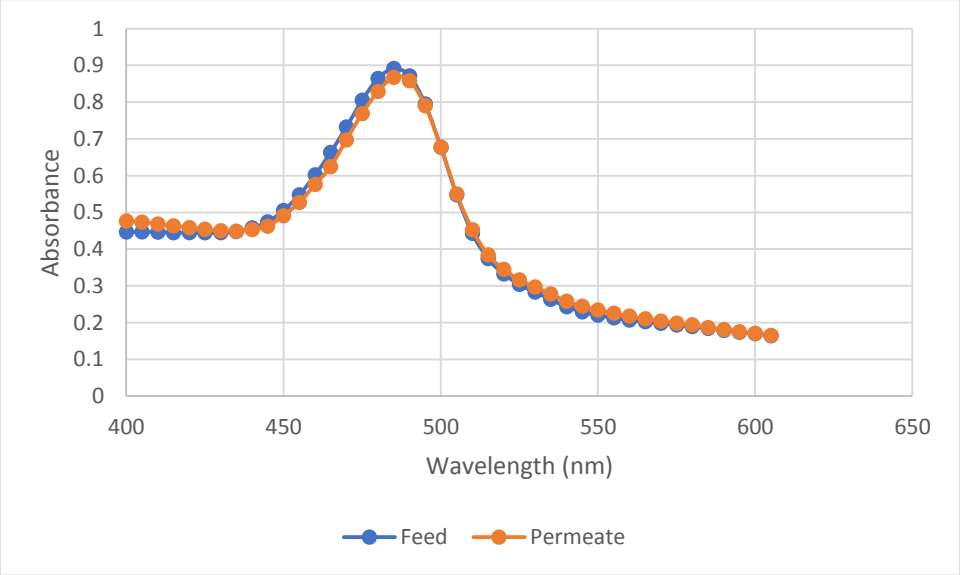


Fig. 7.4 Absorbance peaks for carbohydrate in feed and permeate of MDW

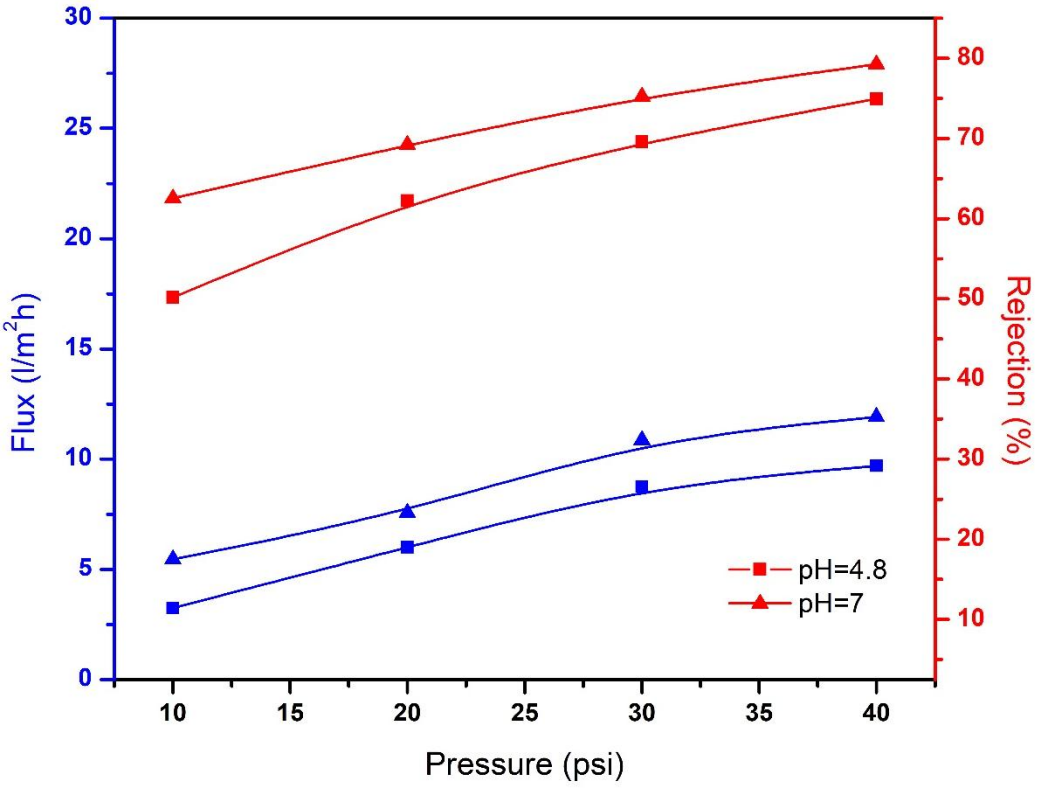
From this above graph we can conclude that there is no significant change in the concentration of carbohydrate after the ultrafiltration operation.

7.3.3 *Wastewater treatment application*

At pH~4.8 (isoelectric point of casein), ultrafiltration of the supernatant MDW fluid gives 74.93% rejection of total protein at 40 psi, at pH~7 the rejection is 79.2%. Here, the permeate flux in both cases increase with increase in operating pressure. The reason for this is low concertation of solute (proteins) in the MDW. From the theory of filtration, we know that Poiseuille's equation states that,

$$\frac{1}{A}\frac{dV}{dt} = \frac{\Delta P}{\mu\,(R_m + R_c)} \quad (18)$$

Here left-hand side denotes the flux, R_m is the membrane resistance, R_c is the cake resistance,



μ is the viscosity of the feed, ΔP is the transmembrane pressure

Fig. 7.5 Pressure vs Flux and Protein rejection of MDW ultrafiltration

Now, the increment or decrement of the flux depends on the ratio $\frac{\Delta P}{(R_m+R_c)}$. If the increase in pressure is less than the increase in cake resistance, the flux decreases with time, but if the opposite happens, then the flux increases. In the previous experiments, where the feed was 1000 ppm BSA solution, we see a downwards trend, but in this experiment, where the feed concentration is 112.5 ppm, it is safe to infer that, the cake resistance build-up is much smaller that it was in case of the 1000 ppm solution.

feed	**112.475**		**R (%)**		**flux (l/m2.h)**	
10 psi	56.03425		50.18071		3.24921	pH~4.8
20 psi	42.46475		62.24517		6.00061	
30 psi	34.19725		69.59569		8.7458	
40 psi	28.195		74.93221		9.69713	
feed	**112.475**					
10 psi	42.13201		62.541		5.45558	pH~7
20 psi	34.62712		69.2135		7.5615	
30 psi	27.87991		75.21235		10.86115	
40 psi	23.33366		79.25436		11.9097	

Table 7.1 Flux and protein rejection values for MDW ultrafiltration

That's why we see an increasing trend in the flux. Also, due to low concentration of the feed, it creates less fouling and thus we accordingly get less rejection than the previous case, due to the absence of a sieving layer created by retained protein molecules. We get a steady state flux of 9.7 l/m^{2}h at 40 psi with pH~4.8 solution and a steady state flux of 11.91 l/m^{2}h at 40 psi with pH~7 solution. The rejection is more in case of pH~7 solution, which is in accordance with our previous results with BSA solution.

The lactose concentration remains almost unchanged with ultrafiltration. The reason for this is the low size of lactose molecules, i.e., 5000Da, which cannot be stopped by the current membrane having a molecular weight cut-off of 14463Da. We'll need nanofiltration membrane to separate lactose from the solution.

Chapter 8.

Conclusion

8. Conclusion

The present work was about manufacturing a modified membrane to be used in a wastewater treatment application. Polysulfone was chosen to be the base polymer for the membrane and polyvinyl pyrrolidone (PVP) was used as the additive, pore forming agent in low to high weight percentage to modify the membrane. Several characterization methods have been taken up to investigate the morphological and permeation-based characteristics of the prepared membranes. The FESEM photographs dictate that all the membranes have asymmetric structure. After, examining all the results, it can be concluded that the use of PVP as an additive increases the hydrophilic nature of PSF membranes and the hydrophilic nature increases with the increasing weight percentage of PVP, but it was also noticed that the rise in hydrophilic properties like PWF, EWC, porosity are less when the PVP weight percentage is getting higher, that tells us, we shouldn't use any higher amount of PVP to modify the membrane; primarily because using more PVP is not yielding much favorable improvement.

The ultrafiltration experiments confirm the rejection properties of the membrane, which reaffirms the molecular weight cut-off we estimated using the empirical equations. We can see that the membrane performs protein separation better in a neutral to basic pH range. The membranes respond well to the chemical cleaning technique we used and gives favorable results in the reusability test where we can see that the membranes retain their permeate flux after repeated ultrafiltration of 1000 ppm BSA solution. We have also given a possible explanation for the pattern of flux and rejection vs pressure graph. After all these we have chosen a best membrane, which is the high PVP membrane. This was used in the wastewater treatment application.

We chose dairy wastewater for the wastewater treatment application as the membranes performed well in standard protein separation. Model dairy wastewater was prepared based on previous works. Isoelectric precipitation was done to separate heavy protein and the rest was subjected to ultrafiltration where we can see 75-79% rejection at 4.8 to 7 pH range. We didn't conduct the experiment in basic pH because, the results of the experiment were already confirming our probable explanation for flux and rejection vs pressure graph for BSA, so we can expect slightly higher rejection in basic pH range. Also, in treating MDW, after performing isoelectric precipitation, the pH of the feed stays at 4.8, to increase the pH would amount to extra cost and will yield little more rejection. So, it depends on the goal of the specific application.

APPENDIX

APPENDIX I: List of figures

APPENDIX II: List of Tables

APPENDIX III: List of References

[1]. Tilley, E., Ulrich, L., Lüthi, C., Reymond, Ph., Zurbrügg, C. (2014). Compendium of Sanitation Systems and Technologies – (2nd Revised Edition). Swiss Federal Institute of Aquatic Science and Technology (Eawag), Duebendorf, Switzerland. p. 175. ISBN 978-3-906484-57-0

[2]. Iyyanki V. Muralikrishna, Valli Manickam, in Environmental Management, 2017

[3]. https://en.wikipedia.org/wiki/Wastewater

[4]. General Characteristics and Treatment Possibilities of Dairy Wastewater – A Review, Aleksandar Kolev Slavov, Food Technol Biotechnol. 2017 Mar; 55(1): 14–28. doi: 10.17113/ftb.55.01.17.4520, PMCID: PMC5434364

[5]. 4. Magdalena Lech et al. "Dairy wastewater utilization: separation of whey proteins in membrane and chromatographic processes", Desalination and Water Treatment, doi: 10.1080/19443994.2015.1117823

[6]. Marcel Mulder: Basic Principles of Membrane Technology, Kluwer Academic Publishers, Dordrecht, Boston, London, 1991, ISBN 0-7923-0978-2.

[7]. Arthanareeswaran, G.; Mohan, D.; Raajenthiren, M. Preparation, characterization and performance studies of ultrafiltration membranes with polymeric additive. J. Membr. Sci. 2010, 350, 130.

[8]. Ju, H.; McCloskey, B. D.; Sagle, A. C.; Wu, Y.; Kusuma, V. A.; Freeman, B. D. Crosslinked poly(ethylene oxide) fouling resistant coating materials for oil/water separation. J. Membr. Sci. 2008, 307, 260

[9]. Park, J. Y.; Acar, M. H.; Akthakul, A.; Kuhlman, W.; Mayes, A. M. Polysulfone-graf t-poly(ethylene glycol) graft copolymers for surface modification of olysulfone membranes. Biomaterials 2006, 27, 856

[10]. Chakrabarty, B.; Ghoshal, A.; Purkait, M. Effect of molecular weight of PEG on membrane morphology and transport properties. J. Membr. Sci. 2008, 309, 209.

[11]. Y. Mansourpanah, S.S. Madaeni, A. Rahimpour, Z. Kheirollahi, M. Adeli, Changing the performance and morphology of polyethersulfone/polyimide blend nanofiltration membranes using trimethylamine, Desalination 256 (2010) 101-107

[12]. Chakrabarty, B.; Ghoshal, A. K.; Purkait, A. K. Preparation, characterization and performance studies of olysulfone membranes using PVP as an additive. J. Membr. Sci. 2008, 315, 36

[13]. Chakrabarty, B.; Ghoshal, A.; Purkait, M. Effect of molecular weight of PEG on membrane morphology and transport properties. J. Membr. Sci. 2008, 309, 209.

[14]. Chen, Zhiwei, et al. "A Novel Membrane-Based Integrated Process for Fractionation and Reclamation of Dairy Wastewater." Chemical Engineering Journal, vol. 313, 2017, pp. 1061–1070., doi:10.1016/j.cej.2016.10.134

[15]. Silva, A.C., Guimara˜es, P.M.R., Teixeira, J.A., Domingues, L., 2010. Fermentation of deproteinized cheese whey powder solutions to ethanol by engineered Saccharomyces cerevisiae: effect of supplementation with corn steep liquor and repeated-batch operation with biomass recycling by flocculation. J Ind Microbiol Biotechnol (2010) 37:973–982.

[16]. Firman, Leticia & Pagliero, Cecilia & A. Ochoa, Nelio & Marchese, J. (2015). PVDF/PMMA membranes for lemon juice clarification: fouling analysis. Desalination and Water Treatment. 55. 10.1080/19443994.2014.925836.

[17]. B.K.Dutta, Principles of Mass Transfer and Separation Processes.

[18]. Zeki Berk, Chapter 10 - Membrane processes, Food Process Engineering and Technology (Third Edition), Food Science and Technology, 2018, Pages 261-287

[19]. Sinha, M.k., and M.k. Purkait. "Increase in Hydrophilicity of Polysulfone Membrane Using Polyethylene Glycol Methyl Ether." Journal of Membrane Science, vol. 437, 2013, pp. 7–16., doi:10.1016/j.memsci.2013.03.003.

[20]. "Performance Improvement of Polysulfone Ultrafiltration Membrane Using Well-Dispersed Polyaniline–Poly(Vinylpyrrolidone) Nanocomposite as the Additive." *ACS Publications*, pubs.acs.org/doi/abs/10.1021/ie202503p.

[21]. "Development of an Integrally Skinned Ultrafiltration Membrane for Wastewater treatment: Effect of Different Formulations of PSf/NMP/PVP on Flux and Rejection." Desalination, Elsevier, 17 Oct. 2005, www.sciencedirect.com/science/article/pii/S0011916405002894.

[22]. R.M. Boom, I.M. Wienk, Th. Van den Boomgaard, C.A. Smolders, Microstructures in phase inversion membranes. Part 2. The role of a polymeric additive, J. Membr. Sci. 73 (1992) 277–292.

[23]. Chakrabarty, B.; Ghoshal, A. K.; Purkait, A. K. Preparation, characterization and performance studies of polysulfone membranes using PVP as an additive. J. Membr. Sci. 2008, 315, 36.

[24]. Calvo, José Ignacio, et al. "Liquid–Liquid Displacement Porometry to Estimate the Molecular Weight Cut-off of Ultrafiltration Membranes." Desalination, vol. 268, no. 1-3, 2011, pp. 174–181., doi:10.1016/j.desal.2010.10.016.

[25]. "Liquid–Liquid Displacement Porosimetry Applied to Several MF and UF Membranes." Desalination, Elsevier, 24Aug. 2013, www.sciencedirect.com/science/article/pii/S0011916413003664.

[26]. Calvo, José Ignacio, et al. "Porosimetric characterization of polysulfone ultrafiltration membranes by image analysis and liquid–liquid displacement technique" Desalination, Volume 357, 2015, pp. 84-92, doi:10.1016/j.desal.2014.11.012

[27]. J.S. Schultz, R. Valentina, C.Y. Choi, Reflection coefficients of homopore membranes: the effect of molecular size and configuration, J. Gen. Physiol. 73 (1979) 49–60.

[28]. R. van Reis, A. Zydney, Bioprocess membrane technology, J. Membr. Sci. 297 (2007) 16–50.

[29]. Marion M. Bradford, "A Rapid and Sensitive Method for the Quantitation of Microgram Quantities of Protein Utilizing the Principle of Protein-Dye Binding", Volume 72, Issues 1–2, 1976, pp. 248-254, doi:10.1016/0003-2697(76)90527-3

[30]. Enrique Antón et al., "Fitting approach to liquid–liquid displacement Porosimetry based on the log-normal pore size distribution", *J. Membr. Sci.* Volume 470, 2014, pp. 219-228, doi: 10.1016/j.memsci.2014.07.035

[31]. D.B. Mosqueda-Jimenez, R.M. Narbaitz, T. Matsuura, G. Chowdhury, G. Pleizier, J.P. Santerre, Influence of processing conditions on the properties of ultrafiltration membranes, *J. Membr. Sci.* 231 (2004) 209–224

[32]. Masuko, Tatsuya, et al. "Carbohydrate Analysis by a Phenol-Sulfuric Acid Method in Microplate Format." Analytical Biochemistry, U.S. National Library of Medicine, 1 Apr. 2005, www.ncbi.nlm.nih.gov/pubmed/15766712.

[33]. Nora'aini Alia, H. Sofiah, A. Asmadi & A. Endut (2011) Preparation and characterization of a polysulfone ultrafiltration membrane for bovine serum albumin separation: Effect of polymer concentration, *Desalination and Water Treatment*, 32:1-3, 248-255, DOI: 10.5004/dwt.2011.2707

[34]. Wienk, I. M., Meuleman, E. E., Borneman, Z., Boomgaard, T. V., & Smolders, C. A. (1995). Chemical treatment of membranes of a polymer blend: Mechanism of the reaction of hypochlorite with poly(vinyl pyrrolidone). *Journal of Polymer Science Part A: Polymer Chemistry*, *33*(1), 49-54. doi:10.1002/pola.1995.080330105

[35]. M.J. Munoz-Aguado, D.E. Wiley, A.G. Fane "Enzymatic and detergent cleaning of a polysulfone ultrafiltration membrane fouled with BSA and whey" *J. Membr. Sci.* Volume 117, 1996, pp. 177-185, doi:10.1016/0376-7388(96)00066-X

[36]. D. Kuzmenko, E. Arkhangelsky, S. Belfer, V. Freger, V. Gitis "Chemical Cleaning of UF Membranes Fouled by BSA." *Desalination*, vol. 179, no. 1-3, 2005, pp. 323–333.

[37]. Xueye Wanga, Jinxing Mab, Zhiwei Wanga, Haiqin Chena, Mingxian Liuc, Zhichao Wua, "Reinvestigation of membrane cleaning mechanisms using NaOCl: Role of reagent diffusion", *J. Membr. Sci*. Volume 550, 2018, pp. 278-285

[38]. C. Regula, E. Carretier, Y. Wyart, G. Ge´san-Guiziou, A. Vincent, D. Boudot, P. Moulin, "Chemical cleaning/disinfection and ageing of organic UF membranes: A review", *Water research* vol. 56, 2014, pp. 325-365

[39]. María-José Corbatón-Báguena, Silvia Álvarez-Blanco, María-Cinta Vincent-Vela, "Cleaning of ultrafiltration membranes fouled with BSA by meansof saline solutions", *Separation and Purification Technology*, vol. 125, 2014, pp. 1–10

[40]. Yongjun Sun et al., "Experimental Study of Fouling Behavior of Main Substances (BSA, HA, SA) of Dissolved Organic Matter (DOM) in Dead-end Membrane Filtration", *IOP Conf. Series: Materials Science and Engineering* 301 (2018) 012031 doi:10.1088/1757-899X/301/1/012031

[41]. Daniel J. Miller, Sirirat Kasemset, Donald R. Paul, Benny D. Freeman, "Comparison of membrane fouling at constant flux and constant transmembrane pressure conditions", *Journal of Membrane Science*, vol. 454, 2014, pp. 505–515

[42]. Chen, Zhiwei, et al. "A Novel Membrane-Based Integrated Process for Fractionation and Reclamation of Dairy Wastewater." *Chemical Engineering Journal*, vol. 313, 2017, pp. 1061–1070., doi:10.1016/j.cej.2016.10.134.

[43]. Jianquan Luo, Luhui Ding, Benkun Qi, Michel Y. Jaffrin, Yinhua Wana, "A two-stage ultrafiltration and nanofiltration process for recycling dairy wastewater", *Bioresource Technology*, vol. 170, issue 16, 2011, pp. 7437-7442, doi: 10.1016/j.biortech.2011.05.012

[44]. Bechold, H., Schlesinger, M., and Silbereisen, k., *Kolloid Z.*, 55 (1931) 172

[45]. Erbe, F., *Kolloid Z.*, 59 (1932) 195

[46]. Munari, S., Bottino, A., Capanelli, G., and Moretti, P., *Desalination*, 53 (1985) 11

[47]. G. Cappanelli, F.Vigo, S.Munari, Ultrafiltration membrane—characterization technique,J.Membr.Sci.15(1983)289–313

[48]. "Chapter 3 - Preparation and Characterization of Ion-Exchange Membranes", *Membrane Science and Technology*, Volume 9, 2004, Pages 89-146, doi: 10.1016/S0927-5193(04)80034-2

[49]. https://photometrics.net/field-emission-scanning-electron-microscopy-fesem/

[50]. H. Strathmann, K. Kock, P. Amar, R. W. Baker, The formation mechanism of asymmetric membranes, Desalination16(1975)179–203.

[51]. https://en.wikipedia.org/wiki/Ultrafiltration

[52]. D.A. Musale, S.S. Kulkarni, Relative rates of protein transmission through poly (acrylonitrile) based ultrafiltration membranes, J. Membr. Sci. 136 (1997) 13–23

[53]. H. D. W. Roesink, Ph. D. Thesis Twente University, Enschede, 1989

[54]. I. M. Wienk, e. E. B. Meuleman, Z. Borneman, Th. Van den boomgaard and C. A. Smolders, "Chemical Treatment of Membranes of a Polymer Blend: Mechanism of the Reaction of Hypochlorite with Poly(viny1 pyrrolidone)", Journal of Polymer Science: Part A Polymer Chemistry, Vol. 33, 49-54 (1995)

[55]. Nielsen S.S. (2010) Phenol-Sulfuric Acid Method for Total Carbohydrates. In: Nielsen S.S. (eds) Food Analysis Laboratory Manual. Food Science Texts Series. Springer, Boston, MA, DOI: 10.1007/978-1-4419-1463-7_6

[56]. Kruger N.J. (1994) The Bradford Method for Protein Quantitation. In: Walker J.M. (eds) Basic Protein and Peptide Protocols. Methods in Molecular Biology™, vol 32. Humana Press