

Fabrication and Characterization of Ultra Filtration membrane and its application for hard water treatment



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Certificate

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DEDICATION

To my lovely parents, respectable teachers and dearest friends.

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'Behold! In the creation of the skies and the earth and the alternation of night and day there are indeed signs for men of understanding.' [Quran, 2:164]

All praise to Almighty ALLAH for his help and utmost support that He gave to me. I present my kindest gratitude to Dr. Muhammad Mujahid, my supervisor, who guided me through their knowledge during the phase of course work and research work. Their guidance has let me reach the point of success which I was looking for.

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Adnan Alam

Abstract

In modern age membrane technology is prevailing due its efficiency, low cost, energy conservation, ease of operation and quality of results. Organic polymers are preferred to choose as a membrane material, among which Cellulose Acetate is the most commonly and widely used material. In Cellulose acetate (CA) membranes, CA being the matrix material shows changed characteristics if blended with additive like Chitosan (CS). The current study was based upon the investigation of effects made by Chitosan and its concentration on CA membranes. It was derived that variation in concentration of Chitosan (CS) is the key to control porosity in CA membranes. Six Cellulose acetate (CA) membrane were synthesized by varying CS in each membrane and relative characteristics such as porosity and pore size were investigated. Formic acid was used as a solvent and Chitosan as a pore forming agent in membrane fabrication. Flat sheet Membranes were synthesized with phase inversion method. These membranes were characterized with SEM, AFM, XRD, FT-IR, tensile behavior, absorbed water content and pure water permeation flux. Membrane was also tested for treatment of hardness in tape water. Hard water treatment results were used for the evaluation of fabricated membranes.

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CHAPTER 01

INTRODUCTION

1.1 Historic Development

The membrane history can be traced down way back into the ancient times, where desalination of sea water was in practice. The records of history explain that some of the ancient nations like Persians, Romans and Latin have made development in treating sea water.

A well-known Greek philosopher, Hippocrates observed that “vapor produced from seawater when condensed is no longer salty” and taught his students the concept of desalting. To make desalination easier and simpler, the scientific word moved to explore membrane technology [1].

The first recorded history of membrane phenomena was the middle of eighteen century, where membrane was used and process of osmosis was discovered. In the same decade the separation of ethanol from pig’s bladder was done using semi impermeable membrane. Hence a relation between semi permeable membrane and osmotic pressure was developed [2].

During the 2nd World War the fabrication as well as application of membranes technology progressed more significantly. Many cities in of the war participating countries were being smashed by the aerial attacks, but at the same time variety of membranes were developed and synthesized for water treatment and bacteriological removal study. In the same time United States of America, Russia, France and England developed a ceramic membranes, the purpose of this membrane was to enrich Uranium, so that uranium can be used for war related activities because uranium is a radioisotope. Since the working and separation for isotopic Uranium enrichment is very underprivileged, the membrane area used was about millions of square meters [3].

After 2nd world war, membrane technology was rapidly developed and was used in variety of disciplines of life. Owing to the ease of use, low energy cost, good

efficiency and reliability of results, membrane technology is preferred nowadays over the conventional separation methods because conventional methods involve more cost, energy, cost [4].

1.2 Membranes in Modern Age

Membranes gain an important and significant place in chemical technology for separation and purification, and are used in broad spectrum of applications. The key property of membrane that is to controls the permeation rate of physical and chemical species through it.

Membrane can be used for controlled drug delivery; the basic goal is to control the permeation rate of drug from a source to the body. For separation applications the membrane should behave such that, it permit the solvent to move through the membrane while stopping the solute particles from passing through [5].

The membrane science and technology is going to be an expanding field. It had become a prominent and essential part of various activities and industrial processes [6].

Membranes technology is emerging as an important place in chemical industry especially in biotechnology, where it has been used extensively used in many of applications such as purification, pharmaceutical, and hemodialysis [7].

1.3 Membrane Technology

The term membrane comes from a Latin word “membrane” which means a skin. But nowadays the word “membrane” is extended to define and describe a thin flexible layer or film, which acts as a selective medium between two phases; this is because of the semi permeable properties. It acts as a filtering or separation agent who is very selective due to the difference of permeation and diffusivity coefficient, or solubility and electric current [8].

In reality the membrane has become an essential part of our lives. All animal and plant cells composing living organisms are surrounded with membrane. All biological membranes like cell membranes are very choosy that transfer only specific particular species [9].

For definition purpose, membrane can be termed as semi permeable layers, across which a mixture of solvent with solute is forced through applied pressure, and thus the particle and solute are retained by membrane layer. The aim of membrane use is not only the particle removal but also to eliminate bacteria, organic matter and microorganisms as well. Water quality can be increased by the removal of bacteria, microorganisms and organic colloidal through membrane treatment [10].

Membrane technology uses membrane as a micro and nano scale sieve. So working of membrane can be consider as a filter which allows the solvent or water to flow through it and rejects the follow of macro particles relative to membrane pore size. During the flow it catches small particles and other contaminants. Membrane performance is increased by pressure difference, which is either applied pressure of inert gas or vacuum. Membrane filtration is as an alternative to sediment purification techniques, flocculation, adsorption, distillation and extraction [11].

1.4 Classification of Membrane Filtration

There exist some levels for filtration through membranes. Each level has different characteristics such as separation mechanisms, physical morphology, pore size, flux rate, applied pressure and chemical nature. In general, there are four main types of membrane for filtration. These are microfiltration membrane, ultra filtration membrane, nano filtration membrane & reverse osmosis membrane.

Depending upon the pore size, membrane processes are typically classified by their rejection abilities. Thus membrane processes are classified into following types. The working and relative pore sizes given below in the diagram [12].

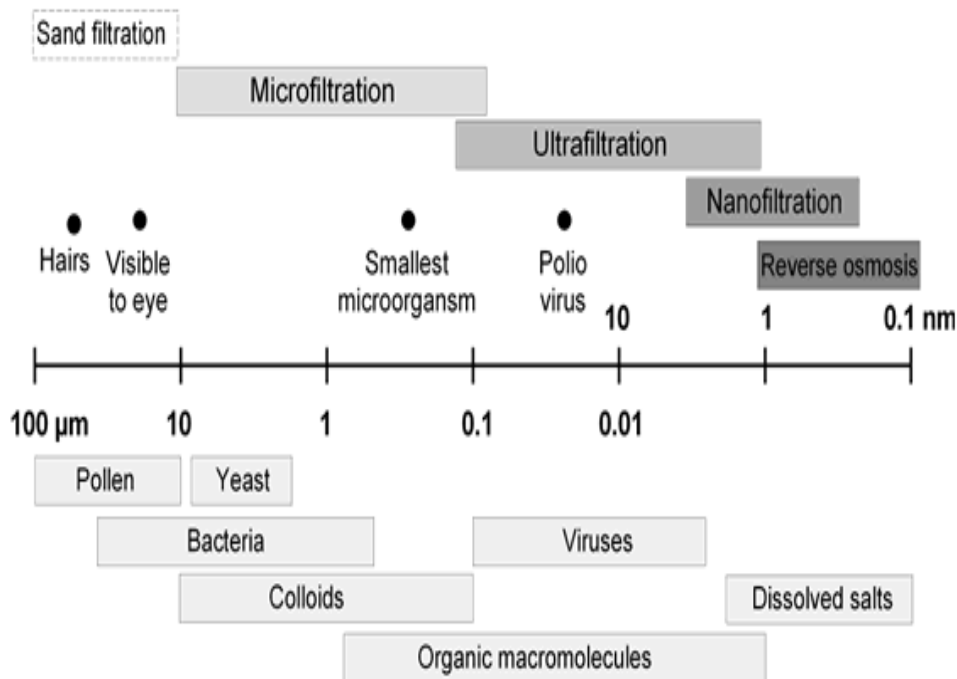


Figure 1: Application of membrane technology relative to the size of contaminants

1.4.1 Micro Filtration

In Micro filtration the membrane used has pore size ranging from 10 to 0.1 micrometer. The particles separated in micro filtration also ranges from 10 to 0.1 micrometer in size. Micro filtration membranes usually operate at low operating pressure. The reason for low operating pressure is the relatively large pore size in these membranes.

The applied pressure ranges approximately between 100 to 300 kPa or 15 to 50psi. We can remove materials such as gravel, clay, silts, and Cryptosporidium particles, small stones, organic colloidal, plant matter and some of the bacteria as well. These membranes are not affective for virus. However using micro filtration membranes in collaboration with anti bacterial agents, the viruses in water is effectively eliminated [13].

It is found that the use of chemicals for water treatment, such as chlorination of water is quite risky and UN hygienic. Chemicals are used to kill micro organisms in water body, but harms and side effects of these used chemicals pose a great threat. Using

micro filtration membranes, organisms, pathogens and other harmful organisms can be eliminated without giving any side effect.

Micro filtration is also used as pre filtration technique for Ultra and nano filtration. Pre filtered solvent will cause less fouling in ultra and nano filtration. Even pretreatment of solvents is done for reverse osmosis. RO and NF are mainly used for desalination of sea water, thus the use of MF is done as a pretreatment filtration. Doing this efficiency and performance of RO and NF is increased [14].

1.4.2 Ultra Filtration

An Ultra filter is defined as a filter whose pores are of colloidal molecular dimensions. Filtration through such filter, ordinarily with the aim of complete or partial removal of the colloidal or molecular particles present in the solvent system filtered, is termed as ultra-filtration.

The pore size of Ultra filtration membrane ranges approximately 0.1 to 0.01 micrometer. In terms of applied pressure, Ultra filtration membrane requires more Tran's membrane pressure as compared to MF, because the pore size in UF is smaller as compared to MF. The applied Trans membrane pressure in UF is about 100 to 600 kPa or 25 to 90 psi. Ultra filtration is efficient filtration technique than MF. It will remove virus as well as all the biological organisms from the feed. If Ultra filtration is coupled with disinfectants, it becomes an absolute barrier for viruses. Therefore it is recommended to use Ultra filtration along with disinfectant, if water quality has to be increased [15].

Following are some of the advantages which UF possess over conventional methods of isolation and purifications,

1. Use of chemicals is prevented
2. Quality of treated water is improved up to a constant standard.
3. Easy to use due to simple assembly
4. Energy conservation and environmental friendly
5. Better results compared with the results of conventional methods

Beside all these advantages, Fouling happens to be the biggest disadvantage of membrane filtration [16].

1.4.3 Nano Filtration

The pore size in Nano filtration membrane is even smaller as compared to UF and MF. The pore size ranges approximately, 1 to 10 nano meter. Due extremely small pore size, NF requires high operating pressure across the membrane. The operating pressure in NF is nearly 600 kpa to 1,000 kpa or 90 to 100 psi. The significance of NF is that it virtually removes all the organic and inorganic particles, which includes bacteria, virus and other biological organisms. Inorganic particles like carbonates, sulfates, nitrates can be removed from feed through NF [17].

Nano filtration membranes are also effective in treatment of alkalinity in the feed solvent. The alkalinity in the feed can be controlled through NF membrane. On the other hand, this filtration is quite effective to control water hardness. Since water hardness is caused by carbonates, NF membranes can remove significant concentration of carbonates from water. Therefore, NF membranes are sometimes referred as “softening membranes”. To get good results, the hard water should be pretreated; this will enhance the life of NF membrane by reducing fouling. In terms of cost and energy, Nano filtration requires more cost and energy [18].

1.4.4 Reverse Osmosis

The Reverse osmosis membranes is non porous, and the solvent molecules pass through RO membrane by diffusion mechanism. RO membrane is semi permeable and selective in nature i.e. it allows the solvent molecules through feed to diffuse but other particulate matter, ions, microorganisms, molecules, hydrocarbons, virus, bacteria etc are retained by the membrane. The spectrum of uses of RO is very broad. It is used to treat and isolate radioactive particles like radium from water. For better efficiency and long lasting life, pretreatment of feed is important before using it for RO membrane. Since no pores available in RO membrane, it operates at a very high pressure; this makes the process more costly [19].

Following are some of the advantages of RO filtration,
RO membrane removes nearly all the dissolved ions and contaminants

It can operate almost without any break in period

It gives very minimum effluent concentration

It actively removes all the virus and bacteria from feed solvent

RO is simple and easy to operate, even less attention from operator is required

It can be used affectively for all system applications

Beside advantages, RO possess short comings as well, which are listed below:

Its operating cost is very high

Almost for every feed, pretreatment is required

Waste water management is a problem

Severe fouling problems are reported with RO [20].

1.5 Materials for Membrane

Usually organic polymers are the base membrane material. Though other forms of polymer material like ceramics, glass or metals are used as membrane material, but organic polymer owing to its cost and efficiency are more widely used. Membrane developed for drinking water quality control is all made from organic polymer. Organic polymers are less expansive and flexible in use as compared to other membrane materials. Therefore organic materials are preferred for membrane fabrication. Organic compound are usually less reactive and are of inert nature most of the time. It is important that membrane material should be inert and non-reactive towards feed and rejected particles, otherwise corrosively in membrane will cause damage to it. Organic polymer material is affective to treat chlorinated water due to inertness of membrane material [21].

The other aspect to consider for membrane is its mechanical strength. Since membranes having more mechanical toughness can survive with more pressure and workable with extreme pressure applied across the membrane. So the strength of membrane allows the process to function with ease.

Membranes having two dimensional strength allow better cleaning and testing, which could be performed either from feed side or filtrate side, across the membrane. Membranes may be embedded with surface charge. This modification will make membrane more workable for the removal of ions or microbial contaminants present

in the feed with the opposite charge. The electrostatic attraction between the oppositely charged ions helps in isolation of undesired components.

It is important to note whether a membrane is hydrophilic in nature or hydrophobic in nature. Because the attracting or repelling nature of membranes defines how well it absorbs or desorbs the water, thus the fouling potential of a membrane can be described. Knowledge of hydrophilic or hydrophobic character of a membrane helps to design for fouling control [22].

The precursors used for Micro filtration and Ultra filtration membranes are of wide range and variety. Some of them are given below,

- Poly vinylidene fluoride
- Poly acrylonitrile
- Poly propylene
- Poly sulfone
- Poly ethersulfone
- Cellulose acetate

These materials are different in properties like surface charge, strength and flexibility, degree of hydrophobicity, oxidant tolerance and pH [23].

Cellulose Acetate and Polyamide are the common precursors for the fabrication of Nano filtration and Reverse Osmosis membranes.

Generally Cellulose membrane has a biodegradable nature, so the operating conditions must be moderate. In severe acidic or strongly alkaline conditions the material may be damaged. The operating pH conditions should range from 4 to 8.

Small amount of Chlorine is useful to control biodegrading of membrane material and also the biological fouling is controlled without giving any damage to the membrane. On the other hand, Polyamide is more flexible material contrary to Cellulose acetate, because wide range of pH conditions can be used for Polyamide, though it shows less resistance for strong oxidizing agents but works well with weak oxidizing agents. Polyamide membranes require less operating pressure so their use makes the process cost effective [24].

1.6 Modules for Membranes

There are different kinds of membrane module, manufactured according to the desired results and available facilities. Following are the few important modules,

- a. Hollow fibers module
- b. Spiral wound module
- c. Flat sheet module

Module construction involves sealing and potting the materials into an assembly. Modules are designed in order to make fabrication for long standing, ease of operation and use in multiple laboratories.

For long lasting use usually the spiral wound modules are preferred, though the spiral wound modules are together with an independent chamber for pressure which is isolated from the module as well, and works separately[25].

The details of each module is given as under,

1.6.1 Hollow Fiber Module

Most of the Micro filtration and Ultra filtration membranes are made in hollow fiber modules. Such modules are applied for quality control of drinking water applications, and micro level particles can be filtered effectively. These modules comprise of are thin and elongated tubes which are fabricated by any suitable organic material. The module is constructed by bundling up the fibers in different symmetries.

The bundling arrangements of fibers could be longitudinal or sealed with resin in a pot from both ends or could be enclosed in pressure chamber. The modules may have different mounting arrangements i.e. mounted vertically or horizontally. Another way of constructing module is to bundle up hollow fibers into a basin where pressure chamber is not required.

Usually more than ten thousand fibers comprise a hollow fiber module. The size and proportions of hollow fibers is dependent on manufacturer and requirement, however the average requirements are given as under,

- a. Outer span about 0.4 to 2.0 mm
- b. Inner span about 0.2 to 1.0 mm
- c. Fiber wall thickness about 0.2 to 0.6 mm
- d. Length of fiber about 1 to 2 meters

1.6.2 Spiral-Wound Modules

Spiral wound modules are mostly used in Nano filtration or Reverse Osmosis filtration applications. These modules were developed to remove molecular scale dissolved solids.

The main unit in the module is pack in of many flat sheet membranes. This unit typically termed as a “leaf”. This unit is wrapped about a pivotal perforated tube. Each leaf is mainly consisting of two flat membrane sheets; these sheets are gapped by a spacer. This spacer is actually a permeate carrier. The working mechanism of spiral wound membrane is that feed solvent is made to enter in the spacer, between two membrane layers. Feed solvent while flowing through the spacer, also permeates through the surrounding membrane layers as well as through permeate carrier. Thus the dissolved components in the solvent and particulate matter are rejected as a waste, while solvent moves out through the membrane layers [27].

1.6.3 Flat Sheet Module

The design of a flat sheet module is analogous to that of a thin flat sheet or a plate. The filtration assembly for a flat sheet membrane usually consists of a deep cup, with rectangular or circular sides. The flat sheet membranes can be fixed or supported to one or both sides of this cup in the flow unit. In the flow unit the membrane is usually supported on perforated plates, this arrangement allows the permeate collection easy and quick.

For filtration, the solvent is forced into the membrane containing unit using inert gas pressure and is collected from the other end of membrane as permeate. In many cases, the membrane modules are made such that the basic flat sheet membrane units assemble in a series connection and thus it forms a cassette.

A commercial scale module usually comprises several cassettes. Thus large quantity of feed can be treated in a single operating time using several cassettes. Main advantages of such modules are that they are easy and simple to use. Moreover, they are easy to clean and ease of replacement and removal of defective membranes. These modules can be effective in handling thick, sticky feeds and the high concentration feeds.

One of the main disadvantages of this module is the low filler density, which means these membranes have low ratio of membrane area to module volume. The flat sheet modules are usually used for Ultra filtration, Micro filtration and Nano filtration [28].

1.7 Modes of Operation

Following operating modes can be used for membrane filtration,

- a. Dead End operating mode
- b. Cross Flow operating mode

Dead end operating mode is the simplest mode of operation in which feed is allowed to pass through membrane perpendicularly. When feed solvent come in contact with membrane's surface area, a pile up of particles start developing. This pile up leads to fouling on membrane surface. So in this operating mode, membrane needs to be cleaned frequently otherwise there would be a significant loss of performance.

For the filtration at industrial scale, the cross flow operating mode is often used; the reason behind this operating mode is that it produces less fouling, while extreme fouling is observed in dead end operating mode. In cross flow operating mode the feed is allowed to move parallel to the surface of membrane. As long as feed move through the membrane, the composition of particles in the feed changes and two streams are created i.e. permeate stream and a retentate stream [29].

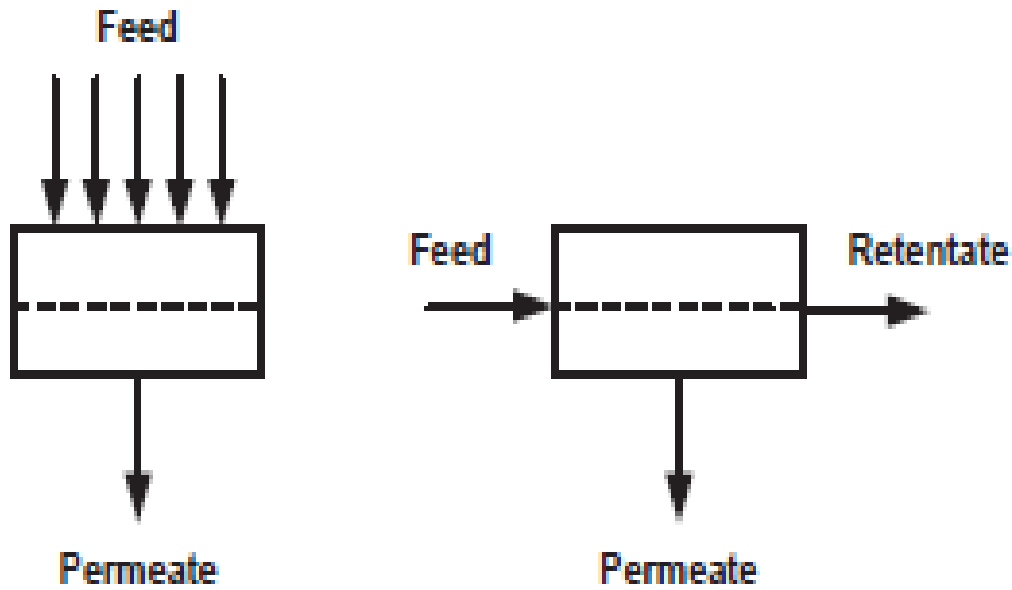


Figure 2: Left: Dead End operating mode Right: Cross Flow operating mode

1.8 Membrane Fouling

Membrane fouling can be explained as a process in which dissolved and solid matter or solute particles accumulates on membrane surface and fill into the membrane pores. This accumulation will result into the decrease efficiency of membrane and limits its wide spread use. As discussed, fouling results in the significant flux decrease and ultimately increases the significant operating costs. There could be several other factors responsible for flux decline in membrane processes like, concentration polarization, surface accumulation with solid, gel layer formation and blocking of orifices.

Membrane fouling can be divided into following types, based upon the strength of contaminants to attach to the membrane surface.

- a. Back washable
- b. Non Back washable
- c. Reversible fouling
- d. Irreversible fouling

Back washable fouling can easily be removed by only reversing the flow of permeates direction across the pore of membrane at the end of each filtration cycle. On the other hand, non-back washable fouling is not removed by reversing the flow direction of permeates between each filtration cycles. However, non-back washable fouling can be treated by chemical cleaning [30].

Irreversible fouling, On the other hand, cannot be removed by chemical cleaning, flushing, backwashing, or any other means, and the original flux of the membrane cannot be restored.

In reversible fouling, membrane original flux can be regained by any suitable physical or chemical cleaning methods. Fouling can be reduced by use of some regular methods like pretreatment, forward washing, cyclic back washing, chemical and physical cleaning, surface modification, ultrasonic etc.

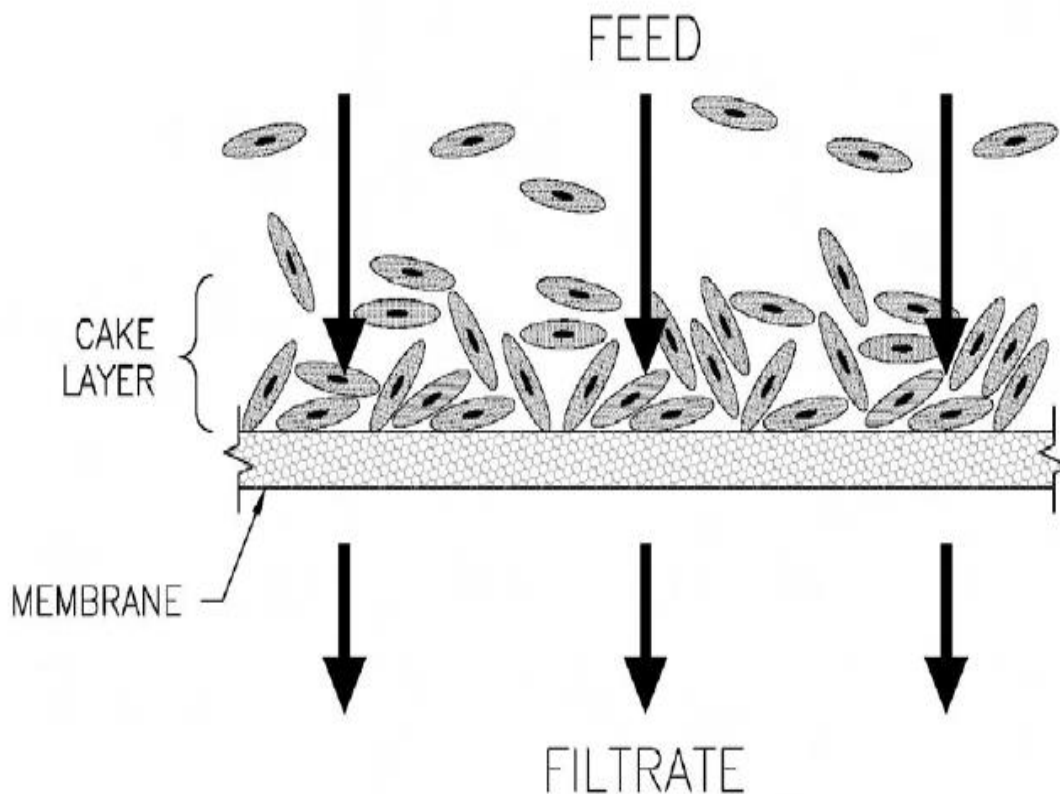


Figure 3: Fouling due to particles in feed

1.9 Applications of Membrane Technology

The study of membrane filtration nowadays is the main concern and interest in the field of purification and isolation. Moreover the area of application for membrane is expanding rapidly day by day. As membrane separations and purification involves moderate conditions, so the use of membrane technology in different fields like pharmaceutical industry, food industry, and biotechnology and water treatment is rising very rapidly. On the other hand, the possibility of membrane to make isolation at low cost and energy makes the membrane filtration superior over traditional separation techniques [30].

1.10 Applications of Ultra Filtration

Ultra filtration has wide variety of application in various disciplines of life, some of which are discussed below,

1.10.1 Environmental Applications

UF can be used for electro coat paint recovery

It is an effective technique for waste water treatment

Oily waste water and oil water emulsions can be treated with UF membranes

It can be used in pulp and paper industry for printing ink recovery

Effluents from leather and tanning industry can be treated using UF membranes [31]

1.10.2 Food Industry

UF can be effectively used in:

- a. Dairy industry for cheese and protein recovery
- b. For sugar refining
- c. For concentration of fruit juices and for the clarification of juices and beverages
- d. For the protein concentration in vegetables
- e. For the egg white concentration [30]

1.10.3 Biotechnological Applications

UF can be used for the harvesting of enzymes and for the separation of microorganisms and enzymes

It can be used for bioreactor and for tissue culture system. Ultra-pure water can be prepared with UF membranes, which find applications in pharmaceutical, electronic and biotechnological industry

It can be used for the separation of micro solutes from blood; such process is called as Hem filtration [31]

1.10.4 Polymer Industry

UF can be used for concentration of latex emulsion [31]

CHAPTER 02

LITERATURE REVIEW

The origin of systematic studies of membrane technology can be traced to around eighteenth century, where large work were reported and the focused was made on Ultra filtration membrane performance for treatment of wastes. Besides this, some researchers focused the membrane fouling control using various techniques [34].

2.1 Membrane's Efficiency

According to the literature review, some of the work mainly focused on evaluating different parameters which may affect membrane efficiency and performance [37]. Johannes de Bruijn et al. [35] evaluated the performance and efficiency of zirconium oxide membranes with molecular weight 15 kDa to 50 kDa, for clarification of apple juice and it was found that high permeate flux is achieved with high velocity of feed solvent and low trans membrane pressure. The optimum permeation was done at 40 kPa and with the speed of 2 m/s, this was 35% less than what could be expected due to extreme fouling.

Hyeok Choi et al. [36] performed experiments to examine cross flow velocity effects on behavior of micro filtration and ultra-filtration membrane for biological suspension. The results show that there is a linear increase in permeate flux having ascending cross flow velocity of feed & peak cross flow velocity has found to have more effecting decreasing fouling of Micro filtration membrane than Ultra-filtration membrane.

Seungkwan Hong et al. [37] studied the behavior of decrease of permeate flux in cross-flow operating mode for filtration of colloidal suspensions. Analysis results demonstrated that increasing feed particles concentration and trans-membrane pressure gives in faster flux declination. It also showed that the cross flow velocity remains ineffective to the permeate flux at transient stages of the filtration.

2.2 Water Treatment

Membranes are extensively used for treating emulsions of oil water, particularly for application where the recovered materials are highly valuable, like recycling the

aqueous cleaners and coolants [38]. Numerous works can be seen in treating oily water, especially using Ultra filtration and Micro filtration [32-34].

Jing Zhong et al. [33] worked on oil waste-water, obtained through processes of refinery with aid of ceramic membrane filtration and flocculation. They reported that doing flocculation as pretreatment, the fouling of membrane is decreased & consequently increase in permeate flux is achieved. The cross flow velocity was suggested for pilot and industrial application.

B.Chakrabarty et al. [34] used poly sulfone for treatment of oily wastewater by modifying poly sulfone Ultra filtration membranes. They observed that the properties of feed of the oily waste-water have a main character in oil separation as well as the rate of permeate flux.

K. Karakulski and A. Kozlowski [39] made comparison study on the oil purification efficiencies of the Ultra filtration membranes. They made experiments on three tubular Ultra filtration membranes which were made of different materials and found that the three membranes with their characteristic pore size can decrease the oil content up to 10 mg/l and then the permeates is allowed to discharge into the sea.

H. Ohya and J.J. Kim [40] studied that how size of micro filtration membrane pore affects the mechanism of separation for oily water by bringing into use, the tubular glass membrane. They determined the transition of separation from blocking to cake formation. Thus they recommended the importance of adjustment of pore sizes of oil concentrations prior to industrial operation.

Shi-Hee Lee et al. [41] fabricated a ceramic microfiltration membrane. They applied the soluble waste oil on filtration membrane and found the optimum composition of the material to be used for this membrane fabrication. They also investigated the effect of back flushing and cross flow velocity on permeate flux & found that permeate flux increases when back flushing was applied. The permeate flux also found to be increased with cross flow velocity.

2.3 Operating Conditions

Mehrdad Hesampour et al. [42] evaluated operating conditions effects, on Ultra filtration of emulsified oil in water. They found that the most significant effect occurs because of temperature, on permeate flux.

J. M. Benito et al. [43] evaluated operating conditions effects, on permeate flux. They used two organic Ultra filtration membranes having different pore sizes. The maximum flux was obtained at a certain temperature and cross flow velocity.

S. Elmaleh et al. [44] investigated the filtration of organic suspension containing hydrocarbons and bio solids using an inorganic Ultra filtration membrane. They found that the inorganic membrane acts as a complete barrier for hydrocarbons and biological suspended solids.

M. Gryta et al. [45] studied the oily waste-water's treatment using a mix of Ultra filtration and membrane distillation. The study showed that the oil content was reduced to about 15 ppm and the using of membrane distillation in a second stage allowed the removal of oil pollutants completely.

2.4 Membrane Fouling

Fouling happens to be a key complication in vast area applications of membrane. Fouling appears to be caused by particle accumulation on the surface of membrane and concentration polarization. Thus fouling decreases the productivity of membrane and decreases the performance of membrane. Methods like anti fouling membrane development [46], techniques like back wash, forward wash, sonication etc [47-48], physical and chemical cleaning were used for fouling control [49-54].

Heng Liang et al. [49] investigated the effect of chemical & hydraulic cleaning of membrane which has been fouled by using reservoir water rich with algae. The conclusion was made that when back-washings have been followed by forward-washing, it becomes is very effective to recover flux. The chemical cleaning using NaOH and NaOCl increases cleaning impact.

Keith N .Bourgeois et al. [50] observed that using a more aggressive backwash removes rapid fouling of Ultra filtration membrane.

J. Paul Chen et al. [51] developed and applied a statistical factorial design on chemical & physical cleaning of Ultra-filtration membrane in municipal waste-water. It was observed that the physical cleaning of membranes was mainly affected by the intervals among the clean, the durations of back-wash & pressure applied at the time of forward-flush. It has been further discovered that chemical cleaning is affected by aggressive pH and high temperature.

Paul et al. [52] produced a control system for optimizing the backwash. It was observed that a periodic backwash can effectively remove the reversible fouling, thus the new approach developed up to 40% decrease in the needed backwash permeate.

MansoorKazemimoghadam et al. [53] studied the chemical cleaning of the Ultra filtration poly sulfone membrane which was fouled due to milk component's concentration. They concluded that using EDTA, sodium dodecyl sulfate & sodium hydroxide for membrane cleaning.

H. Peng et al. [54] filtered oily wastewater with Micro filtration and Ultra filtration hybrid system and indicated that fouling membranes is because, membrane pores containing oil droplets. Cleaning methods, like air back flushing & hot water heating has been proposed to be more effective in restoring the membrane flux.

Fouling control methods [46-51] like pretreatment, cyclic forward washing, back washing, physical & chemical cleaning, membrane surface's modification and ultrasonic cleaning are either time or capital consuming. Hence the needs for improved techniques for controlling particulate fouling still exist [52].

2.5 Factors Affecting Flux Rate

Wayne F. Jones [62] investigated the use of frequent and periodic trans-membrane pressure reversal to decrease resistances of flux and the result shows that cross flow velocity has no effect on non-pulse permeate flux. Trans-membrane pressure could highly decrease fouling of membrane. Other techniques which are reported are on the basis of use of insert [63-65].

B.B.Gupta and J.A.Howell [63] studied the use of helical-baffle for mineralized membrane with baker yeast filtrate & water emulsion of dodecane. Experimental

conclusions depicted about increase of permeate flux up to 50%. They also observed that permeate-flux linearly increased by increasing helices numbers. It was found that when maximum diameter of baffle is decreased by 40%, then small variations occur in permeate flux value.

A.L.Ahmad and A.Mariadas [65] studied the use of a baffle's helical for microfiltration and cross flow Ultra filtration in order to obtain foul decrease. It has been observed that helical insert increases the velocity of fluid. They found that permeate flux increase is over 100%, and flux has found to increase with increasing number of turns.

T.Y.Chui and A.E.James [66] studied & described the effects of axial-baffle in a membrane with non-circular channel. Helical baffles, cylindrical rod and helical baffles with alternating directions were used. The results revealed that there are significant improvements in the filtration process due to the generated turbulence and flow channel mixing.

Yuan and Finkelstein [70] solved the Navier-Stokes equation. They were the first to solve this equation on laminar flows in a tube with pores. They assumed axial flow to be incomplete development & considered that non-dimensional velocity profile's shape does not vary with axial distance.

R. Ghidossi and J.V. Daurelle [71] studied and then applied the computational investigations for UF hollow fiber ultra-filtration membranes. The researcher got flexibility of developed relations for different condition.

Yuanfa Liu, Gaohong He et al. [66] worked to simulate the turbulent flows at baffle filled membranes and inserted wall baffles periodically & repeatedly in tubes of membrane. The research study shows that fluctuation of turbulence and in-wall shear stresses were caused by baffles.

A.L.Ahmad, K.K.Lau [73] studied & investigated the effect of different spacer filament shapes on concentration polarization control. The results revealed that the triangular filaments have higher degrees of concentration decrease abilities & pressure drops.

F.Li [77] studied and applied both simulations as well as experiment for design & optimizes spacer. The research reports that concentration pattern & transfer of mass coefficient distribution over membrane's surface as a feed channel. Numerous numerical works done cannot be validated via experiments. Some inserts like periodic baffle, disk baffle and rod baffle etc. are not that good geometries in real time filtration due to difficulty for installation. It also provides a high cost of material and can provide damage to membrane.

According to literature review given above, limited data is present on membrane application for wastewater refining. Some of the literatures compare the membrane performance with Ultra filtration of various wastewaters where most of the reports only focused on filtration the wastes containing one certain contaminant. But in reality, wastewaters consist of various contaminants so the membrane performance may be drastically changed or influenced by the presence of other contaminants like oil in refinery wastewater. Some factors for example pH, cross flow, temperature, velocity and contaminant's concentration were evaluated in many research works. However, the effect of temperature on wastewater and its importance on membrane filtration process is often disregarded by people.

CHAPTER 03

CHARACTERIZATION TECHNIQUES

Main theme behind characterization is to make a forecast of the membrane performance from its morphological and structural properties. From the characterization the pore model, pore system and the transport mechanism of the membrane can be predicted.

The membrane filtration performances are directly explained through mass transportation properties, i.e. Trans-membrane flux and retention, which are the main characterizing parameters. For a membrane, the latter parameter i.e. retention is often dependent on the investigation of system. It means the type of solute to be separated from solvent also plays a role in characterization of membranes. It is obvious that flux and retention are related to the size and number of the pores in membrane as well as on the size distribution and radius, so measuring these aspects is a doable way to characterize the membrane. There are certain other important factors are also included like, temperature stability, mechanical resistance and chemical resistance [80].

The current study aims to acquire visual information regarding membrane morphology and structure by image processing as well as by permeation flux rate is used to predict the structural porosity of membrane samples. Therefore characterization of samples membranes is done by two ways,

- a. Characterization through instruments
- b. Characterization through permeation flux rate data

The characterization through instruments involves,

- a. SEM
- b. AFM
- c. XRD
- d. FT-IR
- e. Tensile Testing

3.1 Scanning Electron Microscopy (SEM)

The study of morphology of objects and fine structure with the help of microscope is known as microscopy. Electron Microscope images are developed in scanning, with

beam of electrons; lenses focus them as scanning probe. In microscope, electron probe having energy up to 30keV is focused on specimen's surface and it is scanned in a "raster". Numerous phenomenon occur at surface level, for scanning, most important is the emission of secondary electron having energy of few eV and reflection of back scattered electron with high energy from primary beam. Intensity of emission of back scattered electron and secondary electron is highly sensitive to the inclination through which electron beam strike sample's surface. Amplifier collects the emitted electron current; the variation of resolution signal is utilized to vary the trace cathode ray brightness. Thus, electron beam scanning and fluorescent image have a direct positional correspondence. The ratio of final display of image and sample's field scan, is the magnification developed by microscope. Magnification of the image can be altered by changing intensity of scan on sample and maintaining the display size constant [81].

In SEM, the sample's surface is observed by electron beam. For emission of electron beam with specific energy in keV, a cathode gun is used and focusing is achieved using objective lenses and condenser. The beam scans rectangular area of sample. Because of interaction between electron and atoms on sample's surface, emission of secondary electron is produced which could be detected using detectors. When the signal is amplified, a black and white image of sample's surface is developed with resolution ranging in nm. Because of the difference in number of electron and their speed obtained back from sample, different grey scale scanning electron microscope (SEM) image is formed. Lower atomic number appears lighter while higher appears brighter [82].

3.2 Atomic Force Microscopy (AFM)

AFM represents an imaging technique where a cantilever is brought into contact with a surface, and through some type of close-range interaction, an image is produced. A typical AFM setup would be a cantilever with a reflective backside being brought into contact with the desired surface. The sample, or the cantilever itself, is moved in 3-dimensions with the use of very accurate piezoelectric elements. A tip on the end of the cantilever with radius of curvature and an order of nanometer is made into contact with the surface. The tip is then moved relative to the surface, with a laser shining onto the reflective surface on the cantilever's backside, aimed at a photodiode detector. As the cantilever moves due to the contact force, a feedback circuit keeps the deflection of the cantilever constant, based on the location of the laser on the diode. As a part of that

process, the piezo elements adjust the sample height, and a mapping can be generated based on the motion of these elements. There are different modes that an AFM can operate in, and they can operate based on different forces with the surface. Examples of modes are contact and tapping. Contact mode simply means the tip is dragged across the surface for the measurement. Depending on what is being measured, this could cause damage to the sample. Tapping mode means the tip is brought into contact with the surface at a frequency very near the resonance frequency of the cantilever. As the tip impacts the surface, the interactions, as well as the impact itself in some cases, results in changes to the amplitude of these oscillations, which can be measured by the laser to reconstruct images. It is possible to create cantilevers with tips that interact through non-contact forces, such as Coulomb interactions, electrostatic forces, van der Waals forces, and more. Modern day AFMs are generally accurate to a nanometer or better. Suffice it to say that AFM can provide a fairly robust and reliable method of identifying thickness of flakes. Since AFM is fairly time consuming, and requires a fair amount of resources, it is recommended that optical microscopy be used to first identify potential monolayer flakes, and then AFM used to more objectively determine the flake thickness [83].

3.3 XRD (X-Ray Diffraction) Technique

XRD is one the classical characterization technique, due to its significance it is still used and samples are being interpreted with it. Basic mechanism of XRD involves the incident of X-rays on a crystalline material, as a result, the X-rays bent in different direction. This phenomenon is called as diffraction. The incident X rays on sample are diffracted by different planes of atoms in the sample. This diffraction produces a pattern which contains the information about the arrangement of atoms in the plane within the sample. Thus size and shape of the unit cell can determine using diffraction pattern. The pattern also helps to know the spacing between the atoms.

Powdered samples on the other hand, contain numerous crystallites, which are randomly oriented in the sample. The diffraction pattern from powdered samples is used to estimate the crystalline nature of the sample

By XRD we determine the crystalline and crystallite size of the sample under study.

3.4 FT-IR (Fourier Transform Infrared) Spectroscopy

Since IR radiations have low energy and greater wave length, they can neither excite the atoms nor can undergo the bond cleavage. However, stretching and bending of chemical bonds is caused by the IR radiations. These radiations are made to fall on the sample under investigation. IR radiations of certain wave number are absorbed by the bonds and groups present in the sample. The rest of the radiations called transmitted radiations, are than absorbed by the detector. Absorbed radiations by the sample are utilized for the bending and stretching of bonds. Detectors based information is then translated in a graph between transmittance and wave number.

In FT-IR the peak is shown by a dig in the graph. This dig is because of absorbed radiation. FTIR spectroscopy requires spectra absorption in the infrared regions. FTIR spectra give details regarding groups which are functional in a specimen, and can be utilized in the industry of semi-conductor in order to evaluate the existence of impure atoms. It provides all sorts of details regarding functional groups associated to oxygen and carbon. It represents the relation between intensities and wavelength in graphical from [84].

3.5 Tensile Strength Testing of Membrane:

The tensile properties of CA membrane mainly depend on the Average molecular chain length of the polymer and distribution of chain length in the matrix. Sometimes additives are added in Cellulose Acetate material for required tailoring of membrane behavior. This modification make impact on tensile properties are membrane. For example if pore gen is added is membrane material, it tensile strength would most likely to be decrease due to increase magnitude of porosity in it [85].

Specimen preparation is another important area for characterization of membranes. Since Cellulose Acetate membranes are rigid in character, their specimen preparation involves tedious and careful work. Correct dimension of specimen are important for true tensile behavior of membrane [86].

For comparative membrane analysis, care must be made that all membrane samples be prepared with identical procedure. Identical methods for sample preparation are key to make correct comparative analysis. For the current study of membrane the standard

used was “ASTM D638-03, type-V” This standard describes the evaluation of tension properties of membrane when subjected to test under defined conditions of temperature, machine speed and humidity. All the specimens of membranes were made in accordance with afore mention standards.

CHAPTER 04

METHODS AND MATERIALS

To fabricate Ultra filtration membranes, the first stage was to select materials required. For membrane matrix material, Cellulose Acetate was chosen due to the reasons discussed above. Chitosan was used as an additive in Cellulose Acetate matrix.

4.1 Hypothesis

Before selecting the materials for membrane fabrication the hypothesis was developed after making literature review. The hypothesis suggest that,

- Cellulose Acetate membrane is expected to be porous, if Chitosan is added in it.
- Porosity in CA membrane can be controlled through Chitosan concentration.
- Cross linking between CA and Chitosan will give an organize pattern of pores.

To verify the hypothesis, materials were selected and experiment was designed. The detail of selected materials is as under,

S.No.	Chemicals/ Materials	Brand name
1	Cellulose Acetate (30,000 Da)	Aldrich
2	Formic Acid (99 %)	Merck Co.
3	Chitosan	Aldrich
4	Isopropyl alcohol (99%)	Aldrich
5	Hexane (99%)	Aldrich

Table 1: Materials and chemicals used in the research project

4.2 Membrane Fabrications

With the experience of decades of human research, numerous methods for membrane casting have been developed. Each technique is employed to cast selective and desired membrane. The most common method of membrane casting is phase inversion technique. Generally phase inversion technique is divided into three categories; these types of phase inversion are based on the inversion mechanism. The types are as under,

- Temperature Induced Phase Separation
- Reaction Induced Phase Separation
- Diffusion Induced Phase Separation

In the current study Diffusion Induced Phase Separation technique was used. The technique is also known as Liquid-Liquid phase inversion technique. In this particular method, polymer mass is introduced into a precipitation bath contains a non-solvent, the diffusion of non-solvent into polymer mass results into the phase separation and thus the membrane is casted. The non-solvent in this case was taken as de-ionized water, while the solvent used for polymer dissolution was formic acid. Formic acid is insoluble in water [79]. General schematics of phase inversion process are shown in the following figure.

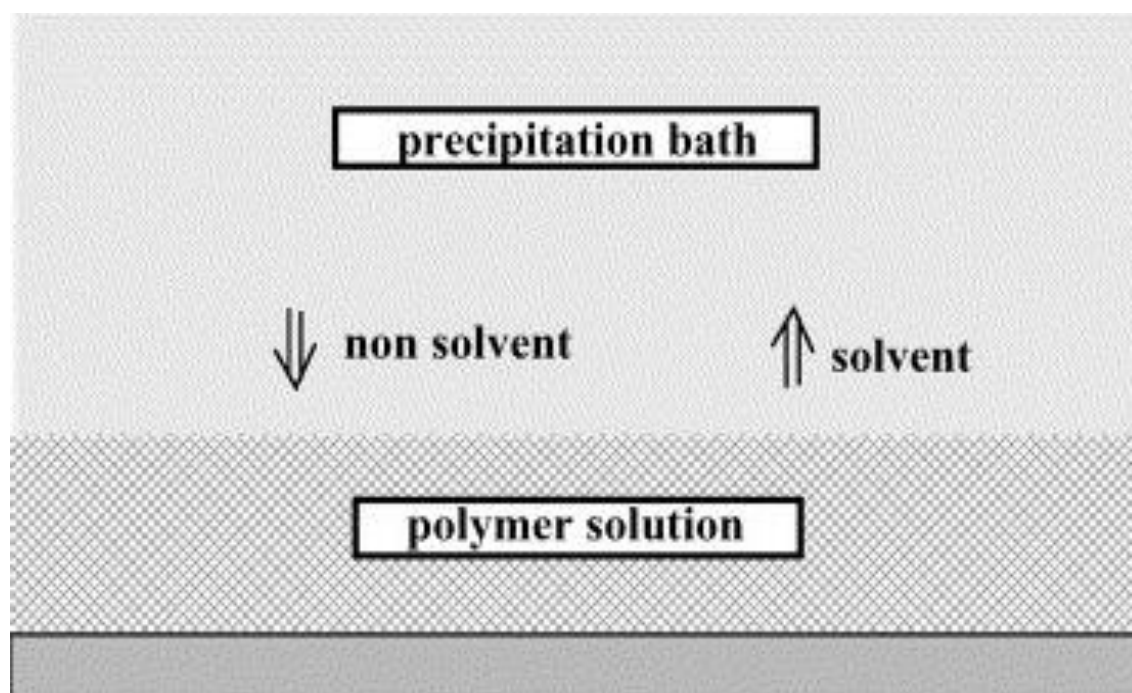


Figure 4: Schematics of membrane casting

4.3 Synthesis

Different concentrations of Chitosan were blended with a constant concentration of Cellulose acetate in formic acid solvent; the composition of each membrane is shown in table 2. A membrane “A” is casted such that it contains no Chitosan content. It is done in order to observe the effect of absence of Chitosan on membrane porosity. The mixtures were kept at constant mechanical stirring at moderate speed for about 24 hours

at room temperature. The aim of stirring is to blend the polymer completely with formic acid. The homogeneous solutions obtained in the process were kept static for about 12 hours in air tight condition to remove air bubbles. With this a homogenous solution is prepared that can be used for membrane casting. For the current project, six different compositions were made for casting purpose; the composition of each membrane is given below,

A*: Membrane without Chitosan

NO.	CA (gm)	Chitosan(gm)	Formic Acid (ml)	Chitosan%
A*	1	0	10	0
B	1	0.1	12	10
C	1	0.2	13	20
D	1	0.3	15	30
E	1	0.4	16	40
F	1	0.5	17	50

Table 2: Formulation of six different dope solutions

4.4 Membrane casting

The homogeneous solution was then casted on glass plat using a casting knife. Thickness of membrane was maintained at 0.2mm. The cast membrane was allowed for evaporation for 30s and was transferred to precipitation bath contains water for phase inversion [80].

4.5 Membrane Drying

A combination of Isopropyl alcohol and Hexane was used for membrane drying. The membrane samples were immersed in aqueous Isopropyl alcohol with increasing alcohol content. The membranes were first kept in 25% aqueous Isopropyl alcohol for 24 hours, then in 50%, 75% and 100% isopropyl alcohol respectively for each 24 hours. In this way water is removed from membranes. To remove alcohol, the membranes were then kept in a mixture of Isopropyl alcohol and Hexane with increasing Hexane content i.e. 25%, 50%, 75% and 100% Hexane respectively for each 24 hours. The membranes were then kept in desiccators until they become completely dry [81].

4.6 Pure water flux

After fabrication the membranes were subjected to pure water flux study at different pressures i.e. from 0.5 to 2 bars. The flux rate was calculated using the relation [82],

$$J_w = Q/A \cdot dt$$

JW: Pure water flux rate ($Lm^{-2}h^{-1}$), Q: Amount of water permeates (L), dt: Permeate time (h) and A: Area of membrane (m^2)

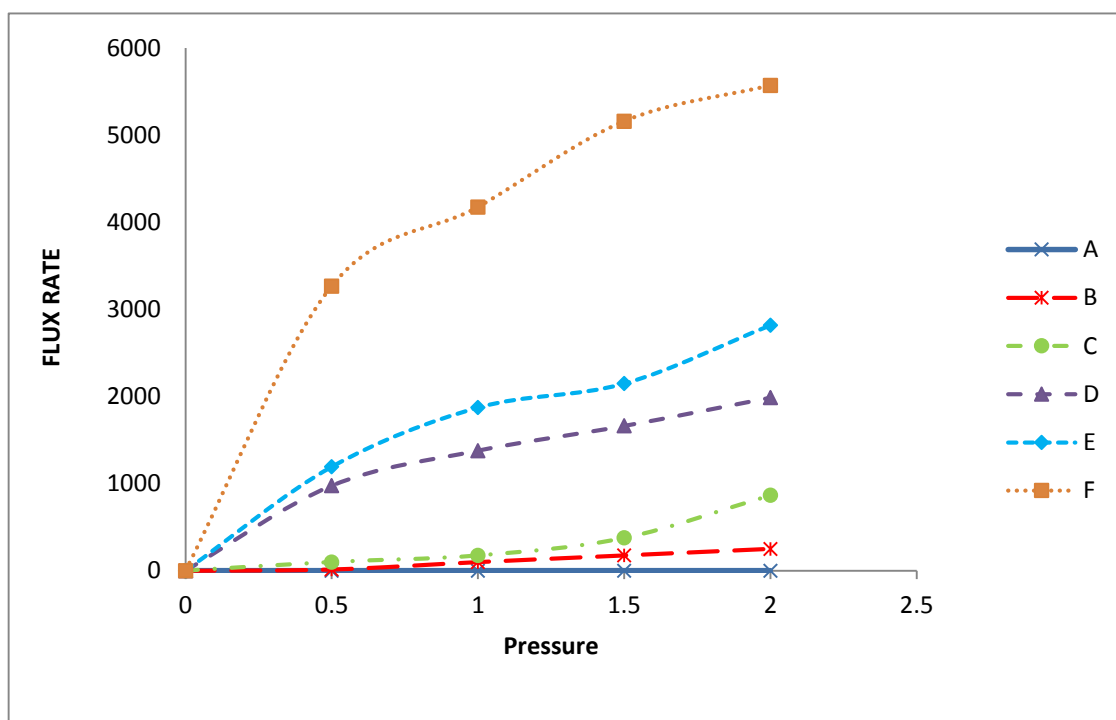


Figure 5: Shows variation of flux rate ((Lm-2h-1) relative to pressure (bars)

Under the given pressure, the flux rate through membrane “A” and membrane “B” is zero, this concludes that the flux rate for these membranes could be studied under high pressure. For membrane “C” to “F” a gradual increase in flux rate is observed. This proves that porosity is increasing from membrane “C” to “F”. This variation is attributed to Chitosan concentration which varies in membrane B to F.

4.7 Percentage water content

Water content is an important parameter to investigate porosity. For percent water content, the membranes were cut into a size of 5cmx 5cmx0.02cm and were soaked in

water for 24 hours and weighed, and then they are dried in oven at 75c^o for 48 hours and reweighed again. Following equation is used to calculate percent water content [83],

$$\% \text{ water content} = \frac{(\text{Wet sample weight} - \text{dry sample weight}) \times 100}{(\text{Wet sample weight})}$$

Membrane	% water content
A	73.6
B	86.9
C	88
D	90.9
E	93.1
F	94.2

Table 3: Absorbed water data

The increase in percent water absorbed by the membranes indicates increased porosity in them as shown in figure 3.

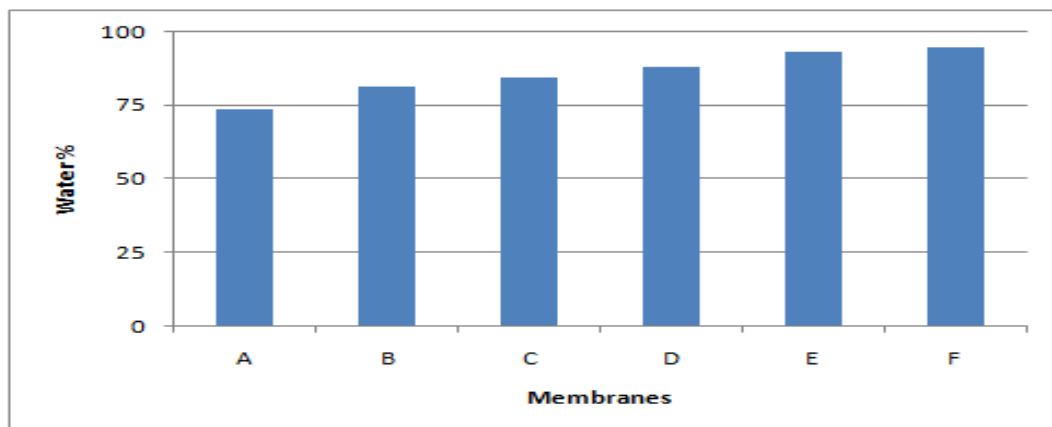


Figure 6: Absorbed water by the membrane

CHAPTER 05

RESULTS AND DISCUSSION

The current research work was an attempt to evaluate the role of Chitosan as a pore forming agent. Various concentration of Chitosan was use in the polymer Cellulose Acetate. As shown above, the increase of flux rate in CA membranes as a function of Chitosan concentration was observed. This suggests that porosity has increased in membranes with increasing Chitosan content. Similar observation is made from percent water content in membrane, which appears to be rising with increase in Chitosan content. This indicates that porosity in CA membranes is controlled by Chitosan.

Characterization is an important tool knows the chemical composition and insight of any material. Synthesized membrane was characterized using the available tools and techniques in school of chemical and material engineering, NUST. The detail of each characterization is given as under,

5.1 Scanning Electron Microscopy (SEM)

High Resolution Scanning Electron Microscopy i.e. 64904-Analytic Scanning Electron Microscope JEOL Japan was used to observe the pore size and morphology of fabricated membranes. The membrane samples for SEM analysis were gold coated to thickness of about 250Å, with the aid of Ion Sputtering Device i.e. JFC-1500, JEOL Japan Quick Auto Coater. The purpose of gold coating is to make membranes conductive for electron beam of SEM. The membranes were then subjected to electron beam for morphology, porosity and structural analysis [84].

Scanning electron microscopy is usually used to observe the membrane structure. Morphological feature of micro filtration membrane & to lesser extents of Ultra filtration membrane could be studied with relative ease. SEM is particularly effective for Ultra filtration membranes. The suitable resolutions of Scanning Electron Microscopy could be around 5 nm, and for qualitative analysis of membrane structure, it may be sufficient. Due to high field's depth, around 150 pm, sharp image can be obtained for rough membrane surfaces. On the other hand, TEM (Transmission Electron Microscopy) contains high resolution power i.e. 0.3 nm than Scanning

Electron Microscopy, but field's depth is limited to around 2 μm . Beside this, very special method of preparation must be required to be adopted to develop a sample which could efficiently be used for Transmission Electron Microscopy [85].

Scanning electron microscopy images were taken in order to verify the effect of Chitosan concentration on porosity of membranes. The images were taken both from the surface and cross section to investigate porosity. A sample membrane "A" is taken as reference because it has 100% CA content and no Chitosan is present in it. This reference membrane "A" is taken as reference in order to make comparison and relative evaluation of all the membranes samples. Pore forming agent i.e. Chitosan was mixed in membrane material in experimental design. SEM is an effective tool to evaluate, how pore forming agent is changing membrane's morphology and structure.

Thus the role of Chitosan as pore forming agent will be thoroughly studied. It is clearly evident from the images, given below, that a gradual increase in porosity is occurring with increase in Chitosan content.

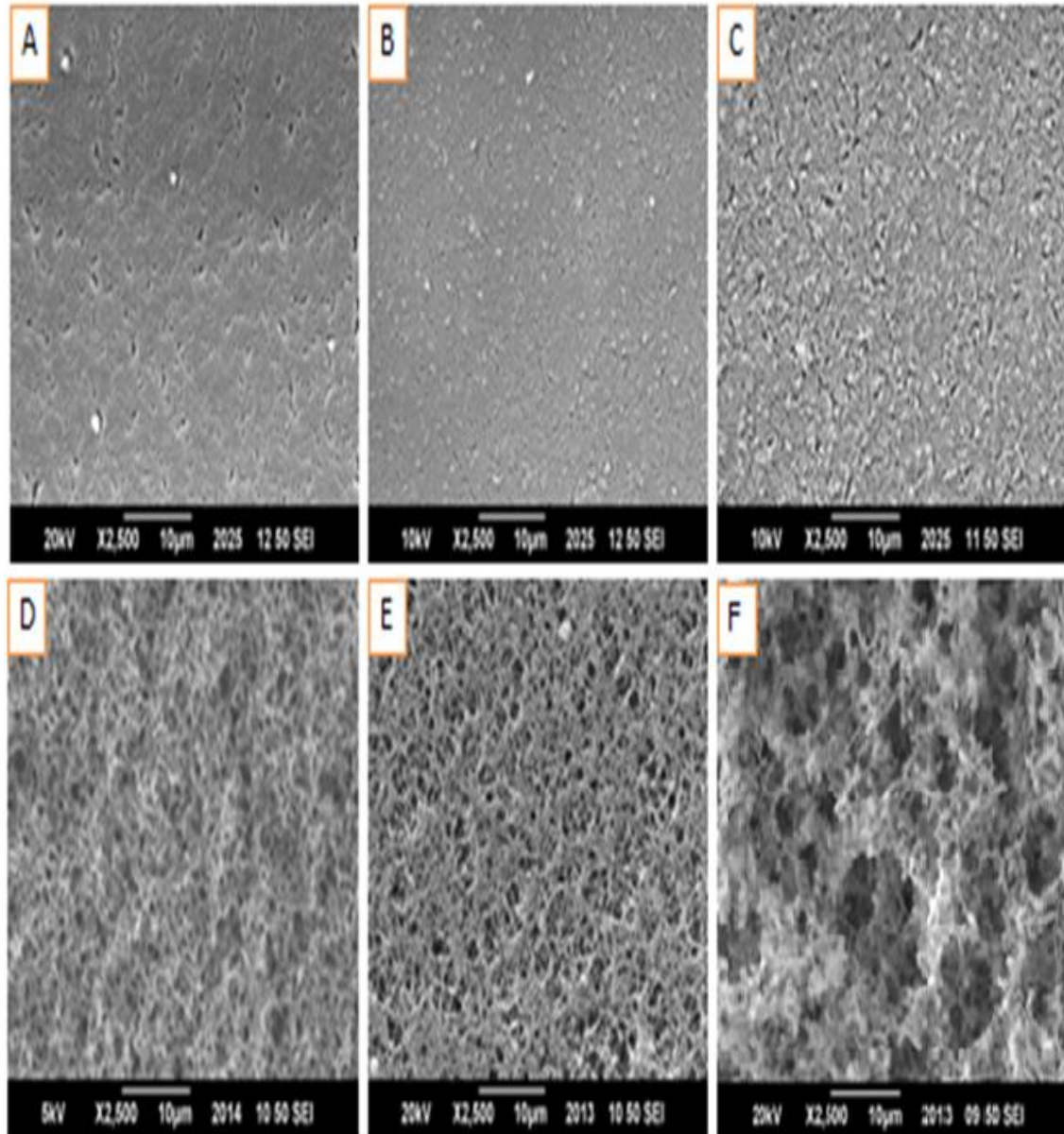


Figure 7: SEM surface images membrane at lower magnification of 2,500 times.

The SEM images are indicating that the porosity is increasing in membranes from A to F respectively; the conclusion is evident even at a lower magnification. A significant change in membrane morphology can be noticed, if membrane “A” is compared with membrane “F”. Thus the results reveals that pore forming agent has affected the structure and morphology of membranes.

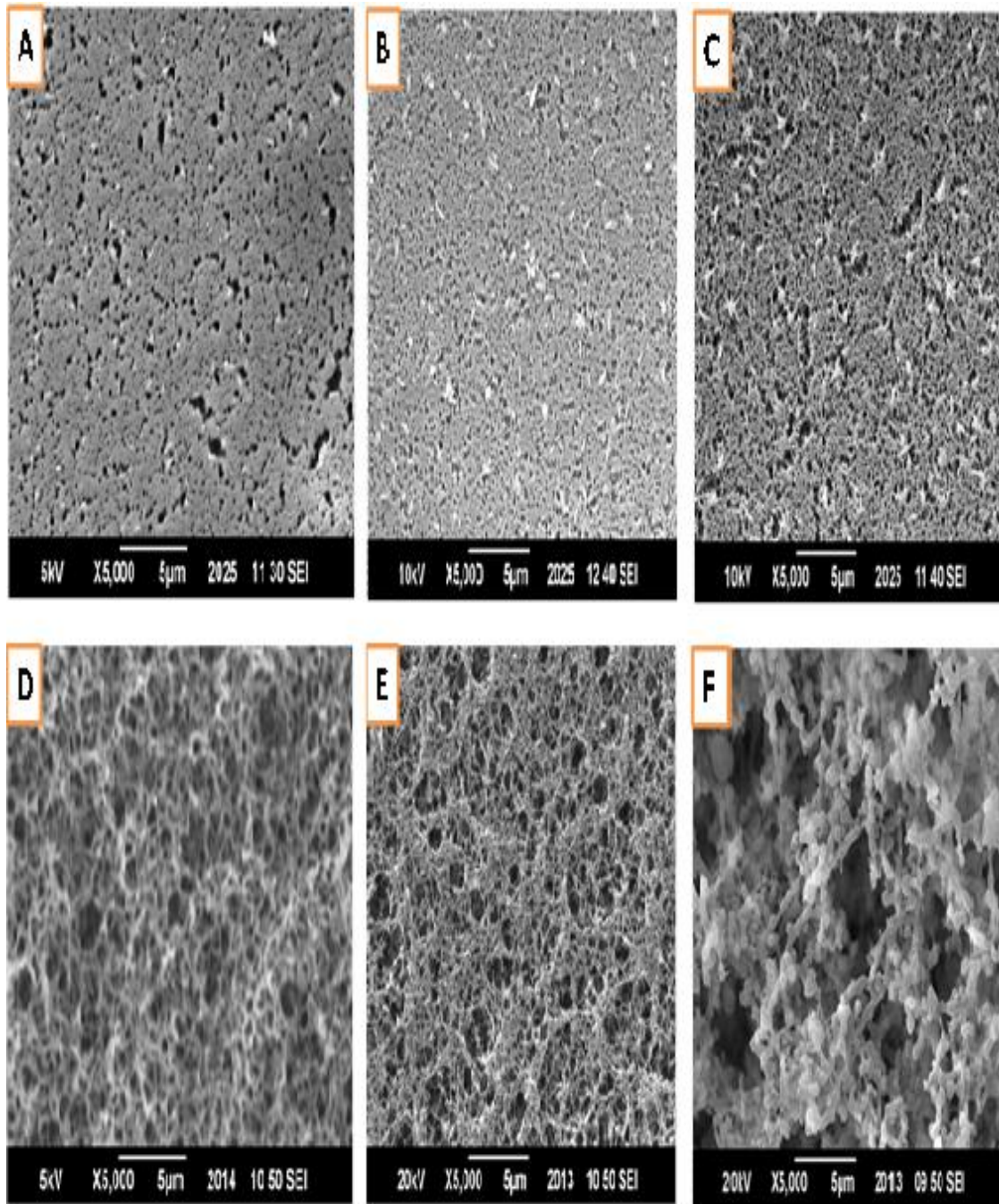


Figure8: SEM surface images membrane at lower magnification of 5,000 times.

Higher resolution images on SEM provides the fine inner details of membranes. As discussed above, the water soaking ability increases in membranes from “A” to “F”. SEM justifies the above shown behavior of membranes, as membrane “E” and “F” has more space to accommodate water molecules than membranes “A” and “B”.

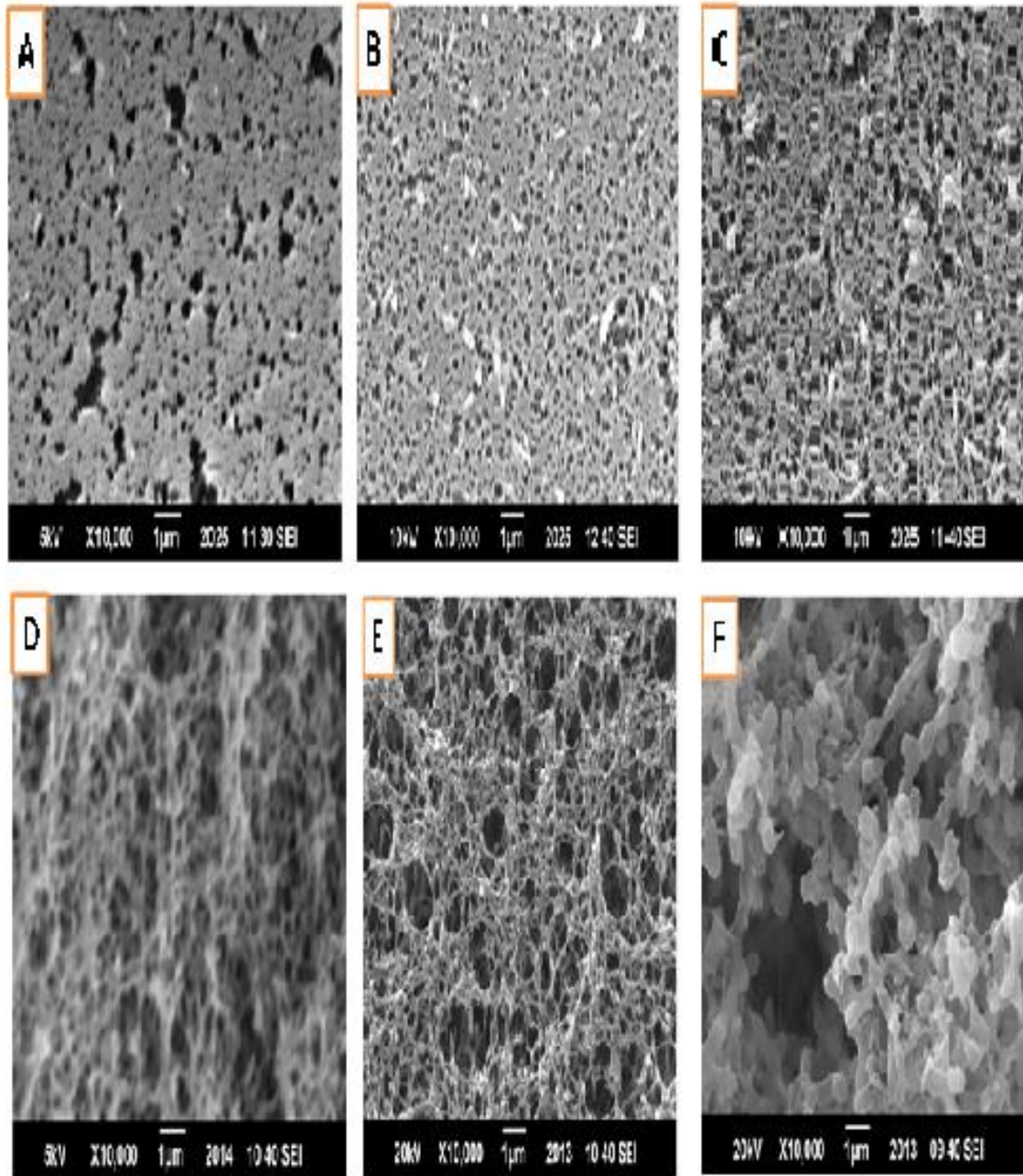


Figure 9: SEM surface images membrane at lower magnification of 10,000 times.

Comparison of membrane 1A with that of membrane 1F, clearly shows the impact of Chitosan on porosity in Cellulose Acetate polymer, as large voids can be observed in membrane 1F due presence of 50% Chitosan in it.

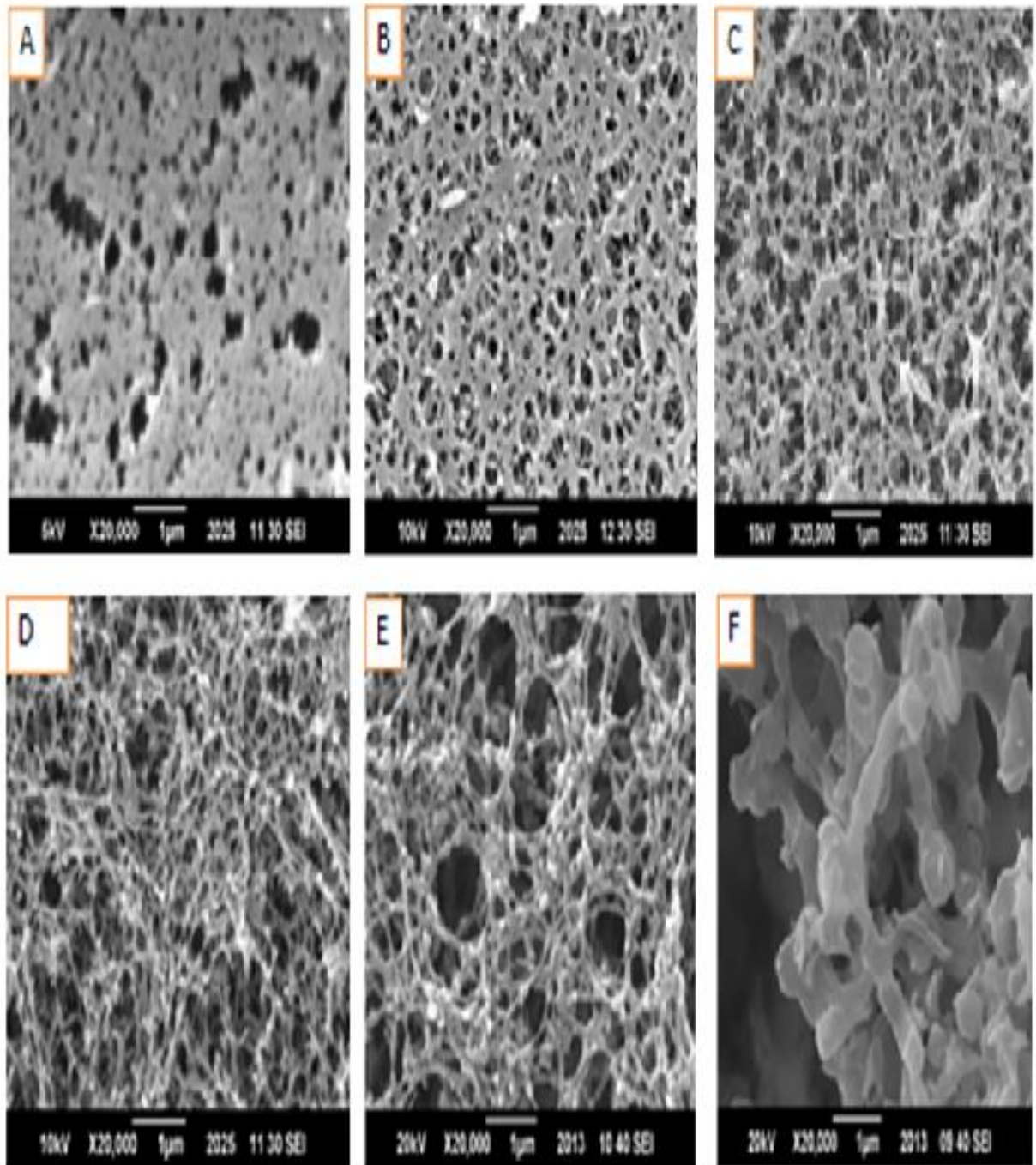


Figure10: SEM surface images membrane at lower magnification of 5,000 times.

A thread like structures, which is characteristics of organic polymer, can be deduced from SEM images. Water permeation data (given above) and tensile strength of membranes (will be discussed below) can be justified from SEM images. Greater permeation rate and low tensile strength of membranes “E” and “F” is because of large voids present.

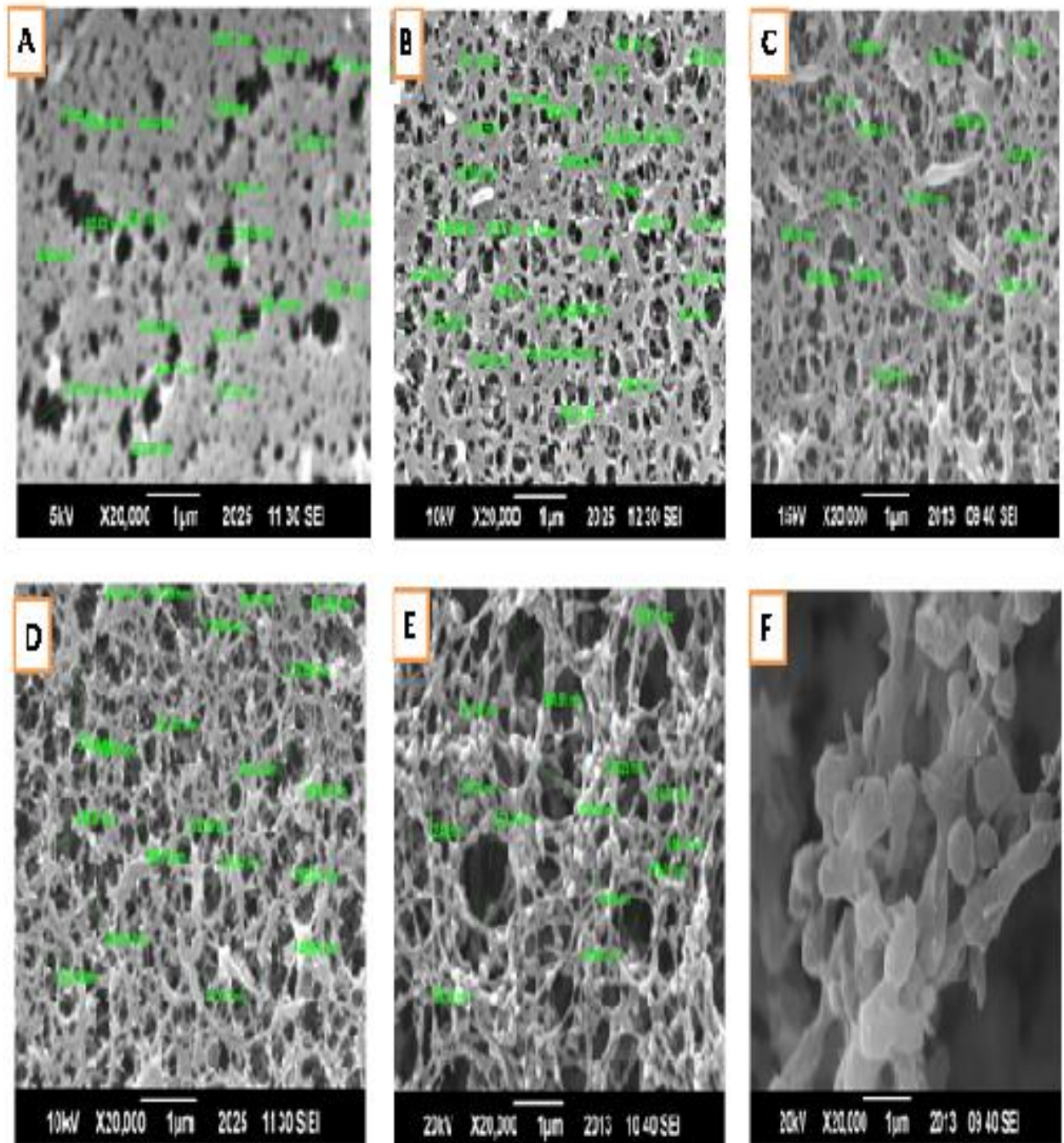


Figure11: SEM surface images membrane for pore size

It has been observed that pore size has been gradually increased in membrane “A” to membrane “F”. This justifies the hypothesis, that Chitosan can be used to control porosity and pore size in CA membranes.

5.1.1 Cross-Sectional Study of Membrane

In general, the study and investigation of structures of Ultra filtration membranes is a difficult and delicate work by using electron microscopy. A number of problems are responsible for this difficulty, for example resolution along with depths of field & investigation of membrane sample's structure create the difficulty to investigate porous membrane with the electron microscopic techniques. Further problems include, micrograph's interpretation is quite complicated, analyses of membranes are local & computation of data is often time consuming.

A brief summary of problems are as,

1. Porosity in the surface of membrane could be separated and may not be connected with entire porous medium in membranes.
2. The resolution for method considered in this research has low intensity in order to identify extremely fine details and small pores.
3. Techniques of preparation of sample may produce artefacts which may affect final output [84].

Beside all these problems, the only suitable method for pore's estimation, porosity of surface and direct investigation is SEM. Though the microscopic analysis is local and laborious to make a reasonable level of precision, because counting and measuring a large number of pores is required for accuracy of results. However, the derivation of quantitative value for porosity of surface is out of practice.

A modern approach to determine the porosity in the Ultra filtration membrane is on the basis of filtration and colloidal particle's penetration with a definite sizes & narrow sizes distributions in to porous layers of Ultra Filtration membranes. Particles penetrating into surface of porous membrane layers penetrate until the small pore near the skin has been achieved. So if pore's sizes in membrane are smaller than penetrating particle's size, then particles are considered to be stuck near the skin of membrane, forming a thin layer of colloids on membrane surface [85].

The thickness of such formed layers could be studied and measured through SEM. SEM can be used in following two ways;

- 1) Secondary electron image mode i.e. SEI mode
- 2) Backscattered electron image mode i.e. BEI mode

The rough morphological structure is examined from the micrographs obtained in Secondary Electron Image mode; these graphs have been considered topographical, On the other hand, backscattered electron image modes give topographical information as well as analytical details about membranes [86].

However in current studies, membrane is investigated from surface as well as from cross section. Cross sectional study is aimed to know the inside of membrane.

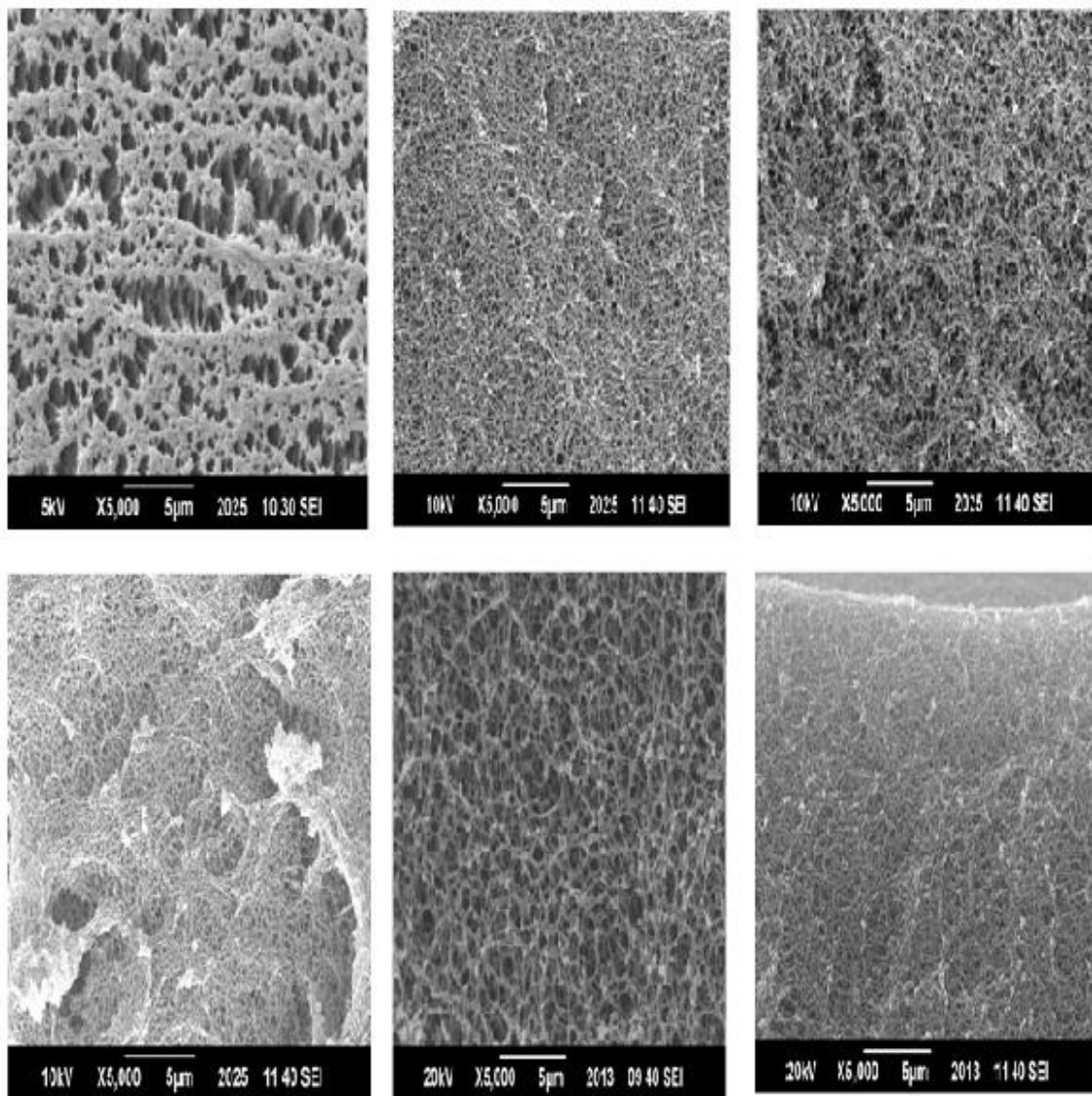


Figure12: SEM cross section images membranes at magnification of 5,000 times

SEM images are indicating that the membrane is porous from inside as well. It can be seen that the first membrane in the above images contains locking portions, which hinders porosity in this membrane. But, gradually the porosity and layer like character of membrane increases, which can be due to increase Chitosan content.

The porosity detail and further information can be made by studying at higher magnification.

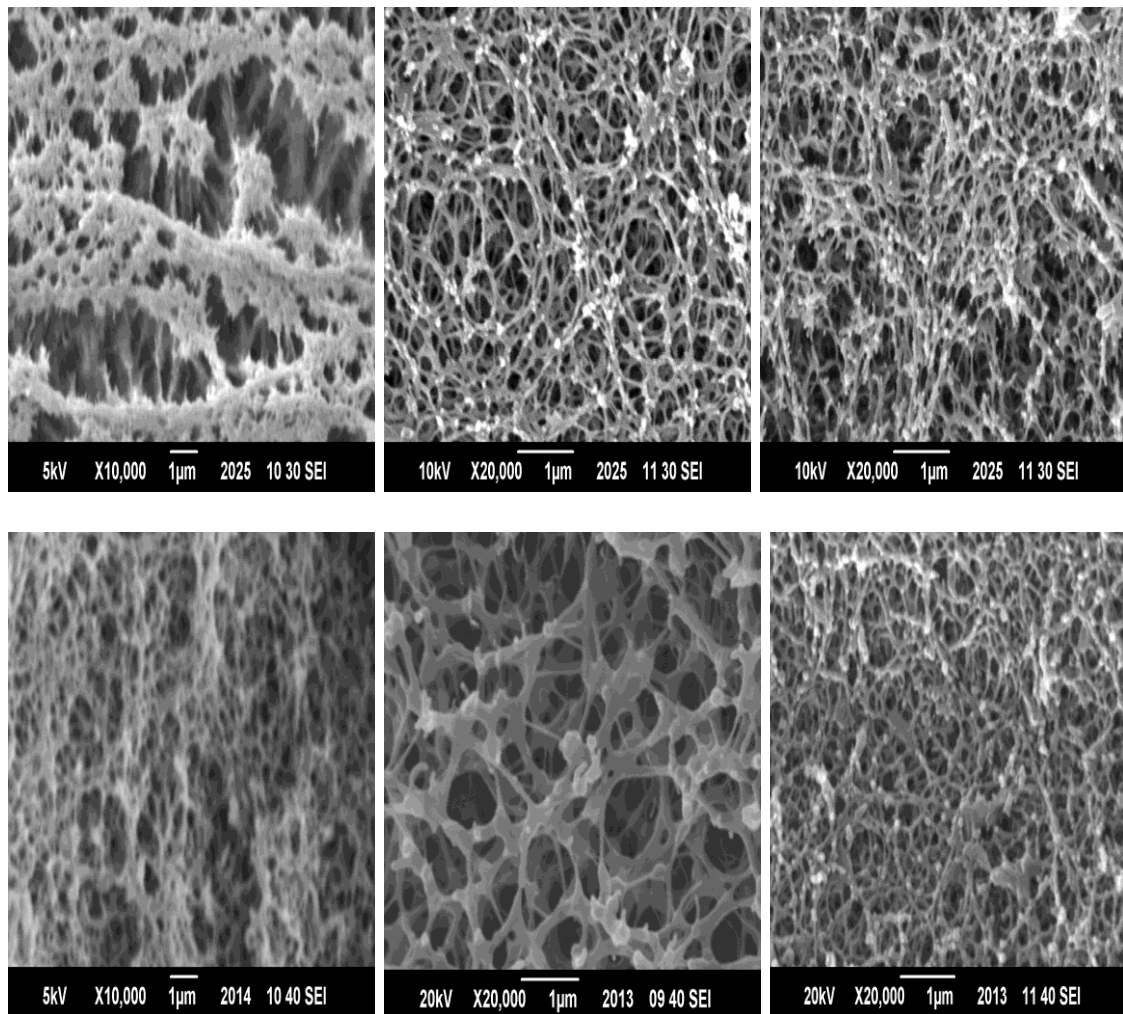


Figure13: SEM cross section images of membranes at higher magnification

Higher magnification provides smaller and finer details. Above images confirm that membranes are porous from inside as well.

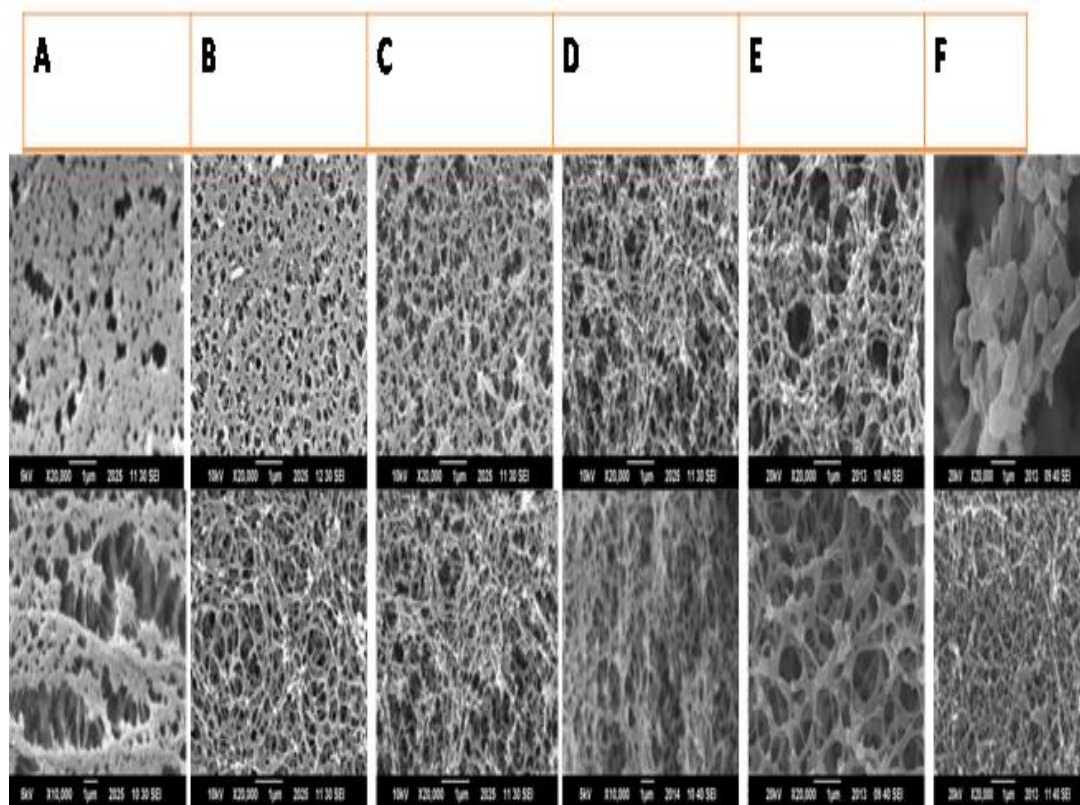


Figure14: SEM surface images in comparison with cross section images of membranes “A” to “F”

The comparison of membrane “A” with membrane “F” signifies the role of Chitosan as pore gen. The variation in tensile properties, permeation flux rate and absorbed water in the membranes is because of variation in pores and voids in the developed membranes. Thus it can be concluded that Chitosan can not only be used to induce porosity in polymer membrane but also can be used to control pore size in the said membranes. Controlling pore size to the desired range would be big step forward for atomic and molecular level filtration.

5.2 Atomic Force Microscopy

The Atomic force microscopic studies on membranes were made on a tapping mode at the surface of fabricated samples. The mean surface roughness (Ra) was used to represent the membrane surface morphology. As mean surface roughness is a mean value of the membrane surface relative to the center plane. Parameter of roughness

merely depends on treatment of captured surfaces data such as plane fittings, filtering and flattening. So the roughness achieved through AFM's results need not to be considered as values of absolute roughness. Since, in this research of membranes, same procedure has been followed for all the sample's measurements, so the captured surfaces of membrane were evaluated and dealt the same way.

Atomic force microscopy images of membranes were taken to observe roughness at membrane surface. It is obvious that membrane porosity would cause surface roughness, so AFM study is another tool to observe the morphology of membrane. The surface study may give the idea about the pore symmetry and pore distribution [87].

Atomic force microscopy images of membranes were taken to observe roughness at membrane surface. AFM is selected for imaging membrane surface due to various reasons. AFM provides resolution up to nanometer scale, thus greater resolution is beneficial in detail study of membrane surface. Contrary to SEM, little effort is required to prepare sample for AFM; moreover imaging through AFM can be carried out for samples in liquid conditions as well. Another aspect of AFM study is that, the three dimensional study and surface imaging can be carried out [88].

It is obvious that membrane porosity would cause surface roughness, so AFM study is another tool to investigate surface and hence porosity. The experiments were planned in a way to induce porosity with the aid of pore gen, and the consequent effects of pore gen are investigated here. The under study membrane samples were investigated through,

- 2-D imaging
- 3-D imaging
- Surface features height
- Pore size
- Mean surface roughness

In the following figures, the AFM results are shown,

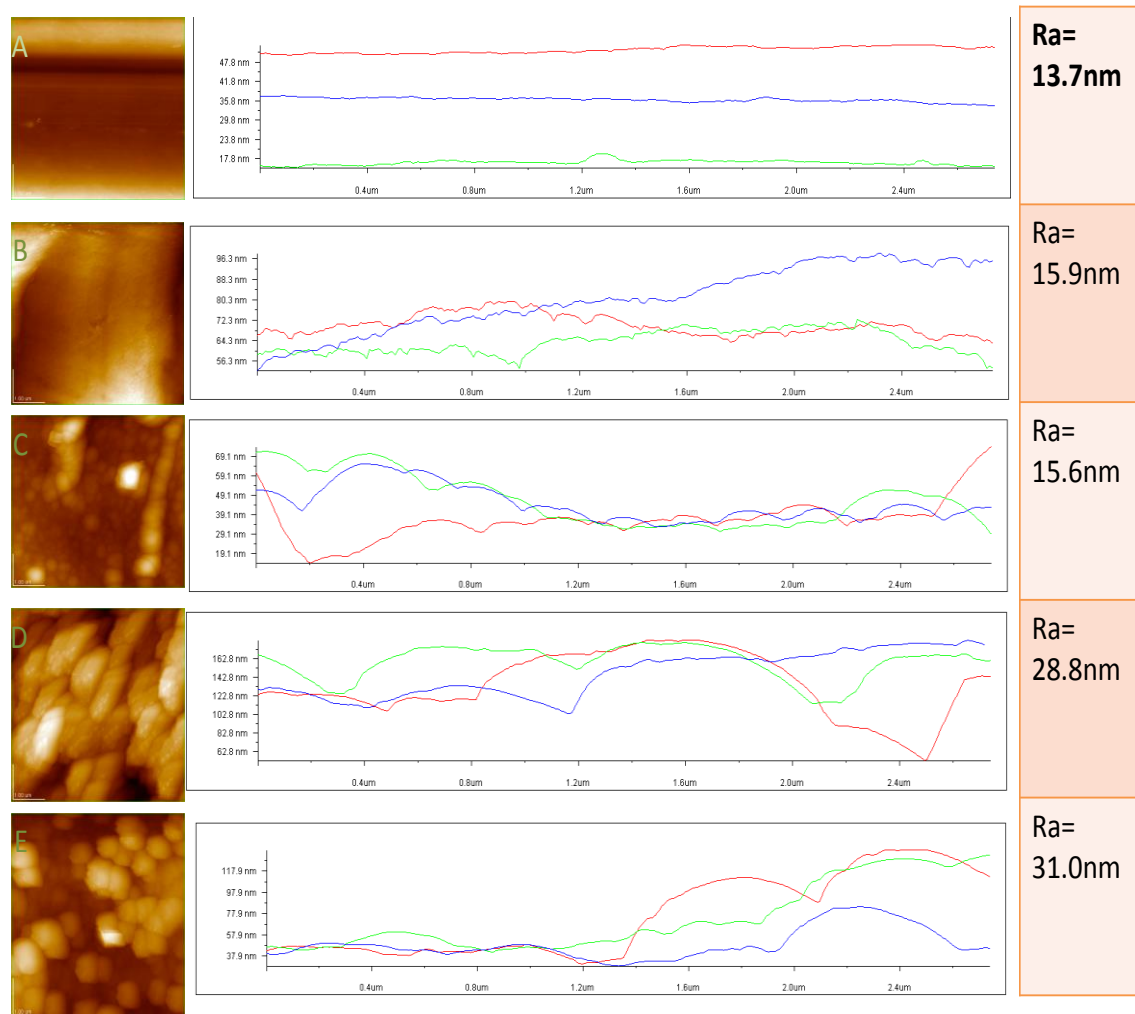


Figure15: 2-D images of membrane samples against their average roughness

Since comparison of surface membrane surface is being done above, the care must be taken for synthesizing the membranes. All membranes were fabricated in an identical way; only the percentage of Chitosan content is varied. The numerical value of surface roughness can be seen to increase in above figure. Since Chitosan is the only factor, which is varying in above samples, so the variation in surface is because of it, because rest of the factors like matrix membrane, solvent, casting conditions, Fabrication technique and Characterization techniques were identical [89].

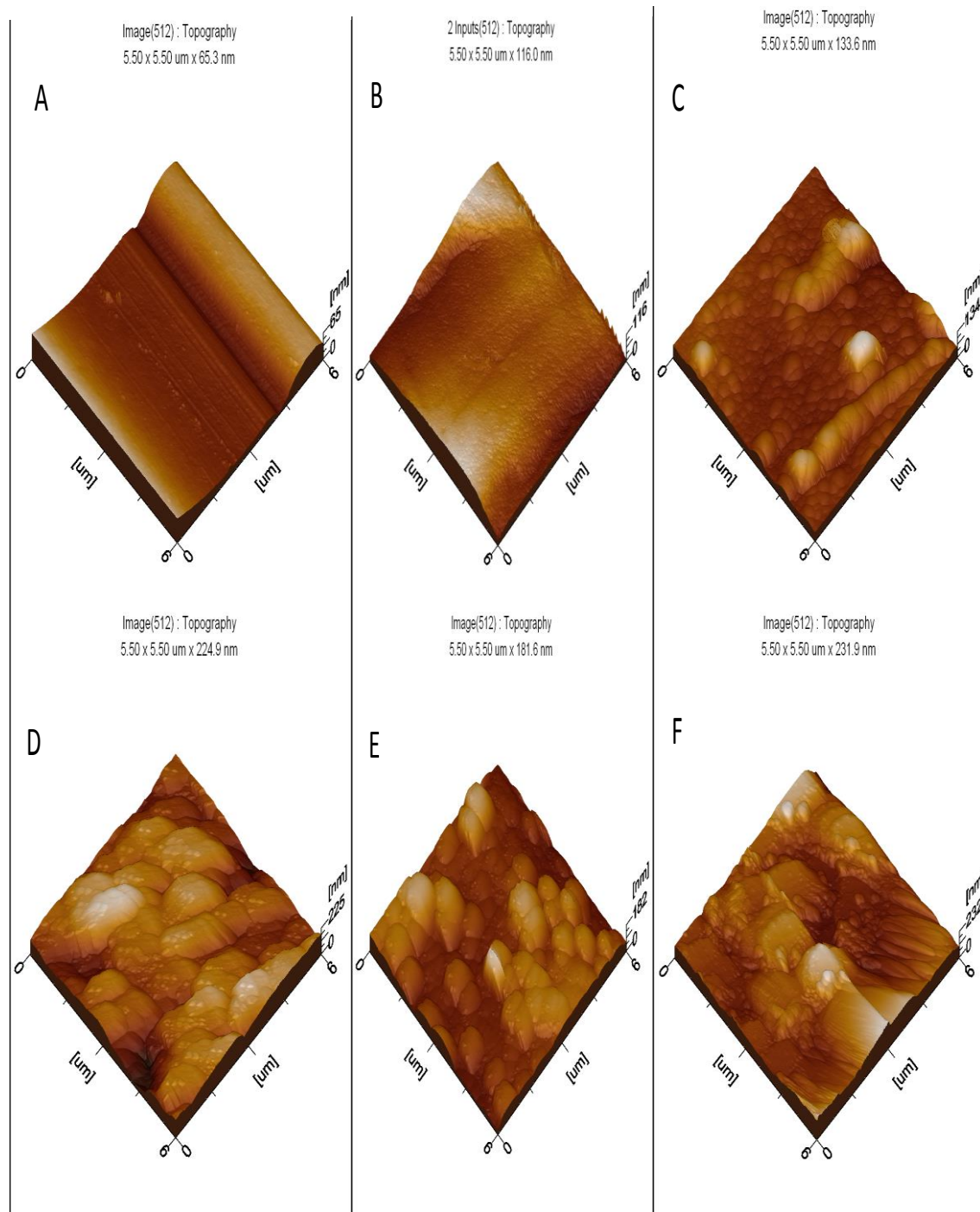


Figure16: 3-D images of membrane samples against their average roughness

The 3-D images show better interpretation about the sample surface as it includes feature heights as well. A gradual increase in feature heights can be seen in the results above. This increase suggests the change in morphology and topography of studied samples. Feature heights study concludes the evidence of porosity in the samples. Comparing membrane “A” to membrane “F” clearly indicates a significant increase in

surface roughness, which is infect, due to increase porosity at membrane surface. Unfortunately, AFM Characterization is limited to surface study only, and inside of membrane cannot be evaluated through it. But a mutual discussion between AFM results and Flux rate permeation confirms that the membranes are porous both at surface as well as from inside [90].

The following table shows a comparison of numerical interpretation of studied samples, which are concluded from AFM studies.

Membrane Type	Average Roughness (Ra)	Surface Feature Height	Pore Size
A	13.7 nm	65.3 nm	-----
B	15.9 nm	116.0 nm	0.065 μm
C	15.6 nm	133.6 nm	0.091 μm
D	28.8 nm	224.9 nm	0.161 μm
E	31.0 nm	181.6 nm	1.0 μm
F	28.4 nm	231.9 nm	1.26 μm

Table 4: Comparative data from AFM about membrane samples

The table above indicates a complete change in the properties of samples as we move down the table, thus the data verifies the assumption that porosity in membranes is proportional to Chitosan concentration. The pore size given in the table is interpretation and discussed be

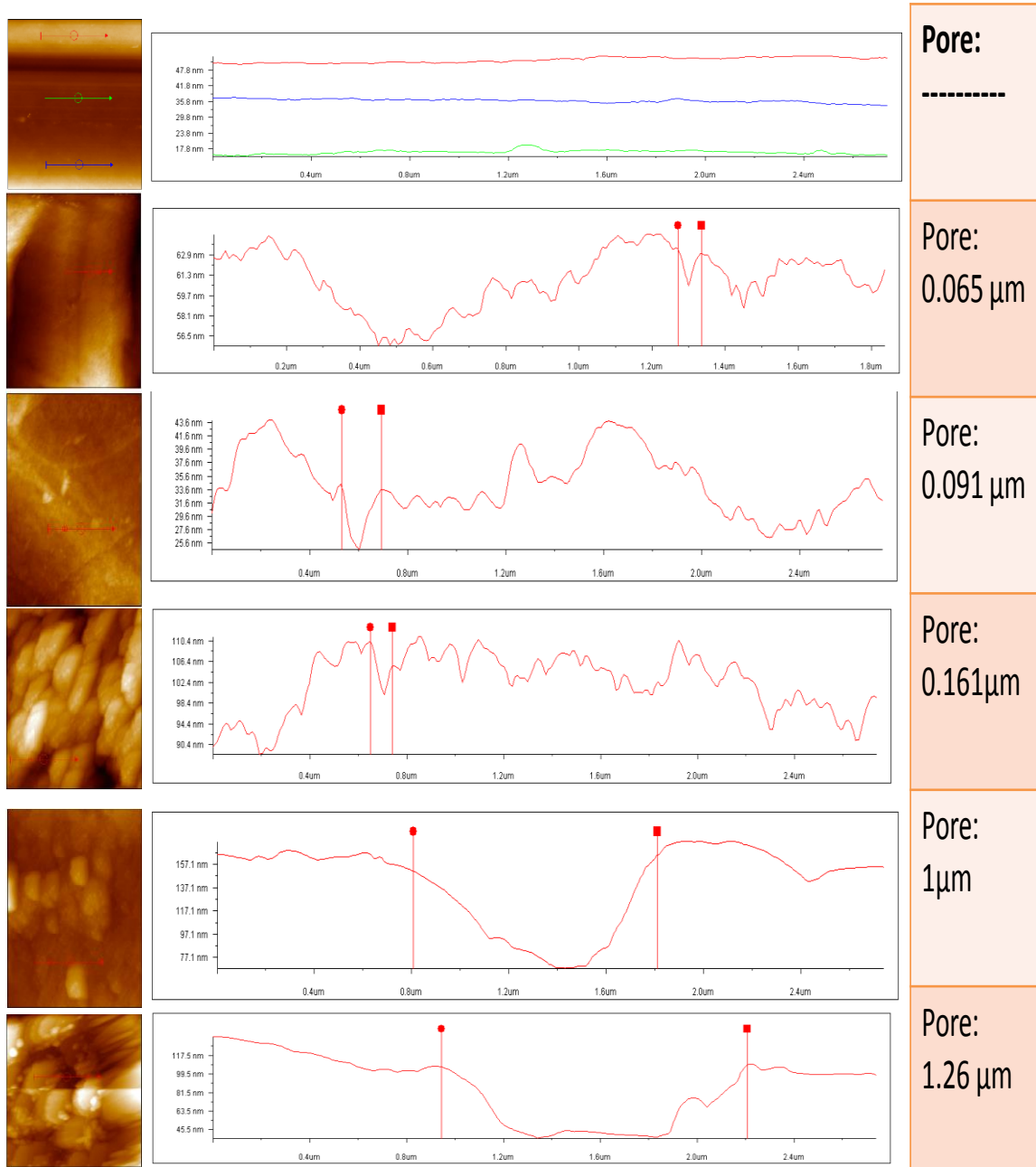


Figure17: Pore size through AFM

The interpretation of pore size of sample membrane is very important and critical for membrane efficiency as well as for flux rate permeation. Too small pore size will cause hinders and would affect the timely release of feed through membrane. On the other hand, very large pore size would cause leakage and the purpose of isolation would die. Pore size distribution and alignment of pores in the membrane are mainly

done by imaging techniques and flux rate data. The alignments of pores and pore size distribution vary with different characterization techniques.

The scan areas of membranes in the images are a mixture of bright and dark portions. The surface features are more defined in the samples “E” and “F”, where more pore gen was added in the membrane. Dig down dark portions of the images are corresponding to pores of the membrane. For pore size, one cannot rely on AFM alone. In order to get accurate information, membrane is characterized with other techniques [90].

In the following figure a comparison between SEM and AFM images is made. AFM has the benefit of its ease in operation and sample preparation. AFM can investigate membrane surface either in dry or wet environment. On the other hand, SEM cannot be used to investigate wet samples; moreover sample preparation is required for SEM which involves gold coating. For AFM operation, very small piece of sample is selected, while in SEM, relatively large samples can be evaluated [90].

Contrary to SEM, the time required to scan a sample in AFM is intensive and laborious. Other factors such as operational set up, difficulty of scanning the area, as due to roughness contact may be lost between surface and tip and the chances of tip damage due to roughness, makes the limitations of AFM. SEM operation is rather easy and fast since it involves electron beam for scanning rather than tip [91].

Thus for accurate evolution both SEM and AFM images are compared in the following figure. Both characterization images are suggesting that porosity, surface roughness, pore size distribution is increasing as we move from membrane “A” to membrane “F”. Hence it easier to conclude that chitosan is a pore controlling agent in the Cellulose Acetate membrane matrix. It can be seen in SEM image for membrane “F”, that voids and gaps are present instead of pores. The related AFM images of membrane “F” are suggesting the same voids in terms of surface roughness.

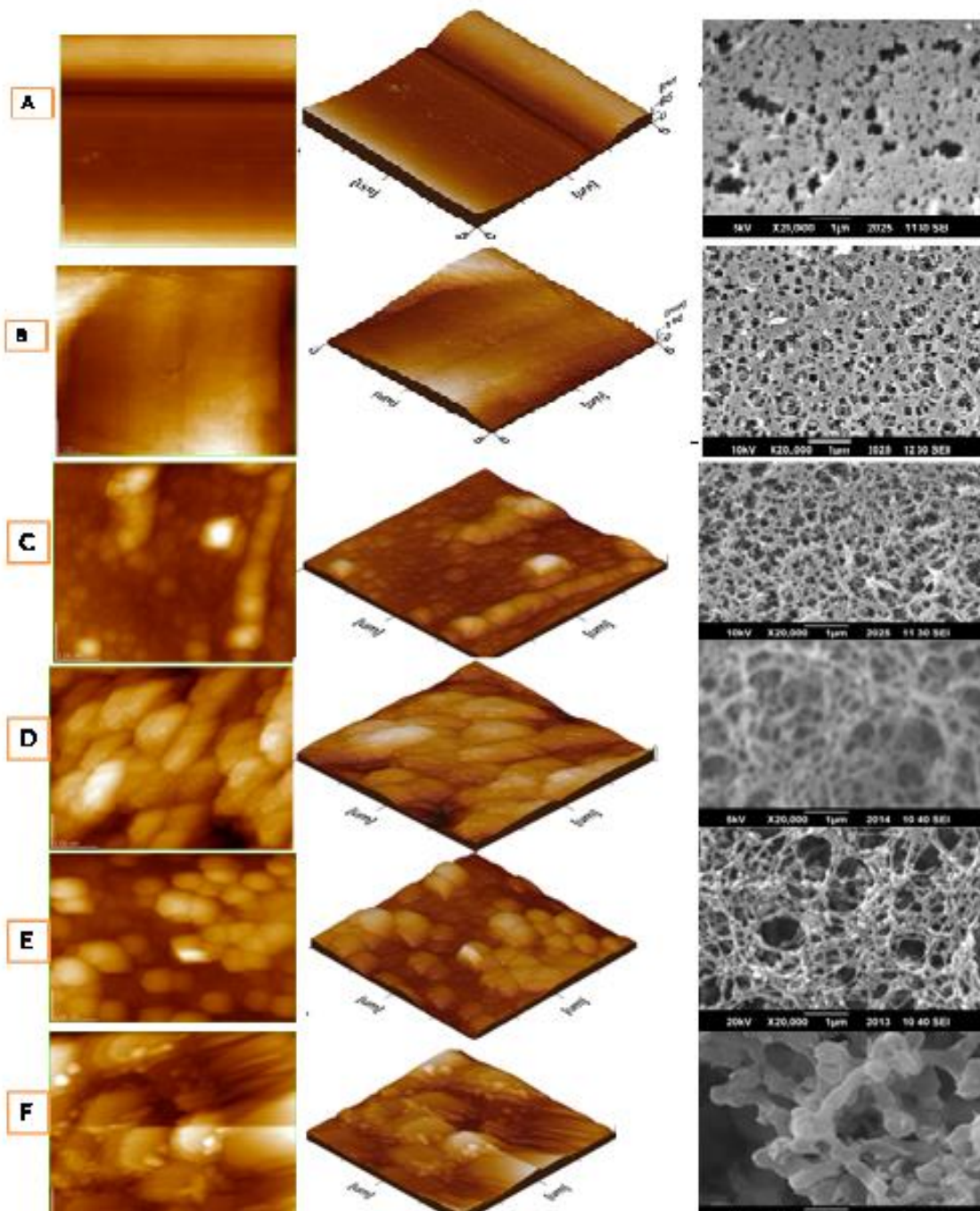


Figure18: A comparison between 2-D and 3-D AFM images Vs SEM images

5.3 Fourier Transform Infra-Red Spectroscopy (FT-IR)

The purpose of FT-IR study is to evaluate the chemical changes that are occurred during the membrane fabrication. It is quick and simple instrumental technique, which is very much effective for the functional group identification of organic compounds in particular. The peaks in FT-IR spectrum are due to the absorption of IR radiations.

The IR studies of sample membranes were done from 4000 to 500 cm^{-1} at room temperature [92].

Though the FT-IR spectra give immense help to understand structural information, it will not only explain the presence of functional groups but also clarify which groups are not present. In the present case membranes are fabricated as a blend of Cellulose acetate and Chitosan, so the FT-IR of powdered Chitosan and Cellulose acetate were done separately and then compared with FT-IR spectra of membranes. Following table shows the absorbed frequency of various organic functional groups, the data helps us to interpret the absorption spectra in the following pages.

Frequency, cm^{-1}	Bond	Functional Group
3500–3200	O–H stretch, H–bonded	alcohols, phenols
3400–3250	N–H stretch	amines, amides
3300–2500	O–H stretch	carboxylic acids
1760–1665	C=O stretch	carbonyls (general)
2260–2100	–C(triple bond)C– stretch	alkynes
1370–1350	C–H bend	alkanes
1250–1020	C–N stretch	aliphatic amines
690–515	C–Br stretch	alkyl halides

Table 5: Relative absorption range of organic functional groups

The IR spectrum of powdered Chitosan is shown below; it reveals the presence of OH Stretching and NH stretching at 3400 cm^{-1} , because a sharp peak is observed at 3400 cm^{-1} , the peak for Alkyl group can be seen less and close to 2850 to 3000 cm^{-1} , the N-H bending and NH wagging peaks can also be found. NH bending peak at 1560 cm^{-1} while NH wagging peak at 668 cm^{-1} . Further peaks are, OH bending around 1400 cm^{-1} while C-O-C stretching and bending peaks around 1,000 to 1230 cm^{-1} .

FT-IR gives no information about the structure of organic compound; it only helps to investigate the types of bonds and functional groups present.

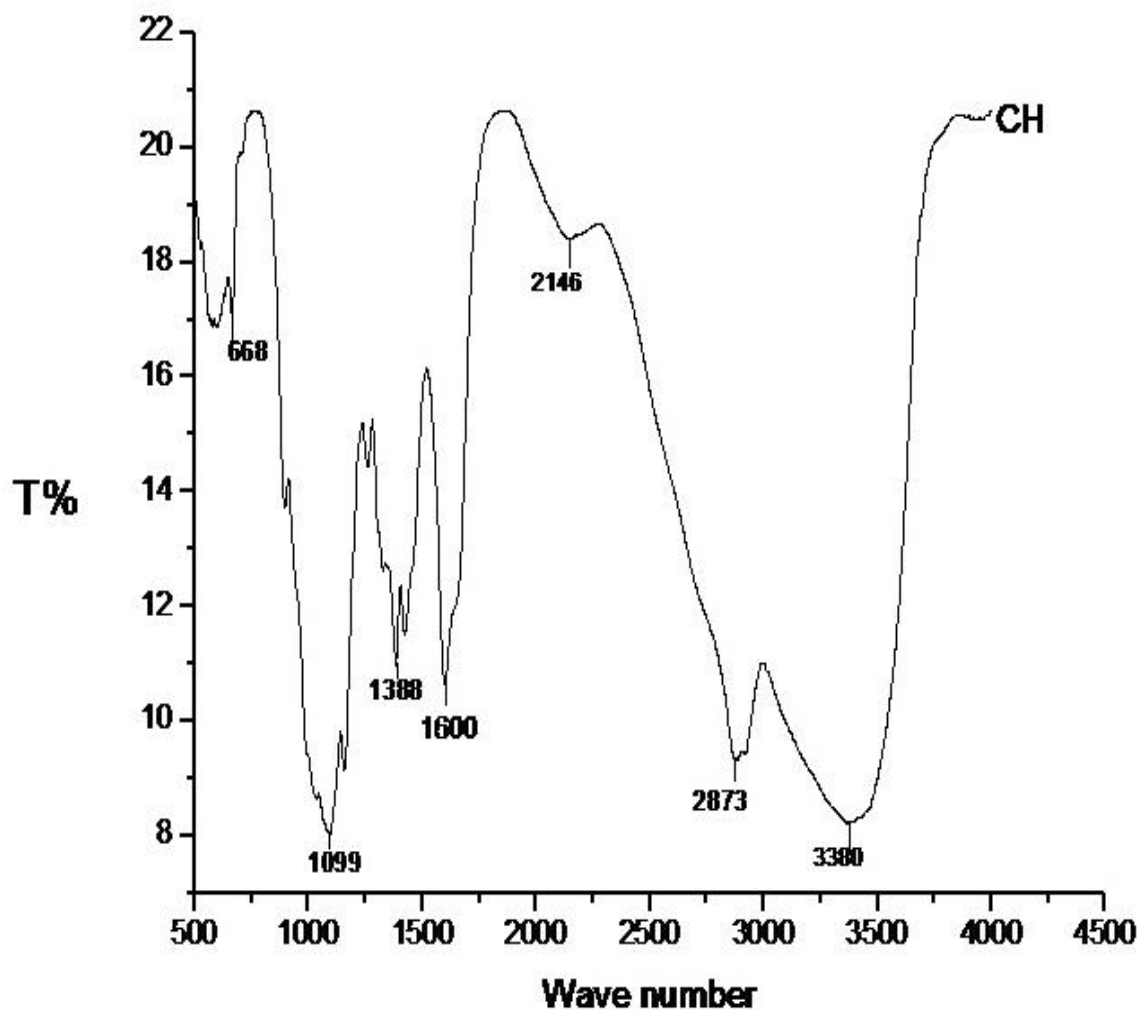


Figure 19: IR absorption spectra of powdered Chitosan

Like Chitosan, The IR absorption spectrum was taken for powdered Cellulose Acetate. The peak around 3400 cm^{-1} in CA spectrum is a broad one, while a narrow peak was seen at 3400 cm^{-1} in Chitosan spectrum. This indicates the presence of Carboxylic group/ Acetate group in CA. The alkyl group stretching is observed at around $2850\text{ to }3000\text{ cm}^{-1}$, while carbonyl group stretching is observed at around 1744 cm^{-1} . The bending peak of OH can be seen around while C-O stretching at around $1,000\text{ to }1230\text{ cm}^{-1}$. The comparison of spectra between Chitosan and CA shows that both have different functional groups. The aim of this comparison is to evaluate, the absorption spectra of membranes which comprises both CA and Chitosan.

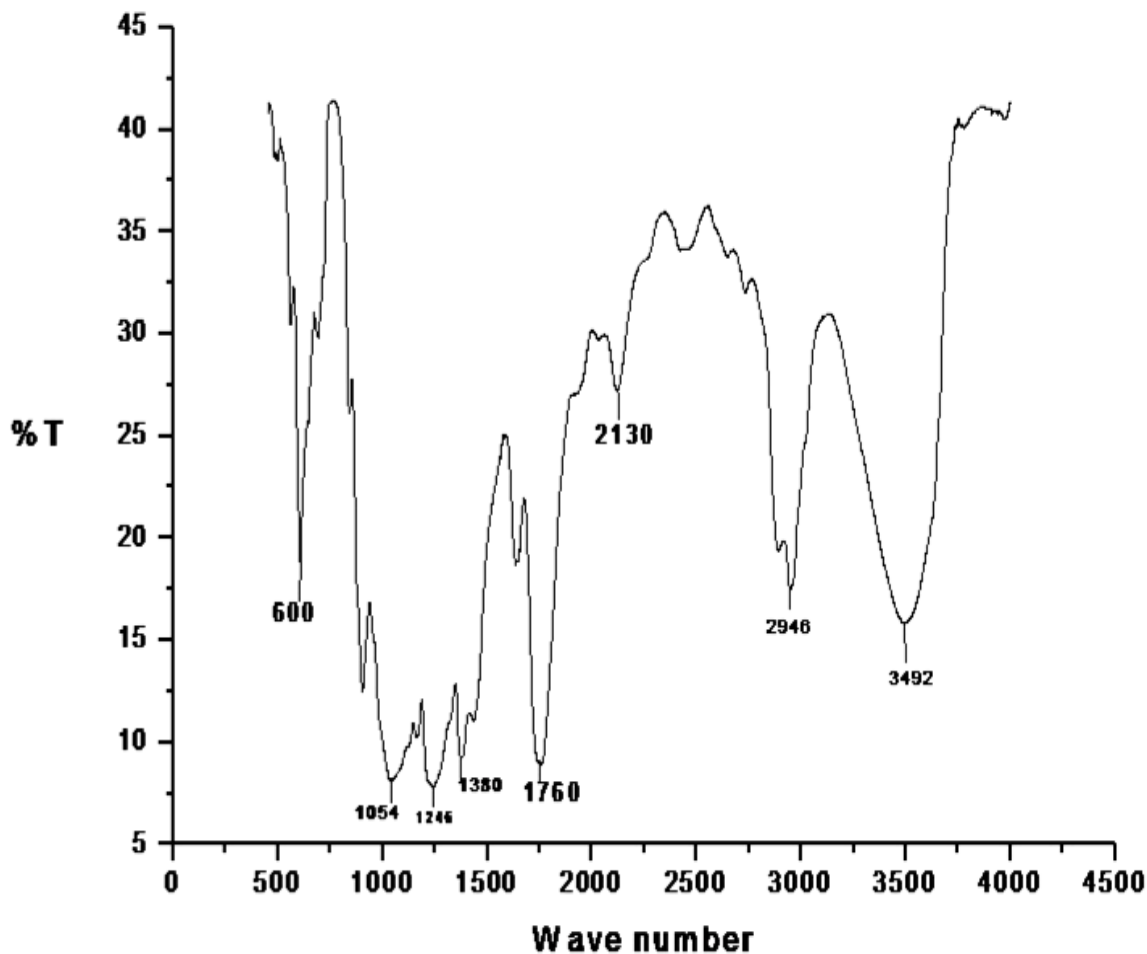


Figure 20: IR absorption spectrum of powdered Cellulose Acetate

In the current study, membrane “A” comprises 100% Cellulose Acetate, while membrane “B” is a blend of Cellulose Acetate and Chitosan. Both membranes were casted in similar solvent. Ft-IR helps us to interpret whether the precursors are completely blended or not. If intensity of particular peak is varying or a certain peak get disappear, this will lead to conclusion of complete blending of membrane material.

The figure below concludes that membrane “A” contains all the peaks possessed by CA powder, but intensities of peaks in membrane “A” is changed, this shows complete blending of polymer with solvent [92].

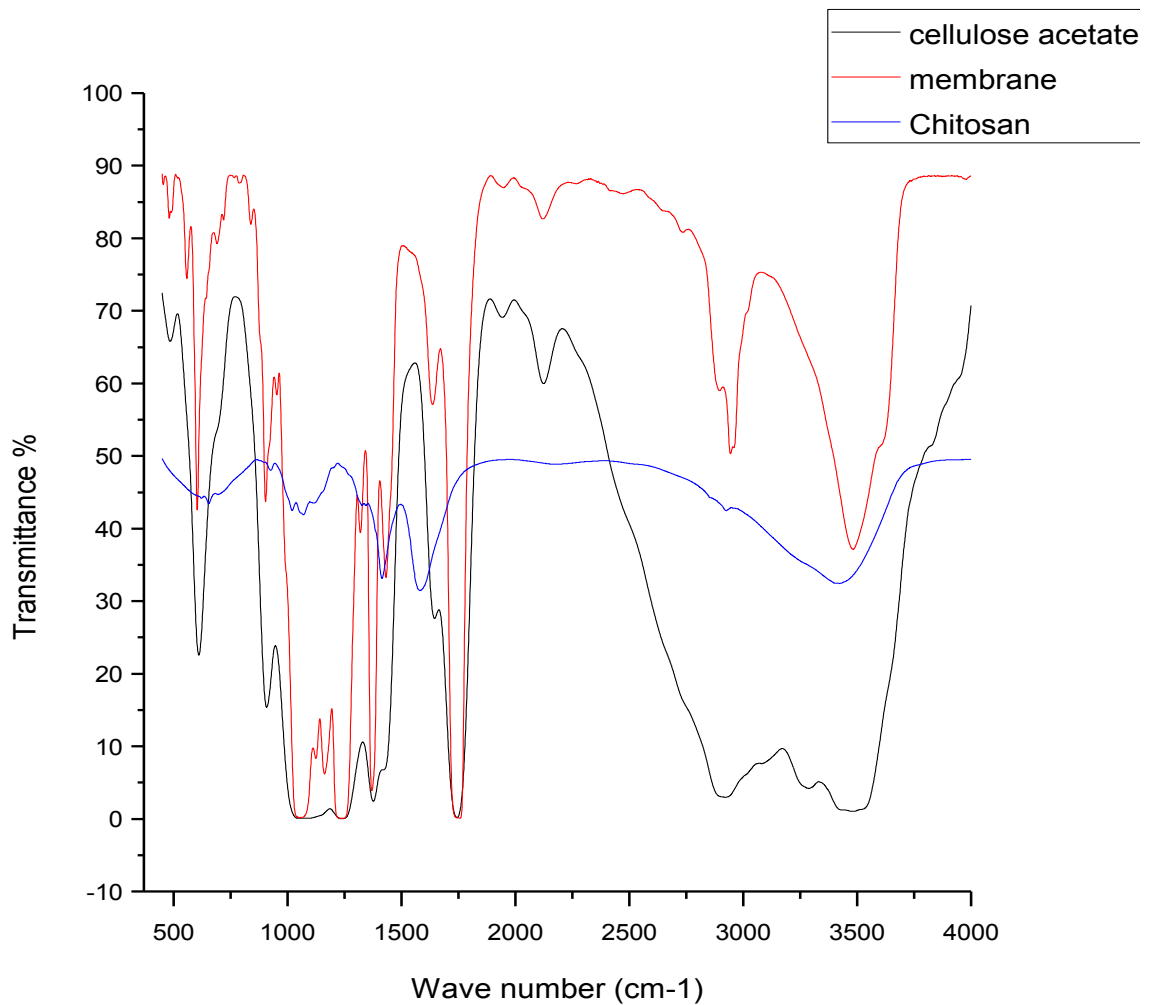


Figure21: IR absorption spectra of powdered Cellulose Acetate, Chitosan and membrane “A”

In the following figure, a comparison is made between the spectra of powdered precursors and membranes. Since membrane “A” is 100% Cellulose Acetate, its spectrum resembles with CA, however the sharpening up of the peaks around 3400 cm^{-1} and 2900 cm^{-1} indicated that CA material was completely blended with the solvent. On the other hand, membrane “B” contains slight content of Chitosan, as a result, a peak around 1100 cm^{-1} is introduced in membrane “B” which was absent in membrane “A”. This confirms that Chitosan is present and became a part of membrane “B”

All these observation leads to conclude that the pre cursors were blended completely during membrane casting.

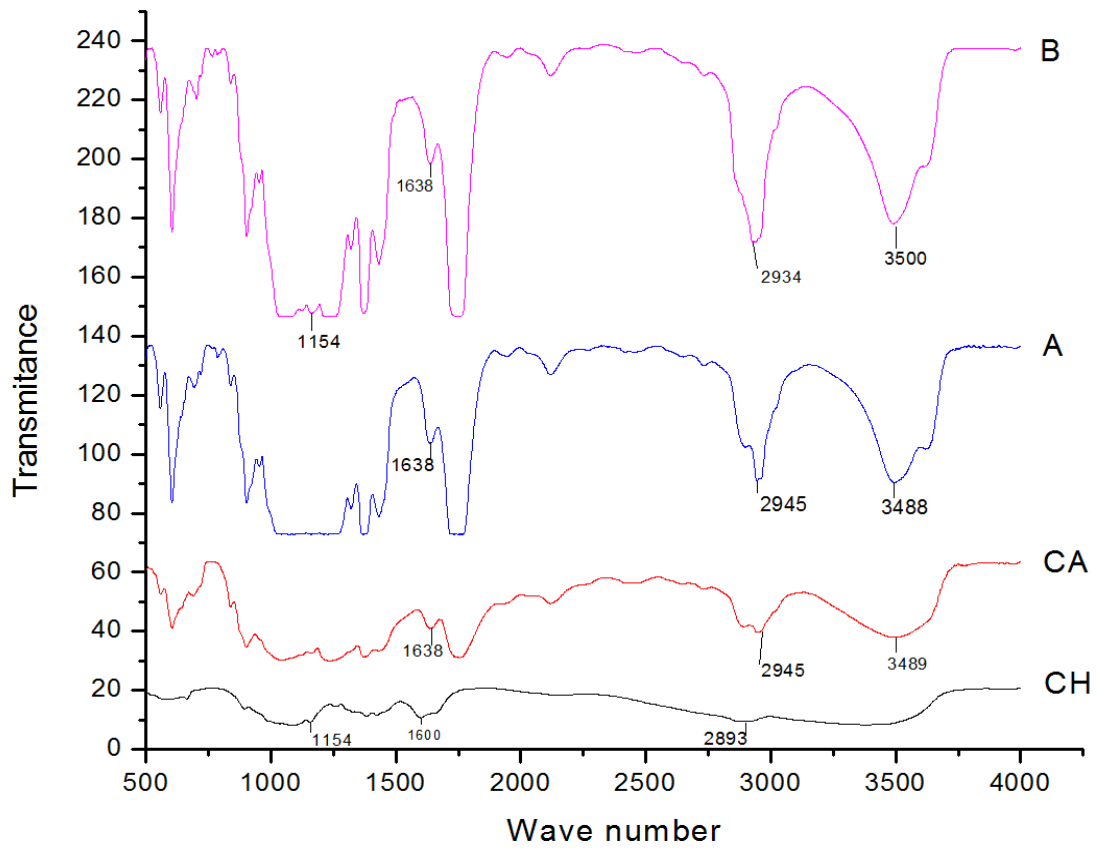


Figure22: IR absorption spectra of powdered Cellulose Acetate, Chitosan, membrane “A” and membrane “B”

In short it can be concluded from the figure below that,

All prominent peaks in both cellulose acetate and Chitosan are present in membrane spectrum, also broad hydroxyl peak in cellulose acetate become narrow and shift in Position.

Therefore, these changes in the IR spectra suggested that there is homogenous blending between Chitosan and cellulose acetate in membrane [93].

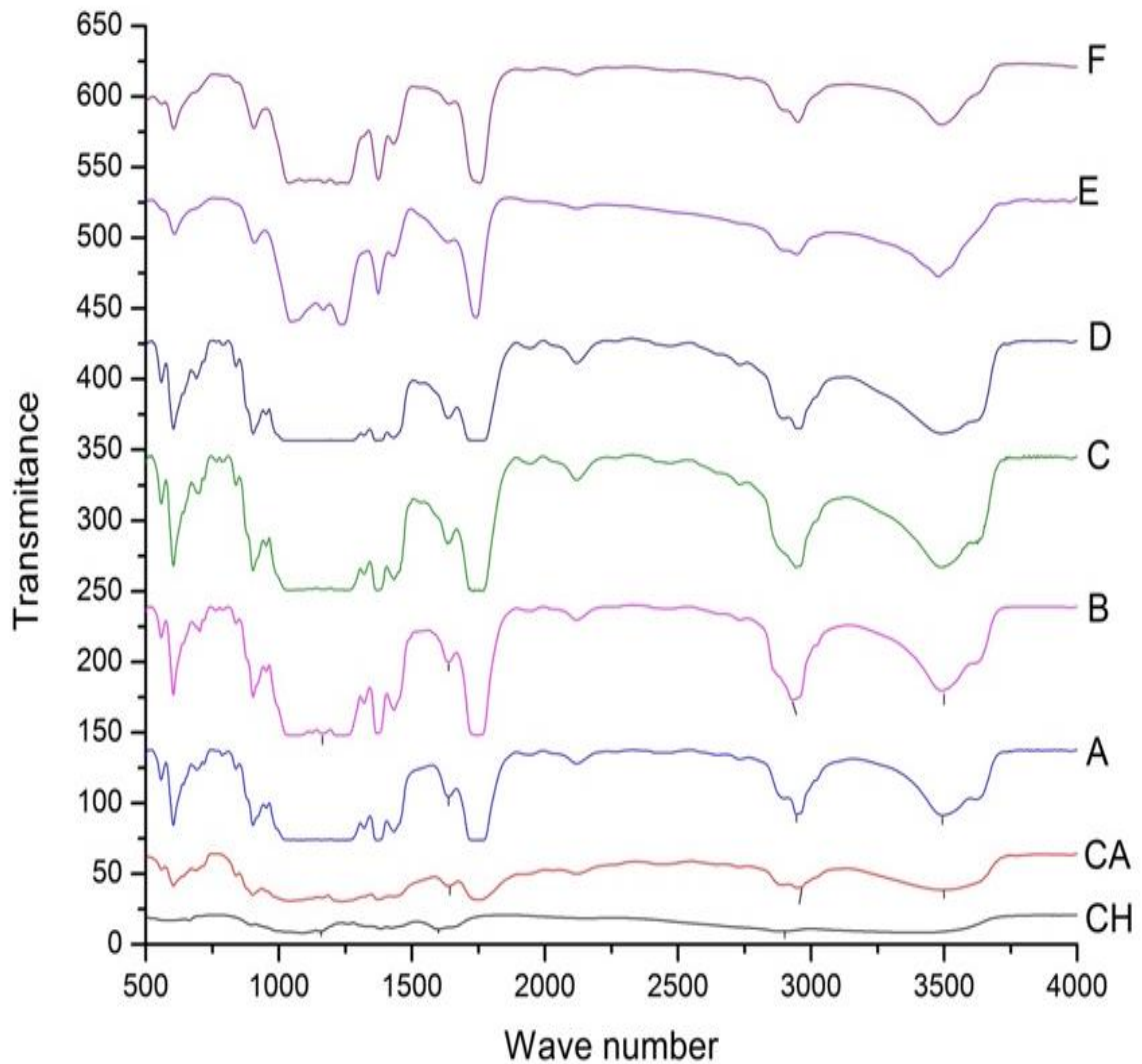


Figure23: IR absorption spectra of powdered Cellulose Acetate, Chitosan and membrane “A” to membrane “F”

5.4 X-Ray Diffraction

The purpose of XRD study of membrane samples is to determine the magnitude of crystalline in the samples. The study helps us to understand and predict, wheatear membrane is amorphous, crystalline or semi-crystalline. In the following figure XRD patterns of powdered Cellulose Acetate and Chitosan are given.

XRD pattern of Chitosan exhibited characteristic crystalline reflections at approximately 21°.

Cellulose acetate XRD spectrum indicates an obvious broad peak at 22° and this peak verified that Cellulose acetate had denser semi crystalline structure. The XRD patterns suggest that Chitosan is more crystalline than Cellulose Acetate.

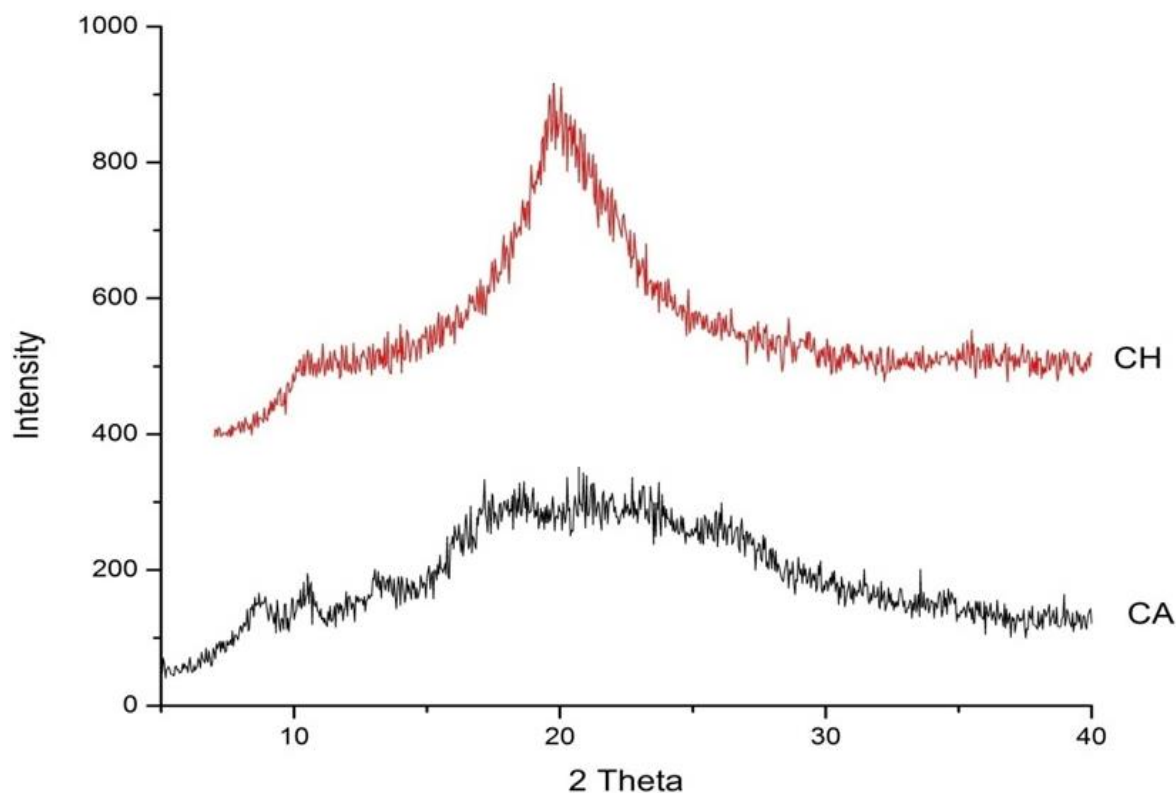


Figure 24: XRD patterns of powdered Cellulose Acetate (CA) and Chitosan (CA)

Chitosan was blended with Cellulose acetate in different proportions to form membranes. The following figure compares the XRD results of powdered Chitosan and Cellulose Acetate to membrane “A” and membrane “B”, where membrane “A” is a blend of Cellulose Acetate with the solvent only, while membrane “B” is a blend of Cellulose Acetate and Chitosan along with the solvent [94].

In membrane “A” a sharp peak at 17° shows an increased in crystalline nature of the sample membrane. Interestingly, CA powder appeared to be semi crystalline due single broad peak, but the same material, when casted as membrane is giving increase in the peak intensity. This increased crystalline behavior may be attributed as heterogeneous nucleation between CA and solvent. Due to solvent interaction, the

alignment in the CA crystals may also be increased, which results in the form of increased crystalline reflection of membrane “A” [95].

Membrane “B” on the other hand, is casted by blending CA and Chitosan in the solvent i.e. formic acid. This membrane appears to be completely amorphous. It means that Chitosan was uniformly dispersed in CA matrix. This regular and uniform dispersion cause misalignment in the planes of CA and resultant membrane turned as amorphous [96]. Remember that membrane “B” contains the least concentration of Chitosan. So it is easy to predict that CA membrane will remain amorphous if more Chitosan is added in it. For comparative description, XRD results are given as under,

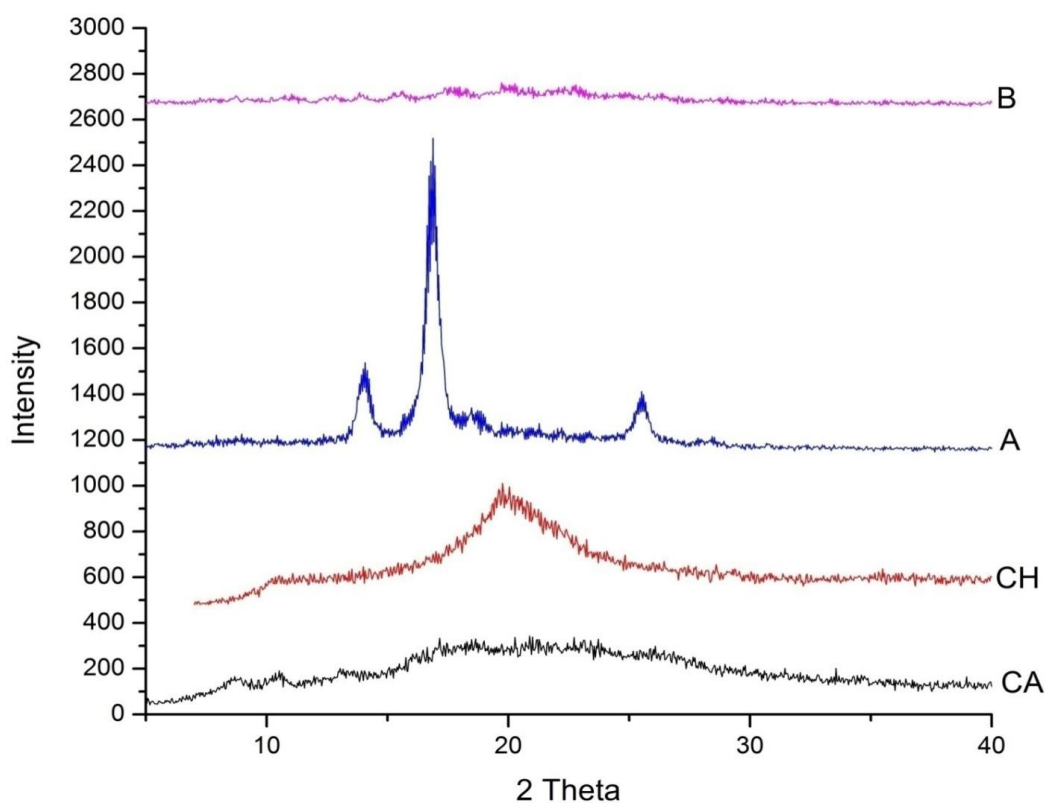


Figure 25: XRD patterns of powdered Cellulose Acetate (CA), Chitosan (CA), membrane “A” and “B”

As it was confirmed from FT-IR results that Cellulose Acetate contains the Acetate or carboxylic group i.e.-COOH, and these acetate group are very reactive. When Chitosan is made to blended with Cellulose acetate, the –COOH groups acts effectively as nucleation centre. This makes the homogeneous dispersion of Chitosan

in CA matrix possible due to reactivity with $-\text{COOH}$ [97]. Due to the same reason, membrane “B” to “F” shows amorphous nature, as shown in the following figure.

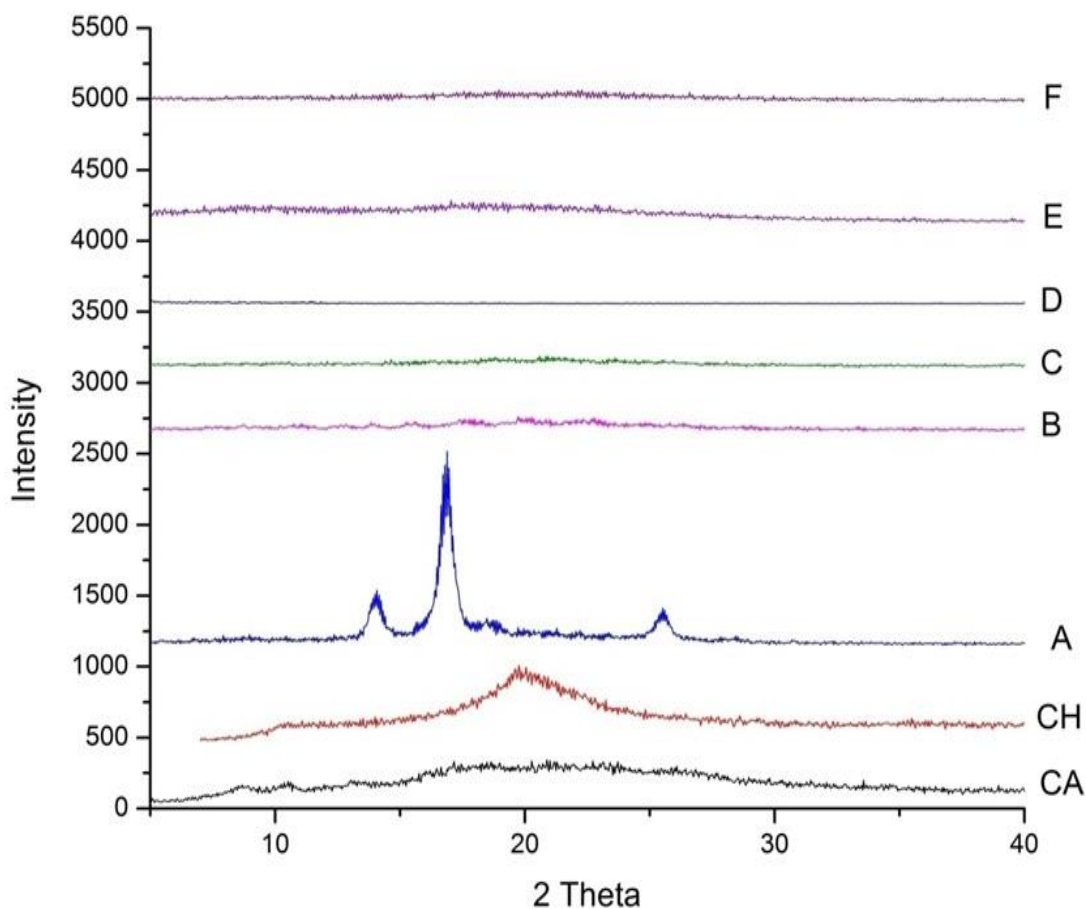


Figure 26: XRD patterns of powdered Cellulose Acetate (CA), Chitosan (CA) and membrane “A” to “F”

Membrane A contains 100% Cellulose acetate with no Chitosan content that is why it is showing crystalline character with a sharp peak. However peaks disappear in membrane B-F. This change clearly confirms successful blending of both Chitosan and cellulose acetate in membrane.

5.5 Tensile Behavior of Membrane

It is important to understand the tensile behavior of fabricated membranes, because membrane has to bear trans-membrane pressure under operating conditions. The tensile study can be used to predict the life and durability of membranes. Since Cellulose Acetate is organic polymer, the fabricated membranes were brittle in nature. Therefore, as per guidelines given in ASTM D 638-03, type V sample, membrane

specimens were made. The dimensions of specimen are given below in the figure. Tensile tests were conducted on six prepared specimens.

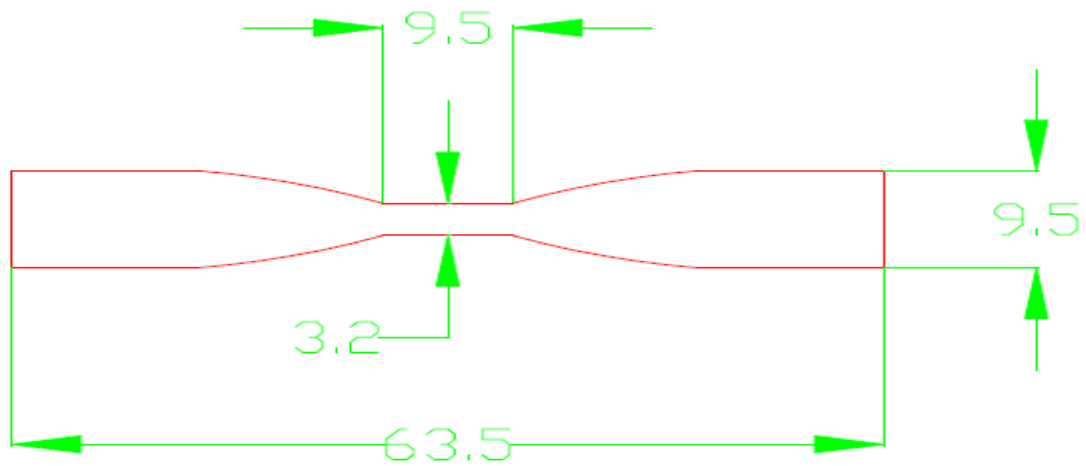
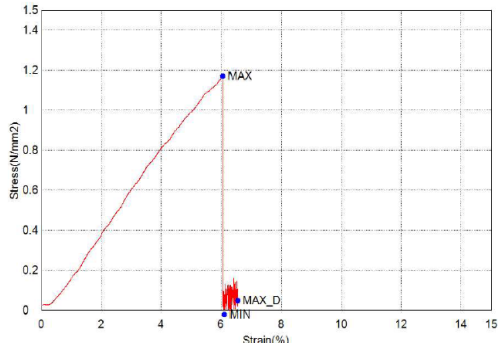


Figure 27: Type V sample

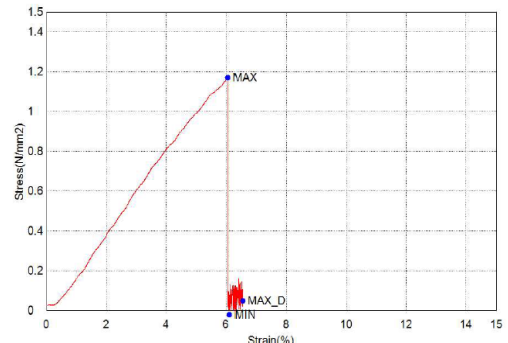
Porosity of each membrane is increased by the addition of Chitosan, this fact was justified in the characterization techniques discussed above. Increased porosity results in decrease strength. Experimental results verified the gradual decrease in strength of the membrane. Figures below show that tensile strength vigorously decreases for membrane “E” and “F”, hence use of such membranes in operating conditions become difficult. Experimentally evaluated tensile strength of each sample is presented in table below.

Membrane Type	UTS N/m²
A	1.2
B	1.2
C	1.0
D	1.0
E	0.7
F	0.3

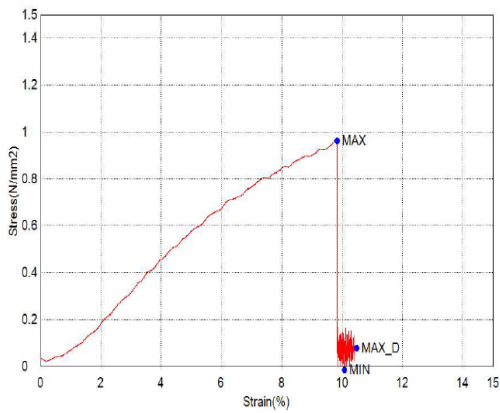
Table6: UTS of membranes



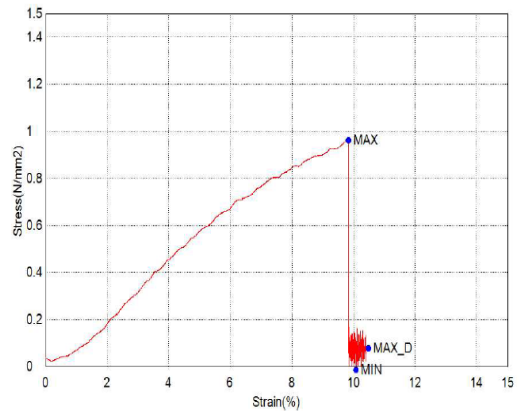
MEMBRANE A



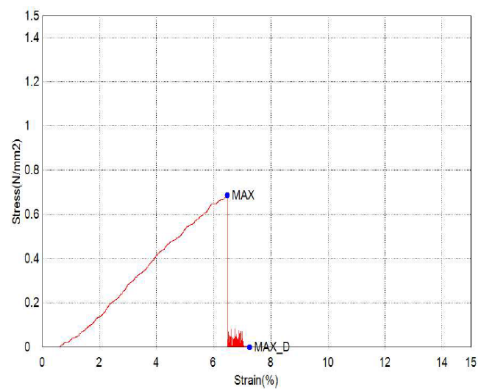
MEMBRANE B



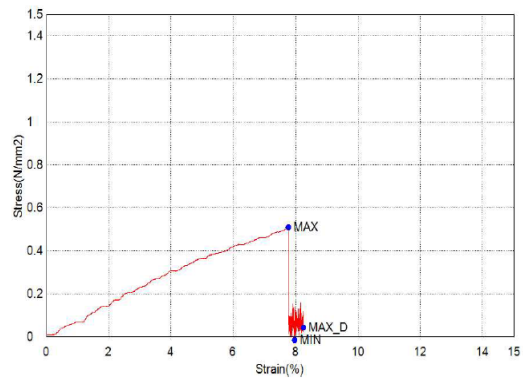
MEMBRANE C



MEMBRANE D



MEMBRANE E



MEMBRANE F

Figure28: S-S curves for membrane samples

5.6 Membrane Performance Test

5.6.1. Water Quality

Providing clean and hygienically pure water to the poor people of third world countries is a burning global issue. With the advent of industries as well as population growth, the under developed countries, especially Pakistan is facing several problems regarding drinking water. Various waste and products from industrial effluents, local sewage, contribute to ground and surface water pollution. Moreover, major part of the country has saline underground water [98]. Therefore the fabricated membranes were used to decrease water hardness.

5.6.2 Aim

Fabricated membranes were tested for tap water hardness. The total water hardness is the measure combines calcium and magnesium ions in milligrams per liter present in water. Water hardness is reported as ppm of CaCO_3 . The tap water samples were taken from National University of Science and Technology Islamabad, and hardness in them was measured by titration analysis [99].

5.6.3 Methods

Since water hardness is caused by carbonates of calcium and magnesium, so ethylene diamine tetraacetate (EDTA) is used as a reagent. EDTA forms a complex compound with both calcium and magnesium ions. Thus titration method can be used for the reaction between EDTA and water samples. One of the requirements of this titration is pH 10, so water samples were maintained at pH 10, which was achieved with $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$ buffer of pH 10. Tap water was then passed through membranes and permeate was titrated against EDTA at pH 10. The difference in hardness was the performance and efficiency of membrane [99].

Membranes	Water hardness before permeation (mg/l)	Water hardness before permeation (mg/l)	% Hardness decrease
A	300	0	0
B	300	0	0
C	300	135	55
D	300	180	40
E	300	200	33
F	300	270	10

Table7: Shows efficiency of membrane towards hardness reduction in tap water

Since membrane A and B gave no permeation because they required more pressure for permeation, and laboratory apparatus was not sufficient to provide that pressure. It is recommended for future studies that membrane A and B should be tested under high pressure. The efficiency of membrane F found to be very low for water hardness, this fact can be related to greater pore size and pore distribution in membrane F.

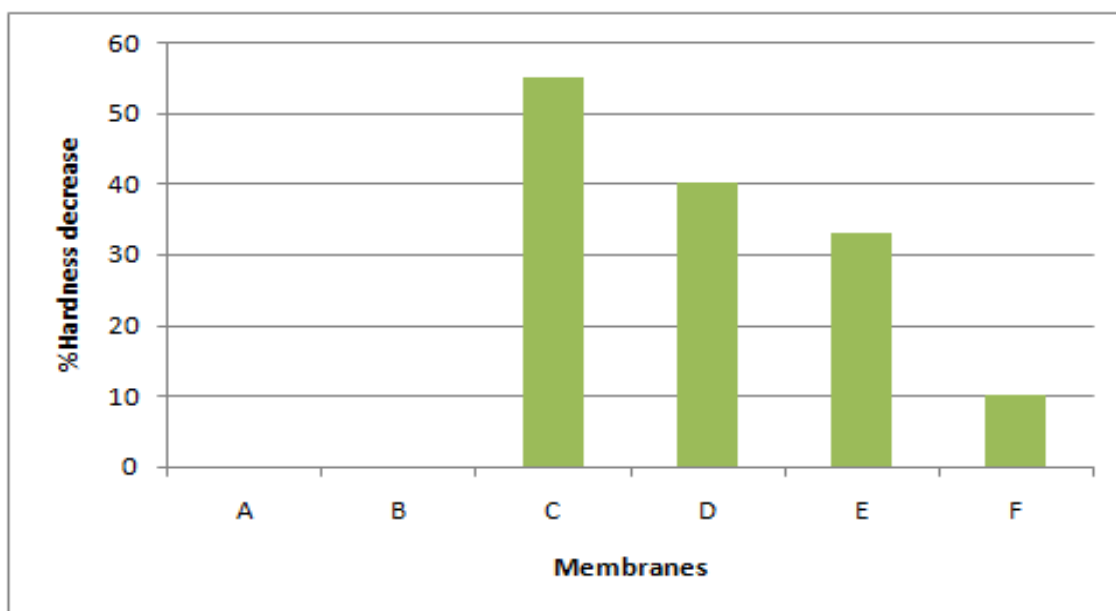


Figure29: Graphical interpretation for water hardness response

Summary

In this study, membranes were fabricated by phase inversion method. The precursors used were Cellulose Acetate and Chitosan. . In Cellulose acetate (CA) membranes, CA being the matrix material showed porosity with Chitosan (CS). It was derived that variation in concentration of Chitosan (CS) is the key to control porosity in CA membranes. Six Cellulose acetate (CA) membranes were synthesized by varying CS in each membrane and relative characteristics such as porosity and pore size were investigated. Formic acid was used as a solvent and Chitosan as a pore forming agent in membrane fabrication. Flat sheet Membranes were synthesized with phase inversion method. These membranes were characterized with SEM, AFM, XRD, FT-IR, tensile behavior, absorbed water content and pure water permeation flux. Membrane was also tested for treatment of hardness in tap water. Hard water treatment results were used for the evaluation of fabricated membranes.

Future Work

1. Fabricated membranes could be used and tested for protein separation in milk and related solvents
2. Membranes performance for separation of oil suspension, could be checked
3. Fabricated membranes contain Chitosan, which has anti bacterial action. So the membranes behavior towards bacteria removal needs to be studied.

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