Reusable Water and Mineral Recovery from Acid Mine Water Drainage Treatment Through Integration of Adsorption and Antifouling Membranes processes

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2024

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NUST-2020-328264NSE08SCME

This thesis is submitted as a partial fulfillment of the requirements for the degree of

MS in Nanoscience and Engineering

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Jan, 2024

This thesis is dedicated to *my family* ...

Acknowledgements

All thanks are due to the Almighty ALLAH, who is loving and merciful. He gave me the strength to work on this thesis because he is the source of all wisdom.

My major source of inspiration has been my supervisor Dr. Nasir M. Ahmad not only for their guidance and support in the preparation of this thesis but also in enhancing my learning in this area. His skills in reviewing my work and his suggestions contributed a lot to improving my work standards and to providing necessary laboratory facilities.

I want to thank my family for the patience and sincerity they showed. I thank my father, my mother who generated radiance to work hard and for their prayers towards my studies.

I am also indebted to Dr. Azhar Mehmood (SNS), my co-supervisor, Dr. Iftikhar H. Gul and Dr. Farhan Javaid. Their dedicated professionalism and enthusiasm for work has been a driving spirit behind the preparation of this thesis. I express my deep gratitude to Dr Amir Azam Khan (Principal SCME) for their efforts to keep the environment congenial for research and study. Mention needs to be made of all the seniors, especially Mr. Imran for valuable discussion and their time-to-time cooperation.

Abstract

Exponential growth in world population has led to the scarcity of natural resources. The most affected one is drinking water out of these natural resources. This chain reaction has produced adverse effects by fouling our natural resources of water. Due to the exponential growth of industries, concentration of heavy metals has increased. This situation can be addressed by introducing nanoparticles in the sample water that can remove hazardous contaminants from water such as viruses, metals, and nitrates. Various traditional and non-conventional methods have been in use such as reverse osmosis, nano-filtration, disinfection, using absorbents such as metals, micro-organisms, and dyes to obtain clean drinking water. This research focusses on this issue by adopting antifouling nanofiltration Polyethersulfone (PES) membrane using phase inversion methodology using Activated Carbon (AC) and Chitosan as main composites and individual fillers on the membrane matrix acting on acid mine drainage water. We have embedded nanoparticles and polymeric composites in the membrane matrix. The yield of this research is to enhance the antifouling behavior as well as flux and salt rejection. These membranes were embedded with concentrated PES, PES with 0.75% chitosan and 0.25% AC, 1.25% chitosan and 0.75% AC and 1.75% chitosan with 1.25 % Activated Carbon. To achieve high efficacy of the adopted methodology, diverse characterization techniques have been opted explicitly Scanning Electron Microscope (SEM), Fourier Transform Infrared (FTIR) spectroscopy, Antibacterial analysis, contact angle measurement, salt rejection, water retention, flux measurement, and mechanical testing. A comprehensive comparison of the acid mine water has been presented in this aspect. The results have clearly indicated an increase in the amount of porosity channels of the membranes having chitosan/AC as composites that explicitly demonstrates higher permeability. The results indicated an increase in water flux from ±4.56 $mL.cm^{-2}.h^{-1}$ to ±17.5 $mL.cm^{-2}.h^{-1}$. This rush in the values and decrease in contact angle ±66° to ±50° values clearly demonstrate that membranes became hydrophilic in character. Similarly, removal capacity for phosphate (99.99%) nitrate (99.80%) and ammonia (66.5%) contaminants were yielded. Tensile strength for PES membranes embedded AC and chitosan showed 4 times more strength as well. Bacteriostatic rate for E. coli and S. aureus bacteria has increased from 52.63 to 90.67.

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List of Abbreviation

CNT	Carbon nanotubes
Acid Mine Drainage	AMD
PES	Polyethersulfone
WHO	World Health Organization
UN	United Nations
SEM	Scanning electron microscopy
ATR- FTIR	Attenuated Total Reflection Fourier Transform Infrared spectroscopy
Nm	Nanometer
C	Celsius
Ml	Milliliter
Ml	Microliter
G	Grams
Sec	Seconds
Rpm	Rotations per minute KBr
P	Membrane code for PES
PCH	Membrane code for PES embedded with chitosan
P-CH-AC	Membrane code for PES embedded with chitosan and Activated Carbon
AFM	Atomic Force Microscopy
S_r	Surface Roughness
EM	Elastic Modulus
UTS	Ultimate Tensile Strength

Chapter 1: Introduction

1.1 Background

Depletion of natural resources is an ever-growing challenge for our current and future generations. There are many factors contributing to this cause explicitly exponential growth in population, commercialization, urbanization, technological advancements, and others. While earth is covered with 72% water, only 0.5% water is available for human consumption [1]. Oceans, glaciers, and mountains are the principal storage system. 30% ground water accounts for fresh water, while other sources such as lakes, streams and rivers provide just 0.26%. Not only water scarcity is the issue, water contamination that is leading to severe diseases is also becoming more and more challenging. Water should be prerogative for all life on earth, especially human beings [2]. Especially country like Pakistan in which water quality is ranked 80 out of 122 countries is a worrisome situation. This poses serious challenge to us and especially in an underdeveloped country like Pakistan.

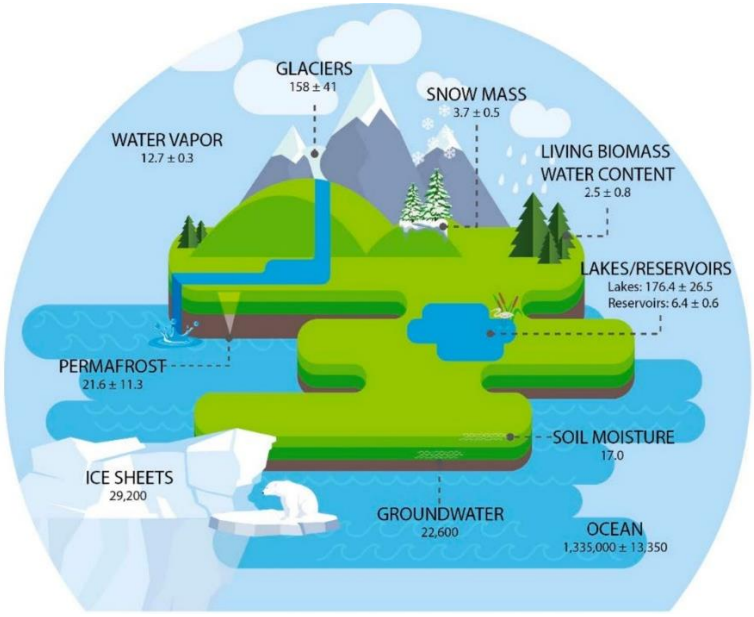


Figure 1.1 Composition of Earth's Water

1.2 Critical Water Situation in Pakistan

In our country industrial waste does not go through proper waste management procedures and as a result it gets mixed up with our natural resources, especially water. Other natural

resources and our fertile land also gets affected by these waste materials [3]. Nitrate abundance in our drinking water may cause blue-baby syndrome, which results from the conversion of hemoglobin into methemoglobin, which is incapable of carrying oxygen. This contaminated water is causing high mortality and morbidity rate whilst causing diseases such as cholera, typhoid, and hepatitis [4].

1.3 Nanomembrane Technology: Vital to our Existence

Depending upon the total dissolved solid concentration, water can be categorized into brine, brackish, fresh, and saline [5]. Cleansing AMD water through natural processes could take decades. Scientists and researchers have done quite remarkable work in this regard but there is still a lot of work that can be done to optimize this problem. Transformation of such hazardous water into portable drinking water could serve human species [6]. Several heavy metals and metalloids affect our drinking water that needs to be purified on an urgent basis. Significant results can be obtained by introducing nanoparticles that remove viruses, solutes, metals, nitrates, and other hazardous contaminants. Some of the sulfide's that are abundant in AMD water are listed in Table 1. There are several passive sampling devices being employed in our research and industries to eradicate these issues [7]–[10]. These compounds can investigate and remove pollutants from hydrophilic as well as semi-hydrophobic compounds. Their configurations can vary from simple ones to sandwiched ones, in which two microporous polyethersulfone (PES) membranes are held together by some alloy. Chemicals from the water get absorbed on to the sorbent phase. It is a multi-phase mass transfer process in which first the analytes get diffused and then sorbents. Besides their structural functionalities, the membranes also prevent the amalgamation of the receiving phase and environmental matrix. Membrane also enables the extension of kinetic regime by slowing down the diffusion from water to receiving phase. After the accumulation of contaminants, there are three phases that follows, first kinetic, then pseudo linear and finally equilibrium portioning phase [11].

There is a plethora of research data available that indicates the effectiveness of chitosan and AC in absorbing contaminants from wastewater [12]. Chitosan intrinsically has both cationic and anionic moieties that enable it to absorb pollutants from acid mine drainage water. AMD water is the root cause of various diseases that are increasing exponentially

due to the formation of acid lakes. Humans encounter these diseases either through direct or indirect contact. Conventional methods such as chemical precipitation, coagulation, filtration, solvent extraction, ion exchange and membrane methods have been rendered mostly less efficient because of heavy metals that are difficult to be separable [13]. Therse metals and metalloids are effectively being removed from water through activated carbon and several raw materials have also been employed for the purpose of neutralization of pH of water. Such drastic conditions demand drastic measures as well. Chitosan combined with PES membranes plays a significant role owing to biodegradability and biocompatibility factors. Furthermore, its performance can be brought into an even more impressive arena by using fillers like carbon nanotubes (CNTs) [14]. CNTs have great electrical, mechanical, and optical behavior that in turn improves the performance of the process. Some of these nano materials are defined in Table 1.1. Other conventional methods that are being employed include chlorination, chemical treatment, and membrane filtration [15]. Chlorination and chemical treatments have drawbacks such as byproducts that need to be processed before they can be used again [16].

Table 1.1 Sulfide Minerals in AMD Water

Sulfide Minerals	**Composition**
Pyrite	FeS2
Marcasite	FeS2
Chalcopyrite	CuFeS2
Chalcocite	Cu S2
Sphalerite	ZnS
Galena	PbS

1.4 Problem Statement

My motivation is to provide clean drinking water to the masses and based on this motivation I have based my research. I have employed membrane technology accompanied with composites that remove the waste agent from water and provide some critical industrial resources as well. Cost effectiveness, flexibility and high removal capacity has led membrane technology to be highly employed by the researchers. Its modular design, energy efficient, and environment friendly with minimal chemical usage. They are made

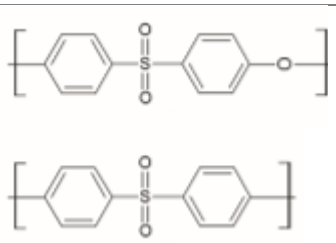
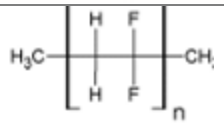
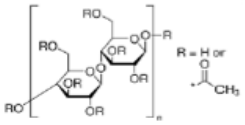
of inorganic or natural materials that improve their effectiveness in the treatment of AMD water.

1.5 Research Structure

1.5.1 Phase-I

This research is based on treatment of acid mine drainage water and recovery of important minerals through adsorption and antifouling membrane process. Producing water with absorbent can purify it [17]. The only drawback of this technique is membrane fouling. This results in adsorption and deposition of multi agents such colloids, macromolecules, and biomolecules (e.g., polysaccharides, enzymes), salts and others. These agents have caused high problems in separability during filtration process and have resulted in reduction of membrane life. Fouling is the direct result of hydrophobicity of membrane materials. This dilemma has been overcome by tailoring membranes to possess certain properties such as antifouling, hydrophilicity, photodegradation and others. In this research membranes have been embedded with AC and chitosan composites that overcome all these issues and remove contamination from water. These modified membranes work on the principle of adsorption and repel certain protein agents. Industrial applications of membrane technology include desalination by reverse osmosis, wastewater treatment, lithium-ion batteries, and membrane-based fuel cells. Membrane materials that have been widely employed in research are cellulose acetate (CA), polyether sulfone (PES), polysulfone (PS), polyacrylonitrile (PAN), and polyvinylidene fluoride (PVDF) [18]–[21]. Membranes need to possess certain properties to achieve requisite objectives such as anti-fouling resistance, mechanical strength, high permeability, and selectivity as well as robust control of pore size over entire surface area. These attributes, if optimized fully can eventually reduce maintenance and ensure sustainability of the process as well. PES based polymeric membranes have shown much better thermal, oxidative, strength, and other properties in comparison to others [22]. Comparison of chemical structure and their attributes of various membranes are as follows:

Table 1.2 Comparison of Various Polymeric Membranes

Polymer	Chemical Structure	Advantages	Disadvantages
PES and PSU		• High thermal and chemical resistance. • Chlorine resistance. • Mechanical Flexibility.	• Low operating pressure limits. • High hydrophobicity.
PVDF		• High thermal and chemical resistance.	• Hydrophobicity.
CA		• Hydrophobicity. • Low cost. • Flexibility in fabrication.	• Low thermal and chemical resistance. • Prone to microorganisms.

1.5.2 Phase-II

Composite hydrogels were prepared for this purpose by wet-casting process by mixing biopolymer such as chitosan with activated carbon. Experimental setup was established in such a way that adsorption properties of these hydrogels were utilized by using different concentrations within membrane matrix [23]. Furthermore, to achieve high efficacy of the adopted methodology, diverse characterization techniques have been opted explicitly Scanning Electron Microscope (SEM), X-ray Crystallography (XRD), Fourier Transform Infrared (FTIR) spectroscopy, Atomic Force Microscopy (AFM), Antibacterial analysis, contact angle measurement, salt rejection, water retention, flux measurement, Thermogravimetric analysis (TGA), Zeta potential, Atomic Force Measurement (AFM) and mechanical testing. In addition, various industrial raw materials have also been obtained as by products such as sterile aggregates (serpentinite, andesite), industrial rocks (magnesite), and other natural and organic materials (peat and biochar) [24], [25]. This process has been depicted in the figure below.

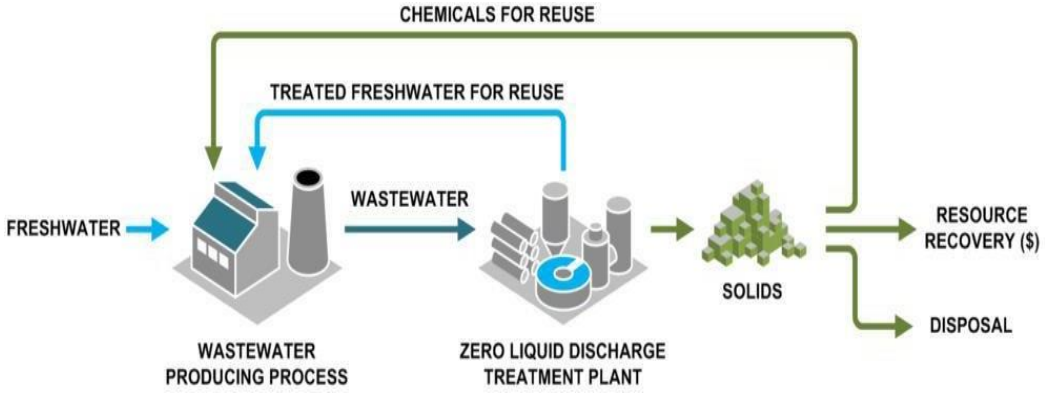


Figure 1.2 AMD Water Treatment Process

Conventional methodologies such as ultrafiltration, reverse and forward osmosis, nanofiltration and others have been widely employed antifouling techniques to elucidate the nitrates and waste particles from water [26], [27]. To conduct our research, model water based on acid mine drainage must be prepared that can be yield through passive fouling resistance, fouling release, active off surface and on surface techniques [28]. One such approach has been opted in our research that can eliminate fouling substances such as nitrate, phosphate, and ammonia, will be discussed thoroughly.

Table 1.3. Nano Technological Methods

Process	Nano Materials	Properties
Absorption	Carbon Nano-tubes	High absorption rates and exponential in cleaning process
Disinfection	TiO_2	Robust and efficient
Photo catalysis	Nano-TiO_2	Effective Photocatalysts, economical and high photo-activity
Membrane	Magnetite	Low toxicity and cost effective

1.6 Aims and Objectives

Following are main aims and objectives of this research work:

• Fabrication of polyethersulphone membrane

• Fabrication of Chitosan and Activated Carbon composite membrane

- Characterization of Fabricated membranes
- Aim of fabrication of composite membrane is to increase

I. Permeability flux
II. Hydrophilicity/ Wettability
III. Salt Rejection Enhancement
IV. Anti-Fouling Membranes

Chapter 2: Literature Review

2.1 Membrane Technology

Acid Mine Drainage Treatment systems have been investigated for quite some time. Many researchers and industrial projects have been dedicated to overcoming this challenge. This research emphasizes that matter and investigation has been done comprehensively to devise a better solution for this problem. This section will focus on the achievement and results evaluated by researchers to optimize AMD water treatment.

In [29], Jainesh and Murthy have published a comprehensive review on anti-fouling nano composite membranes under pressure driven membrane process. Their research highlights the underlying problem in membrane fouling, modified polymer membranes, interfacial polymerization, surface reaction and nanoparticle bending procedures are discussed. Their research overestimates the importance of membrane technology over traditional particle removal methods but also iterates the excessive use of membrane technology can also cause fouling behavior that is unwanted for water purification process. As we all know this fouling behavior is the cause of adsorption of colloids, particles, biomolecules and other proteins and salts. Their research has adopted an anti-fouling method that uses tailored membranes instead of regular membranes to overcome this problem. They have incorporated TiO_2, SiO_2, Al_2O_3, Si and carbon nanotubes. Their research concludes that pressure driven processes such as MF, UF, NF and RO based membranes have a high fouling tendency. By using metal oxide nano particles hydrophilicity of membranes can be increased. TiO_2 based composites have shown higher performance than others. Furthermore, MOFs are also one of the emerging materials deployed for the same purpose.

Another research article [30] written by Abdel Karim and et al, have reviewed modified PES membranes prepared by blending method for AMD water treatment. Their research work sheds light on the modification of polyethersulfone membranes using blending methods to achieve optimum results. According to this paper blending methodology has gained much attraction in industry than other traditional and heuristic methods. Objective of these membranes is to achieve higher water flux, porosity as well as try to improve the fouling parameters of the membrane. This can be achieved using PES membranes as they show chemical stability, thermal stability, and other properties such as oxidation. However,

these membranes are also susceptible to membrane fouling, so to overcome this catastrophic issue researchers have opted for blending PES membranes with different hydrophilizing agents. Their research has concluded that to achieve optimum performance, hydrophilic additives such as PVP or PEG, PES membranes can be rendered more effective for purification of water. However, there is also a catch that these additives can be unstable as they can be easily dissolved in water. So, this issue was eradicated using amphiphilic additives to provide resistance against protein adsorption. Their research also concluded that by opting for nanoparticles-based additives, mechanical, thermal as well as other characteristics of PES membranes can be improved further.

An interactive case study has been conducted namely, Polyethersulfone membranes in polar organic chemical integrative samplers. In this study, preparation, characterization, and fabrication of such membranes have been discussed, there in [31]. The advantage of adopting such a technique is that enclosed integrative samplers protect them from coming into direct contact with the environment matrix. By slowing their diffusion between the water and receiving phases, the extension of kinetic regime of contaminant uptake is enhanced. Furthermore, they have also shed light on the various designs and morphologies of membranes. In addition, they have also provided comprehensive data on alternate membrane manufacturing. Their research concludes that hydrophobicity and charged functional groups affect the PES material, so they must be properly modified selection of such membranes as well is crucial in purification of water.

2.2 Membrane's Classification

This research is based on the removal/adsorption of nitrate components from water to make it purified. One similar research based on PEG-Chitosan and PVA-Chitosan polymer composites has been done by Rajeswari et al [32]. They conducted a series of experiments to study the effects of contact time, adsorbent parameter, and pH of the model solution. They successfully removed nitrate from aqueous solution at pH 3. Their models are confined with Langmuir and Freundlich models. Adsorption rates of PEG-Chitosan and PVA-Chitosan membranes were discovered as 50.68 and 35.03 mg respectively. Furthermore, several characterizations were carried out on the samples such Scanning Electron Microscope, Energy dispersive analysis of X-Rays (EDAX), Fourier Transform

Infra-Red (FTIR), BET and X-ray Diffraction (XRD). The results clearly indicated the efficacy in removal of nitrate ions from model water. Positive values of H^o were detected, indicating endothermic nature of adsorption process. Similarly negative values of G^o at various temperatures demonstrated the spontaneous nature of nitrate on to the composites. Positive value of S^o demonstrates affinity of nitrate ions to PEG-Chitosan and PVA-Chitosan membranes. According to Pseudo-order kinetic, the adsorption capacity of PEG-Chitosan was found to be 50.68 mg higher than its counterpart PVA-Chitosan (30mg).

Anti-fouling is one of the core characteristics of a membrane to achieve purification of water. It must be within the DNA of nano membranes to be anti-foulant. This behavior has been further investigated by Hasan, Zuki and other researchers [33]. They have exploited Chitosan and Powder Activated Carbon composites for this purpose. This experiment was conducted in combination with Polyethersulfone (PES), Chitosan and PAC and the performance was evaluated using various characterization techniques. Various concentrations of PES, Chitosan and PAC were taken, and composites were prepared. These membranes were then further evaluated on river water to examine their effectiveness. Membranes were modified in terms of roughness, surface morphology, functional groups, swelling ration, wettability, and contact angle. Results showed tremendous increase in water flux with increase concentration of chitosan, specifically 0.1%(w/v) (7.36 mL/cm^2) to 1% (w/v) (9.46 mL/cm^2). Water flux increased to a certain extent after that it decreased the water flux to 5.30 mL/cm^2 at 2% (w/v). Also, PAC modified membrane flux was measured to be 6.86 mL/cm^2 which was slightly lower in comparison to un-modified membrane (7.36 mL/cm^2). Chitosan embedded membrane reduced the coliform bacteria to 28% while chitosan-PAC-modified membrane reduced 45% of total coliform bacteria. Thus, the results validated the claim of enhancing anti-microbial resistance of PES membrane by employing chitosan-PAC composite. This research will help in the treatment of water by enhancing anti-microbial resistance. In terms of membrane hydrophilicity, coating membranes did not have significant impact as water contact angle dropped from 78.8^o to 51.2^o. Their cost-effective approach has enabled them to employ these membranes commercially as opposed to other costly fabricated membranes. Further enhancement of these membranes will help in achieving more significant results.

Digging into further research, several papers have been published to exploit the anti-foulant properties of composite membranes incorporated with Activated Carbon, Chitosan and Thiolated Chitosan to enhance the core characteristics such as hydrophilicity, mechanical strength, water flux, contact angle and others. This research is done by Samia Nayab et al of National University of Science and Technology [34]. Membranes selected for this purpose were fabricated at 16% and 20% wt., using Phase Inversion methodology. Experimental setup was conducted on isolated chitosan and AC and then on composites comprised of them. A novel composite consisting of thiolated chitosan/activated carbon was employed in the polyethersulfone matrix to conduct this research which aims at purifying water from acidic and other harmful substances. To validate the claim several characterization techniques were adopted such as Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR), optical profilometry, gravimetric analysis, Scanning electron microscopy (SEM), mechanical testing, water retention and contact angle. SEM showed better channels for thiolated chitosan/activated carbon composites that clearly demonstrate better permeability, and it is further validated by water flux results. Bovine serum albumin flux was also assessed, and their results were quite impressive as it showed an increase from 105 L/m^2h to 114 L/m^2h in water flux and anti-fouling tests conducted also showed better performance in flux that is 51 L/m^2h. Furthermore, water retention tests also demonstrated water uptake increased volume from 22.84% to 76.5% and contact angle from 64.5 to 55.7 degrees. Pristine PES membrane showed lower mechanical strength as compared to their other composites as it is more soluble in water. All these results concluded from their research showed that anti-fouling membrane technology has an upper hand in purification of water from harmful substances. Surface roughness of PES-Thiolated chitosan-AC at 2690nm increased by 20%.

2.3 Filtration Techniques using nanomembranes:

The aspiration of membrane technology comes from the origin of biological reactions in the human body. Exchange between tissues and cells inside many organs to prevent certain particles from passing through while blocking others. Red blood cells act as catalyst to this process known as ultrafiltration [35]. The first commercially prepared membranes were developed from ethyl cellulose, cellulose acetate, and cellulose. Hence completely organic

and as a result they are cost effective as well. Membrane technology as discussed is one of the most efficient and economical, that has been widely employed and inducted in research and development [36]. Membrane technology classification has been demonstrated in Figure 2.1.

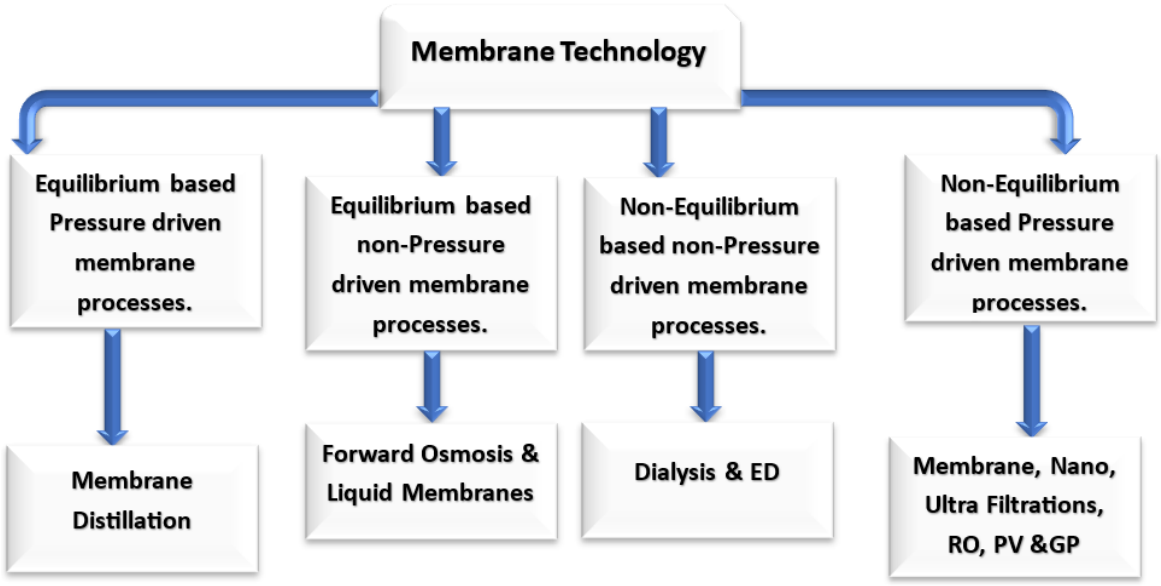


Figure 2.1 Membrane Technology Classifications

Ultrafiltration is also one of the highly employed water treatment processes that grants the removal of multivalent ions and organic molecules. But it can cause severe membrane fouling due to which antifouling compounds have to be introduced in our methodology. PES consists of hydrophobic polymer structure that contains units of phenylene rings that are in turn linked with sulfone groups and ether linkages. The rigidity of aromatic and sulfone groups makes the polymer stiff with the transition temperatures reaching up to 220^{o}C, high chemical resistance and various hydrophobic characteristics [37]. PES polymers are manufactured in different ways. In nucleophilic substitution reaction route, PES polymerization occurs due to condensation of its monomers that is dihydroxydiphenyl and dichlorodiphenylsulfone. In the alternative procedure (electrophilic substitution reaction route), Friedel-Craft type polymerization is performed.

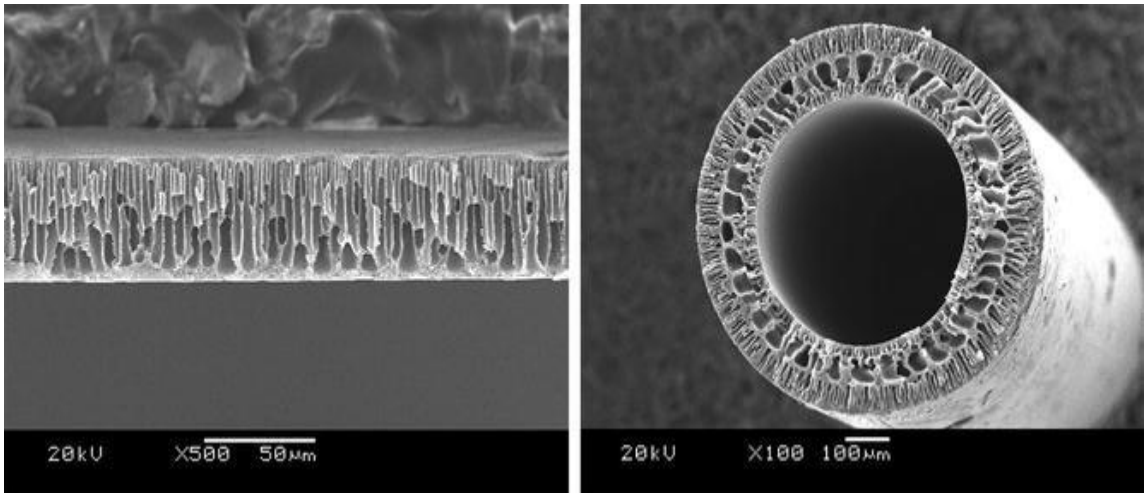


Figure 2.2 Membrane Cross Section View

But despite having such benefits membrane technology suffers from drawbacks as well such as fouling with time, flux slackening, hydrophobicity, chemical degradation under high temperatures, and few others [38]. These drawbacks can be overcome using nano technology. Nano materials can eradicate these setbacks and can purify the water in an optimal way. Several techniques have been devised in response to this requirement such as Ultrafiltration, Reverse Osmosis, Nano-filtration, and Microfiltration that can drive the microbial pollutants out of water. Membrane's basic function is to allow certain particles to pass through while blocking others. Membranes can be classified into natural, atomic, and life-sustaining types. Intrinsically membrane technology is devised based on barrier function. Fouling can influence saturation and penetration rates [39]. Fouling in membranes is caused by the appearance of pores due to the deposition of substances on membrane surface. Indications of fouling include surface charge, hydrophilicity, and other processes. High surface roughness indicates a high degree of fouling as compared to flat membrane surfaces. Membrane fouling can be reversible process depending upon the nature of foulant. Sometimes it can be the cause of flow and module configuration of membranes. Their type includes flat-sheet, tubular or spiral wound. Each membrane has its own advantages and disadvantages such as flat sheets are easy to formulate while hollow fiber is used where larger surface area is needed [40]. Spiral wounds are susceptible to clogging whereas tubular types are employed where cleaning is needed. Similarly, there are other factors that impact such as flow configuration and velocity [41]. To enhance gel

formation and concentration polarization while crossflow obscure solute formation on the membrane surface. Both filtration techniques have been demonstrated in the figure below:

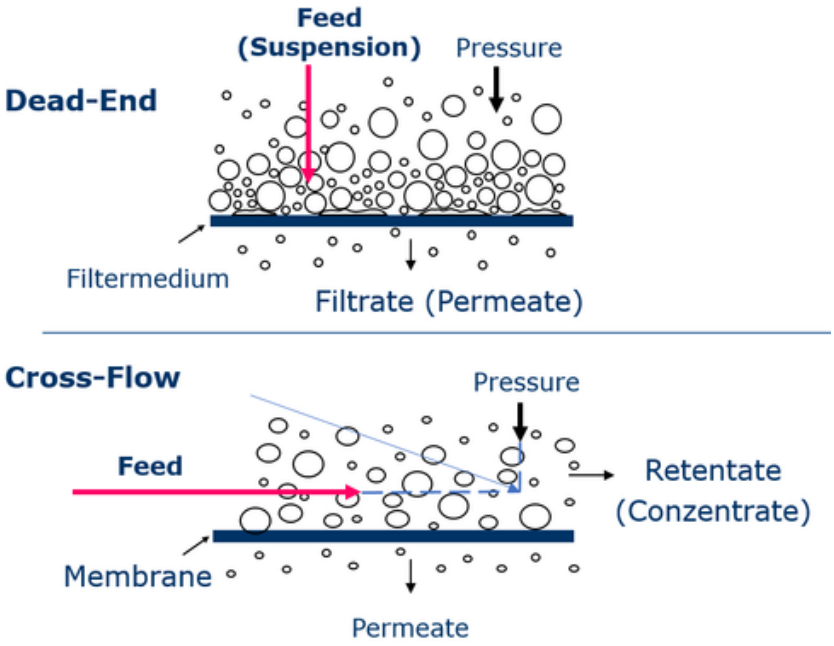


Figure 2.3 Dead-End and Crossflow Filtration Techniques

Hydrophobicity rate in membrane causes the particle to move towards themselves and thus avoiding fouling attack. Reversible fouling is caused by foulant reversible adsorption while irreversible fouling is caused by the solid chemisorption or physio-sorption of foulant atoms on membrane surface [42]. Irreversible fouling leads to a permanent decrease in flux. Methodologies such as back-washing and cleaning can only avoid reversible fouling while irreversible can only be fixed by alteration of membranes. This can be avoided by opting for antifouling membranes [34]. Antifouling membranes can be manufactured by tailoring them with nanocomposites. These inaccuracies of passive antifouling strategies against proliferative bio foulants have led to the innovation of these nanocomposites-based membranes. By employing active-passive and their other combinations can eradicate such issues as well. This challenging task has been considered for this research by opting for a membrane process with carbon nanotubes and chitosan. These synthetic membranes are now commercially being researched or adopted for the purification of water. Polyvinylidene fluoride (PVDF), polyether sulfone (PES), polyacrylonitrile (PAN), polyvinyl alcohol (PVA), polyvinyl chloride (PVC), polyethylene (PE), polypropylene

(PP), polyamide, and chitosan are a few examples of these synthetic membranes [43]. Figure 2.4 shows the fabrication of antifouling membranes for water purification.

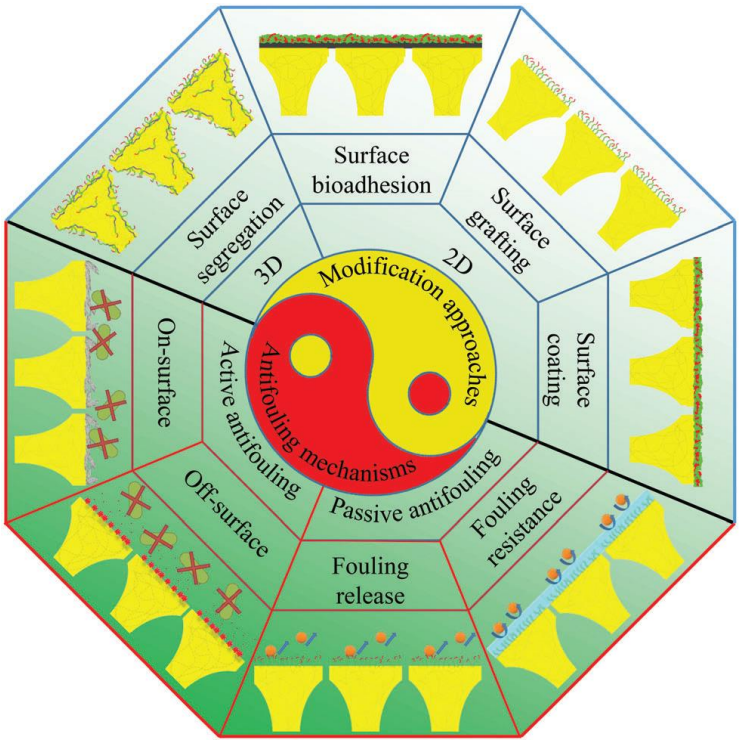


Figure 2.4 Fabrication of antifouling membranes

We have established in our research so far that fouling can cause adverse effects that must be mitigated through fabrication of anti-fouling membranes. Upon further investigation impressive research comprising of comprehensive review of anti-fouling membranes has been listed in this literature review. This research titled “Antifouling membranes for sustainable water purification: strategies and mechanisms” wrote by Runnan and his colleagues shed lights on anti-fouling membranes [44]. As written earlier anti-fouling membranes deal with pervasive fouling problems caused by nitriles, acidic components, and other substances. Their research has exploited basic and advanced filtration techniques such as nano and ultra filtration, reverse and forward osmosis. Furthermore, it also introduces foulants and their mechanisms. Membrane surfaces typically have porous structure, diverse surface physicochemical characteristics and the conditions in which they are being employed. Foulants and more specifically bio-foulants, are ubiquitous in membrane separation processes. These foulants can be characterized into various

categories based on their behavior and environmental conditions. Fouling behavior needs to be exposed from molecular level perspective to get the desired water purification objective. Furthermore, many core characteristics such as hydrophilicity, surface energy, porosity and others also need to be well exploited before employment of them. Homogenous membranes can only cope with limited range of foulants so heterogenous membranes are better suited to adapt against fouling substances. Next step is to further improve these membranes through surface coating, grafting and surface bio-adhesion. Another modification technique is physical blending and surface segregation. These are 2D modification techniques, there are 3D techniques as well that can be blended during membrane fabrication process such as flexible manipulation and self-healing behavior. Nanotechnology has overcome these defects. So, in short nano membrane technologies being investigated further are best there is in purification of water from harmful materials. Farhad Zareei et al [45]have published an article on the enhancement of separation and anti-fouling characteristic of Polyethersulfone nano filtration membrane by embedding functionalized magnetic chitosan nanoparticles. Functionalized Chitosan ($CoFe_2O_4$-CuO) were synthesized in their research and then further fabrication of PES based membranes was done. Validation of the adopted methodology was done by employing various characterization techniques such as X-Ray diffraction, FTIR, SEM, 3D surfaces images, membrane porosity, water flux, salt rejection and few others. Results from their characterization of these membranes showed reduction in water contact angle from 65^o to 36^o for composite membrane. All fabricated modified membranes yielded higher water flux and increased salt rejection than pristine PES membrane. Water flux measured by them is 45.2 L/m^2h and salt rejection as high as 88%. This behavior indicates the increase in hydrophilicity nature of membranes.

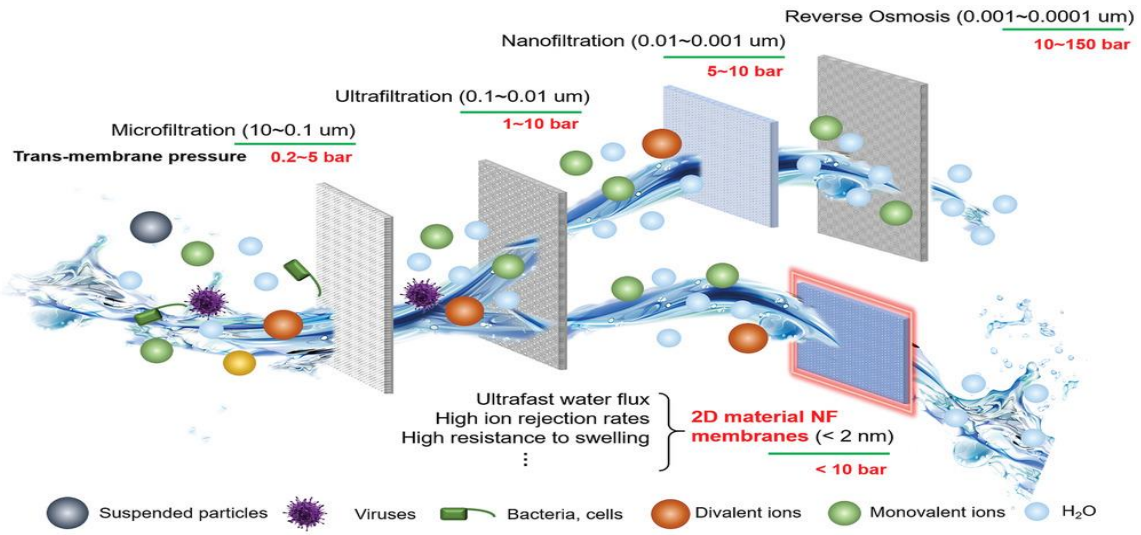


Figure 2.5 Classification of Filtration Techniques

2.4 Polyether sulfone Membranes

Removal of nitrates, acidic and other harmful particles from water is the core objective of our research. Investigating nitrate removal methodologies, I have included this article in literature review because it shows that Chitosan and Activated Carbon based nano-membranes fabricated for this purpose serves the purpose [46]. They have fabricated these membranes and tested them on aqueous solution of fish farm to remove nitrite, ammonia, phosphate, and other pollutants. Adsorbents were prepared with shrimp shells upon converting it to nano-chitosan. For this reason, they prepared a date palm kernel and then activated with oxalic acid and then whole setup along with activated carbon were injected with nitrogen to form nanocomposites. This study was conducted during winter season of 2018 and validation of their efforts were done by measuring pH, effluent concentration, and adsorption time. pH range selected for this purpose was 5-8 and effluent concentration to be 25-100 mg/L. Also contact time for this experiment was also recorded as 15-90 minutes. Their results demonstrated the effectiveness of adopted methodology as pH of water was obtained as 7, concentration as 50 mg/L and contact time as 60 minutes. Similarly, removal percentage of nitrite, phosphate, and ammonia particles were obtained as 99.98%, 99.77% and 65.65% respectively.

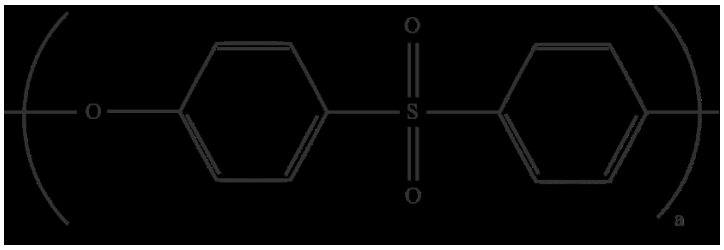


Figure 2.6 Structure of PES


Figure 2.7 PES Powder Form

Bagheripour and Moghadassi et al [47] have presented their findings in the context of fabrication of nano0filtration membranes incorporated with chitosan and activated carbon composites. They have adopted a rather exquisite methodology specifically dip-ping to synthesized nanoparticles comprising of activated carbon and chitosan. These nano composites are embedded in polyethersulfone based filtration membranes to achieve desired purification of sewage water. To enhance the performance of these membranes they have functionalized the nanocomposites and to achieve higher hydrophilicity. These membranes were then further characterized with various techniques such as FTIR, SEM, UV-vis spectra and others to justify the claim. Results yielded from their research indicate the effectiveness of nanomembranes. Higher hydrophilicity and porosity were shown by the fabricated membranes. Similarly, water flux rate also increased from 21 to 30 L/m^2h. Due to higher dispersion of nanoparticles, pore size was considerably decreased. Membrane roughness was also considerably declined from 19.2nm for pristine PES membrane to 5.9nm. Pore size reduction was further validated using Scanning Electron Microscopy. Salt rejection tests conducted on these membranes demonstrated a higher rate,

that is 97%. Lastly, they test these membranes to be anti-foulant which was also successfully achieved.

The objective of fabrication of nanomembranes is to test its properties and effectiveness against acid mine water or other types of contaminated water that cannot be purified conventionally. Shinji et al [48] have shed light on characterization of mine water and acid mine drainage prediction by simple testing techniques. High analytical methods are efficient, but they can be costly and lethargic. Simple methods can be modified in such a way that they can achieve water purification. Fabrication of PES membranes are an efficient methodology that has been in the works for years now. It is an effective method to treat Acid Mine Drainage Water (AMD). This research works on simple testing methods such as leaching test and sequential extraction test with HCL, HF, and HNO_3 to neutralize carbonates. The results demonstrated the Acid Buffering Characteristic Curve test supported the change in pH in the first 10 cycles of leaching test. Net Acid Generating (NAG) pH in the sequential test reflected on the effects of solubility of sulfur in the rocks. This method is proven to be economic and can be iterated further to clean AMD water.

2.5 Chitosan and Activated Carbon

The spread of pathogenic microorganisms in our drinking water and other sources of water has been effectively hindered by antibiotics. However due to the evolution of these pathogenic microorganisms, they have developed resistance against antibiotics which led to the severe infectious diseases and high morality in our societies [49]. Due to these factors researchers have adhered to biopolymer-based antibiotics such as chitosan. Chitosan is a naturally occurring substance with linear polymer nature. It is found in Mucoralean fungi which is chemically composed of glucosamine and N-acetylglucosamine monomers. The N-acetylated form of this polymer, called chitin, which is extracted from lobsters, crabs and shrimps can be converted into a its partially deacetylated form known as chitosan. Chitin is one of the most naturally found biopolymer after cellulose [50]. Chitosan has three nucleophilic functional groups and are modified to produce derivatives consisting of cationic or other hydrophobic characteristics. Therefore, the derivatives of chitosan are aimed at improving the solubility in aqueous mediums as well as enhancing its antimicrobial properties in aqueous medium and other heterogeneous environments.

Chitosan has significant anti-microbial properties and has benefits such as non-toxicity, biocompatible and biodegradable. Naturally found chitosan does not affect aqueous solutions of below 6 pH. However synthetically derived chitosan overcomes these issues. To reduce antifouling behavior of membranes, they have been infused with chitosan and activated carbon. Their key properties include nontoxicity, biocompatible and biodegradable [21], [51], [52]. Chitosan acts as a flocculent that directly results in agglomeration of colloids and eventually resulting in removal of unwanted compounds. Other benefits of chitosan include increased wettability of membranes, hence improving its efficiency by less absorption of protein and reduction in loss of flux. Apart from these characteristics, chitosan is very desirable in multiple biomedical applications because of its ability to bind with metal ions such as Ni2+ and can act as sorbent for arsenic compounds found in drinking water. Its value is further increased when it is incorporated in membranes to increase anti-fouling and anti-bacterial activities. The sulfhydryl group, added in chitosan, increases its hydrophilic nature thus making it more efficient to use in membrane technology. The other compound that is amalgamated in membranes is activated carbon. It also acts as an antifouling agent, and it maintains the odor and taste of water. The presence of van der Waal's forces plays a pivotal role in physisorption [53]. These forces attract pollutants from the model water onto the activated carbon porous surface. Functional groups that are found in chitosan are quaternary, guanidyl, hydroxyalkyl, carboxyalkyl and hydrophobic groups. They have been widely employed as antimicrobials and adsorbents. Chemical structure of chitosan is demonstrated below:

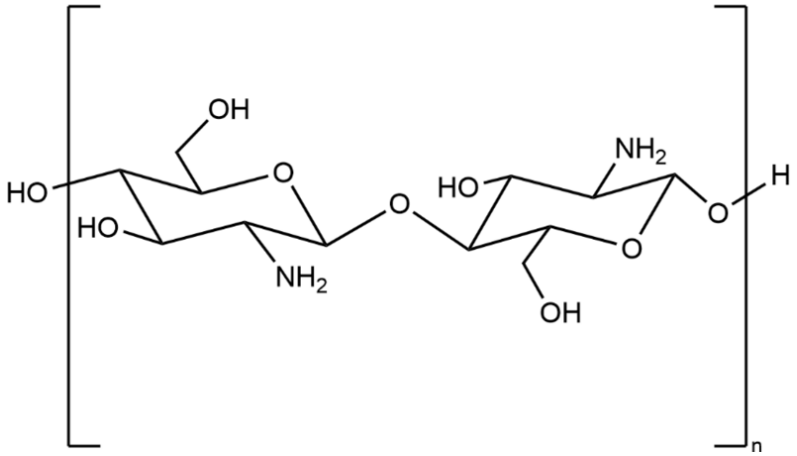


Figure 2.8 Antimicrobial Chitosan

Due to high interest in the chemically derived chitosan, that does not guarantee antimicrobial and low toxicity. In our research by employing activated carbon and chitosan, we are trying to improve the flux rate and anti-fouling properties of our polyethersulfone (PES) membranes. This study has been done by Shahin Hydari et al [53] for cadmium. For this study the removal of cadmium ions from aqueous solution through adsorption on composites of chitosan, activated carbon and chitosan biosorbent. This adsorption study was conducted on a batch and its various effects were studied and recorded such pH of solution, pore size and adsorption rate. The results indicated that optimum conditions for cadmium removal through chitosan and AC were found to be pH 6 whereas adsorbent size was found to be 0.425mm and dose was 6 g/L. Furthermore, Langmuir model was the best to demonstrate the effectiveness of proposed solution.

Another research work based on the applications of chitosan has been presented by Riyan, Tawfiq and Nafisa Click or tap here to enter text.. Shedding light on the applications of chitosan, they have stated that it can be used to treat bio-waste. It is found in abundant and has diverse characteristics. Chitosan is produced from chitin through deacetylation process. It is a biocompatible compound, naturally biodegradable, non-toxic, and many others. It has antimicrobial and antioxidant agents that have a variety of applications. Furthermore, it can be used for drug delivery, bio-nanotechnology, regenerative medicine, numerous industrial applications including gene therapy, environmental and other commercial applications. In short, chitosan can be employed in all fields of biology.

Lin Gu et al have also shed light on this matter in their research in which they demonstrate the fabrication of antifouling membranes based on Lignin, chitosan, and other composites. They have also concluded from their research that these two elements are abundant in nature, so they are economical to harvest for water purification. They have prepared nanomembranes and characterized them through ATR-FTIR, XPS, Zeta potential measurements, AFM, and others. Morphologies and hydrophilicities were recorded to establish the effectiveness of the composites based nanomembranes. In short, chitosan and activated carbon are two of the most effective composites that can be used to cleanse AMD water effectively.

Chapter 3: Experimental Work and Proposed Methodology

3.1 Materials

To conduct our research, model water was prepared, and it was activated with oxalic acid in pyrolysis furnace by injecting nitrogen gas in contact with activated carbon. The membrane casting process was employed using distilled water and the composites were prepared using deionized water. Standard polyethersulfone (58000 Mw) that is used commercially was taken for experiments.

3.2 Chitosan and Activated Carbon Embedded PES Membranes

This experimental work is carried out with various weightages of chitosan such as 1%, 2% and 3%, as well as pristine PES membranes embedded with AC to cleansed AMD water.

3.2.1 Membrane Fabrication

After the completion of the previous process, Nano composites consisting of chitosan and activated carbon were introduced to carry out the cleaning process. Most of the Nano filtration membranes that are commercially utilized belong to thin film composite (TFCs) group. Another form of membrane is asymmetric that has upper advantage to TFC such as higher flux, lower manufacturing cost and others. This research work was carried out in spring, fall and winter seasons. Various batches with pH ranging from 5-9, effluent concentration of 30-100 mg/L and contact time of 30 to 100 minutes, were prepared and tested during these seasons. Phase inversion technique was employed to fabricate nanomembranes. Various membrane batches consisting of PES, PES-Chitosan-AC, PES-AC, and their different concentrations were made using same methodology. Casting solution consisting of PES and NMP solvent was prepared. This solution was then heated at 65^{o} C and then agitated at 250 rpm. This composition has been tabulated below:

Table 3.1 Casting Solution Compositions

Polymer Membrane	PES %	PVP%	AC%	Chitosan%
P_0	16	2	-	-
P_0-CH-AC (1%)	16	2	0.25	0.75
P_0-CH-AC (2%)	16	2	0.75	1.25
P_0-CH-AC (3%)	16	2	1.25	1.75

3.2.2 Chitosan and Activated Carbon Preparation

PES was chosen as desired and then it was spread in 20mL of 1% (v/v) acetic acid solution for 1 hour while stirring. After sonication for 30 minutes at room temperature with ultrasound to aggregate the nano particles. A further 0.75% chitosan powder was added to the suspension while constant stirring and then passed onto sonication process for another 30 minutes. The whole process took more than 2 hours at 65^{o}C while constant stirring. The resulting mixture was then filtered and washed with distilled water until the pH was close to 7. This process has been depicted below:

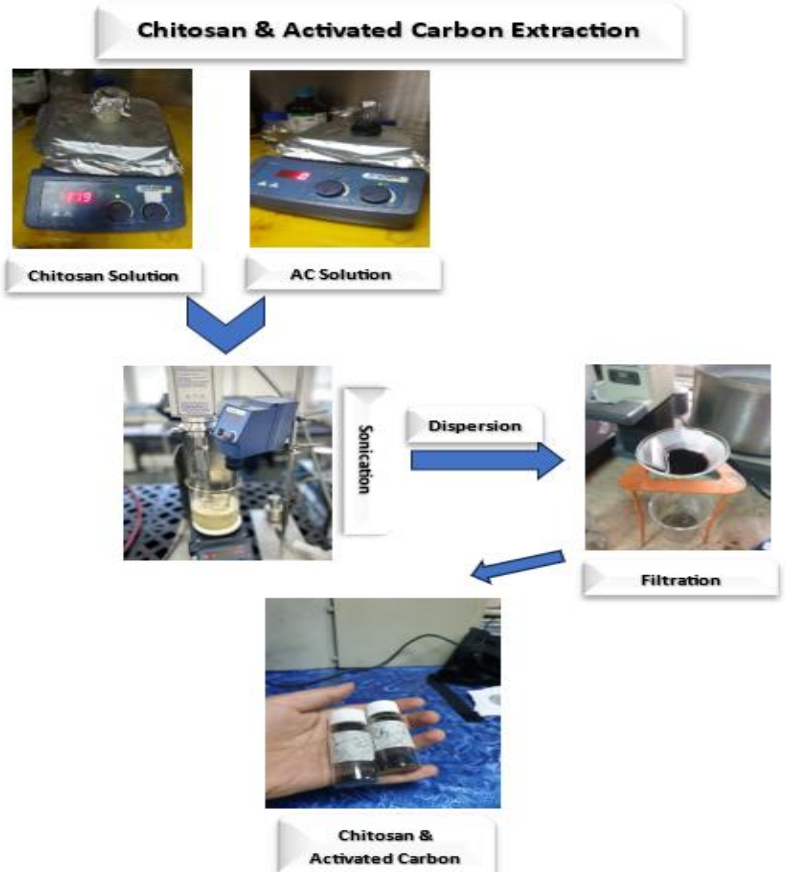


Figure 3.1 Chitosan and AC Preparation

3.2.3 Nanocomposite Mixed Matrix Membrane Preparation:

Solution of the polymer weighing 17.5% w/w was prepared. All chemicals were thoroughly weighed and then added to the solution. 3.5g of PES was dissolved in 12mL of NMP and stirred at 250 rpm for more than 24 hours. Further stirring was done after the addition of chemicals for 120 hours. After that the solution was sonicated and heated for nearly 30 minutes. Trapped air was removed and then the solution was casted on the casting machine as shown in Figure 3.2.

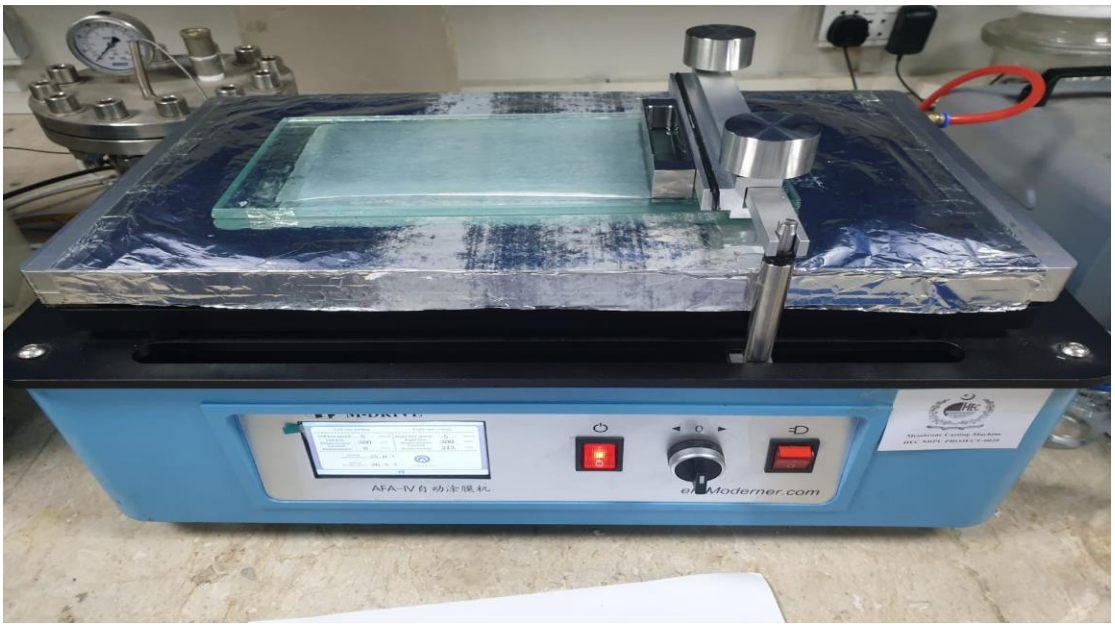


Figure 3.2 Casting Process

The casting procedure was carried out at room temperature at a speed of 50-60 mm/s with water acting as a non-solvent, and then passed on to the coagulation bath for 5 minutes. After that it was dipped in water-isopropanol solution 70/30 for nearly a day. The fabricated membranes were then lastly dipped in glycerol for 4-5 hours. The resulting membranes were then bathed in distilled water and dried to conduct characterizations on them. Whole process has been summarized in Figure 3.3.

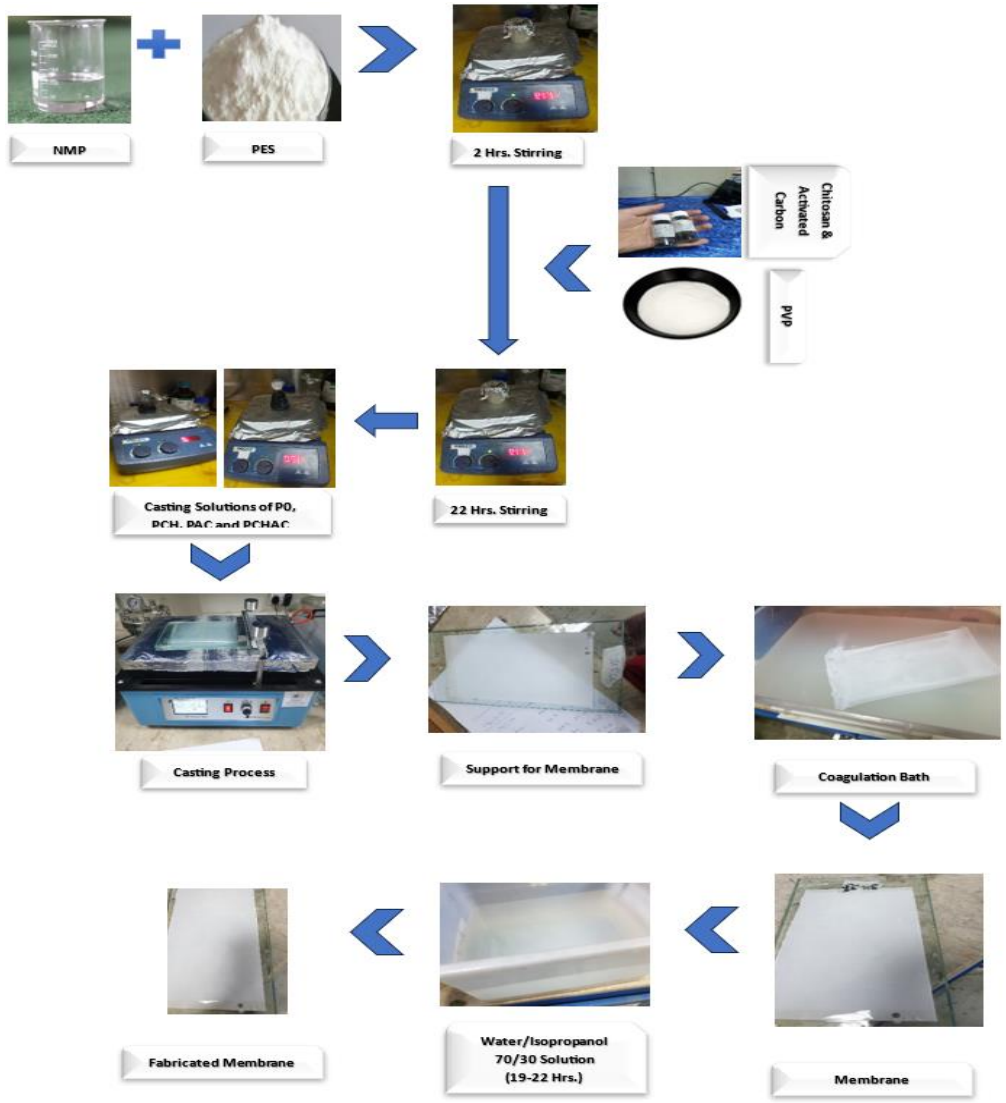


Figure 3.3 Fabrication of Membranes

3.3 Characterization Techniques:

3.3.1 Contact-angle measurement

To measure the hydrophilicity nature of the membranes manufactured, contact angle measurement (sessile drop method) is carried out. A deionized water droplet was carefully injected into a dry membrane sample of approximately 1 cm^2 and the resulting image was captured using standard camera [54]. The sampling rate for contact angle measurement was increased 4-5 times, to reduce error. DSA-25 drop shape analyzer from KRUSS was used to carry out this measurement.

3.3.2 Swelling measurements

Swelling measurements are carried out to measure the extent of swelling of the desired sample. For this purpose, I dried our membranes and then sliced in into thin strips of 5mm x 10mm area. Digitally membranes were weighed and then submerged in distilled water for 24 hours at room temperature. Strips were removed at regular intervals and the placed between two filter sheets to remove excess liquid [55]. Percentage of swelling (SW) can be determined using this formula:

$$SW = \frac{w_s - w_o}{w_o} \quad (1)$$

Where 'w_s' indicate wet membrane weight and w_0 dried membrane weight.

3.3.3 Porosity

Gravimetric analyses are employed in experimental setup to constituent is converted into a substance that can be separately sampled and then weighed. Porosity of the membranes was measured using this technique. Various membrane samples were cut and then submerged in distilled water at room temperature for more than 24 hours [56]. Eliminate any residual liquid after placing them in filter sheets. After measuring the weight of wet (W_w) membranes they were dried (W_d) and their weight was measured again. Thickness of the membranes was analyzed using the following formula:

$$\in = \frac{w_w - w_d}{V_d} \quad (2)$$

Where w_w indicate wet membrane weight and w_d dried membrane weight, 'd' is the water density at room temperature and 'V' shows volume of the membrane.

3.3.4 Scanning Electron Microscopy

To inspect the nature of the membranes manufactured and study their morphology, SEM was employed on the membranes. JEOL-JSM-6490LA with operating system of about 10mm, nominal voltage of 10-20 kV and spot size of 35-60 was used. The membranes were sliced into 1 cm^2 sections and then frozen in liquid nitrogen [57]. To examine the membranes, they were further broken down into miniature segments.

3.3.5 Fourier Transform Infrared Spectroscopy

Functional groups are a vital part of an element, and they can be inspected using FTIR. FTIR was used in our characterization of membranes to identify functional groups. Dried membranes were sliced around $0.5cm^2$ in diameter. Spectral range for this purpose was set as 400 to 3500 cm^{-1} with a resolution of $2cm^{-1}$. BRUKER ALPHA II FTIR spectrophotometer was utilized for this purpose [58].

3.3.6 Mechanical Testing

Mechanical testing was performed to extract the information about tensile strength and other mechanical factors. For this reason, samples were sliced in dog bone shapes as instructed for ASTM D882. The Universal Testing machine (UTS) was utilized to examine the tensile strength of our samples. This study was conducted at a room temperature of 21ºC on Shamizdu AG-X Plus. All samples of different composite concentrations were thoroughly checked prior to testing [59]. Each sample was cut into 25mm x 3mm area with a thickness of about 0.3mm and were assessed using a micrometer. Below figure indicates the testing was done at a strain ratio of 0.5mm/min with a gauge length of 12.5 mm. Young's modulus was evaluated by obtaining the curve of the linear components of stress-strain curvature. Elongation and tension were recorded at the break [60].

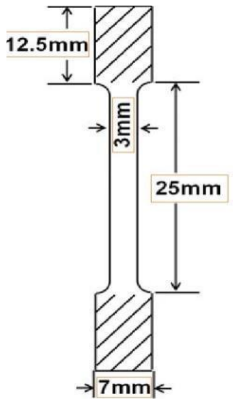


Figure 3.4 Dog-Bone Style Sample

3.3.7 Membrane Filtration Performance Test

To evaluate the permeation of flux of the membranes, flux rate was measured. Laboratory scale dead-end filtration set-up was established. Before the analyzation of membranes, they

were first compacted with deionized water 0.4 MPa for 30 minutes. After that, operating pressure was adjusted to 0.45 MPa for filtration experiments. The resulting water flux was measured. KNO_3 aqueous solution was prepared to estimate the performance of membranes against it [61].

It was determined by the volume of the liquid running through a sample as a function of time, area, volume, and other dependent factors. For this characterization a filtering assembly coupled to a vacuum was set up at various pressures. The passage of running distilled water was timed and measured across the membrane. The recorded data was then evaluated using the following equation:

$$J = \frac{V}{AT} \tag{3}$$

Where 'J' is the measured permeating flux in $L/m^2.h$, 'V' is the volume of the water, 'A' is the area of membrane and 'T' is the permeation flux time. Sample size for recording of data was increased for each membrane to minimize inaccuracies. Lastly, salt rejection was assessed using salt rejection efficiency formula:

$$\%SR = 1 - \frac{Conductivity\ of\ permeate\ (C_P)}{Conductivity\ of\ feed\ (C_f)} * 100 \tag{4}$$

The conductivity of the feed and the permeate solutions was measured using a conductivity meter (Cyber scan PC 300). Feed solution was prepared using distilled water [62].

3.3.8 Water Retention Test

Membrane strips were soaked in distilled H_2O for more than 24 hours to measure the water uptake of membranes [63]. After the requisite time, wet membranes were weighed and then those membranes were evaluated for water uptake/retention using the following equation:

$$Water\ Uptake(\%) = \frac{W_{wet} - W_{dry}}{W_{wet}} * 100 \tag{5}$$

3.3.9 Optical Profilometry

The roughness of the surface of membranes is measured using the optical profilometry technique. In this regard, 0.25 x 0.25 cm^2 pieces of membrane were cut and put on to the glass slide. After that, the slide was examined using the profilometer [64]. The scanned

surface was recorded using NANOVEA PS-50. This way the roughness of the membrane surface was measured.

3.3.10 Anti-fouling Test

Anti-fouling or antibacterial activity of the membranes is one of the essential parameters for the membrane effectiveness against the foul elements of the aqueous solution. In conducting our experiment, all elements of the set up were thoroughly sterilized vis autoclave and all antibacterial tests were performed. The Antimicrobial susceptibility test was carried out using Muller-Hinton (MH) agar plates. E. coli and S. aureus were stored in the solution in 30% (v/v) glycerol solution at about 4^{o}C and then left overnight for growth [65]. They were then grown in MH Broth at about 36^{o}C with rotary agitation at around 140 rpm. The yielded solution containing the desired bacteria was diluted with MG medium to the estimated value of 106-108 cfu/mL. After performing this test, the second stage was to conduct a Diffusion test (Kirby-Bauer test). For this technique, E. coli and S. aureus were first soared onto the MH agar plates through cotton swabs via bacterial suspensions. PES-Chitosan-AC membrane disks were cut into equal sizes and were put in the center of the petri dishes. Incubation of the petri dishes was carried out at about 37^{o}C for 24 hours [66]. After the time elapsed, the petri dishes were observed thoroughly and recorded the growth of colonies. The inhibition zone diameter was calculated. The final suspensions were incubated for more than 15 minutes on a rotary shaker. The final equation for the evaluation of antibacterial activity is as follows:

$$Reduction\ rate(\%) = \frac{N_{control} - N_{sample}}{N_{control}} * 100 \quad (6)$$

Where '$N_{control}$' and 'N_{sample}' represents the number of colonies derived from control and experimentation of PES-Chitosan-AC composites.

Chapter 4: Results and Discussions

In this research work I have successfully implemented the treatment of acid mine drainage water system. This treatment was carried out in SCME laboratories. For this purpose, I have proposed antifouling nanofiltration Polyethersulfone membrane using phase inversion methodology based on Activated Carbon (AC) and Chitosan acting as main composites and individual fillers on the membrane matrix. These membranes were acted upon acid mine drainage water. Membrane technology is flexible, robust, and cost effective but possesses hydrophobicity [67]. To overcome this drawback, we have embedded nanoparticles and polymeric composites in the membrane matrix. The yield of this research is to optimize the pH of water and recover critical industrial raw materials such as sterile aggregates (serpentinite, andesite), industrial rocks (magnesite), and other natural and organic materials (peat and biochar). These membranes were embedded with concentrated PES, PES with 0.625%, 0.0125% and 0.01875% chitosan, PES with 0.625% and 1.25% Activated Carbon. To optimize the conceived methodology, diverse characterization techniques have been opted explicitly Scanning Electron Microscope (SEM), Fourier Transform Infrared (FTIR) spectroscopy, Antibacterial analysis, contact angle measurement, salt rejection, water retention, flux measurement, Thermogravimetric analysis (TGA), and mechanical testing.

4.1 FTIR

The FTIR spectrum shown in Figure 4.1 (a, b, c) shows the distinctive pattern of our materials taken whereas Figure 4.2 shows the FTIR of our research samples. All sampled membranes have peaks around 1576 cm^{-1} showing the strong C=C bonding strength (benzene ring). At 1485 cm^{-1}, C-C bond stretching is visible, which is consistent to the PES structure. These peaks are also visible in PES-Chitosan-AC composite membranes as well. The other bands shown at 1200 cm^{-1} are validation of the C-O structures of the ether and carboxylate. The elongation at 1246 cm^{-1} is the identification of aromatic ether phase (C-O-C). It is due to the presence of sulfone component of PES framework. The final prominent peak at 1150 cm^{-1} is the effect of sulfonyl component (O=S=O). At 873 cm^{-1}, there is a sharp peak which identifies as C-O and C-H which in turns is the identification

of Activated Carbon. Peaks at 1578 cm^{-1} are the attributes of conjugated hydrogen bonded carboxyl group. The spectrum of chitosan composites is visible at 1656 cm^{-1} and 1582 cm^{-1}. These peaks are the identification of C=O, expansion of the N-acetyl group [68]. Furthermore, the peaks at 708 cm^{-1} and 1152 cm^{-1} are due to the presence of -N-H and -C-O-C ether linkages. Similarly, 3100 cm^{-1} to 3400 cm^{-1} signifies the presence of amino acids.

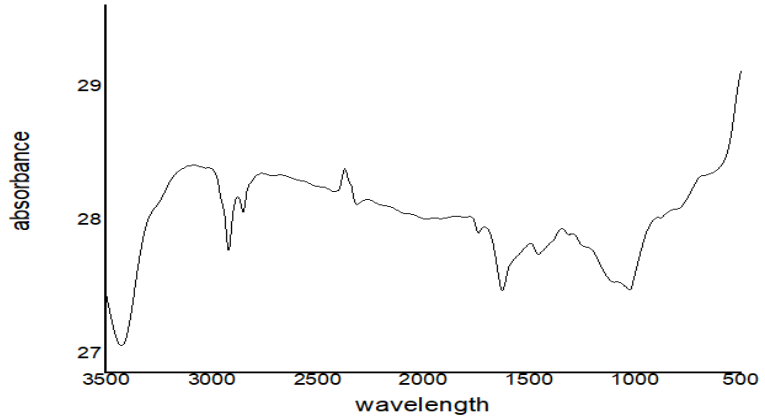


Figure 4.1 (a) FTIR of Polyether sulfone

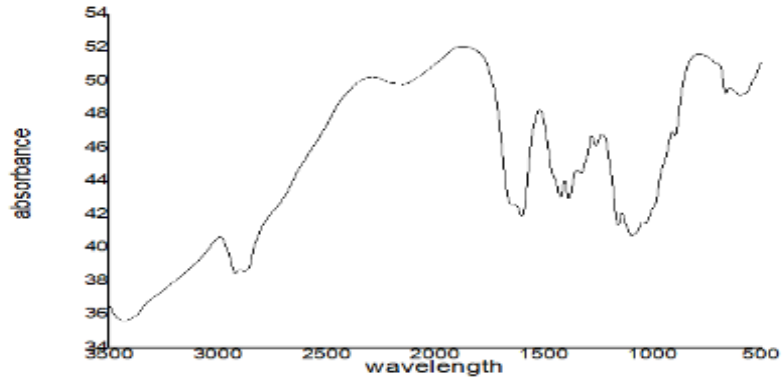


Figure 4.1 (b) FTIR of Chitosan

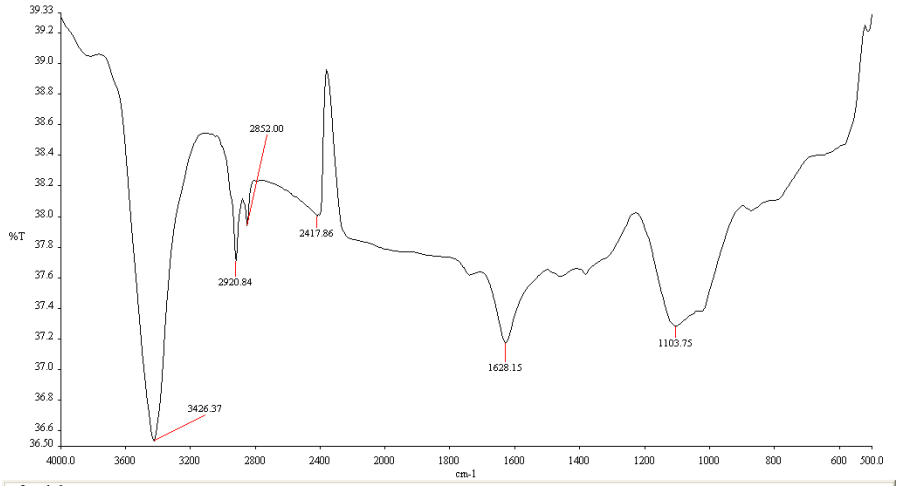


Figure 4.1 (c) FTIR of Activated Carbon

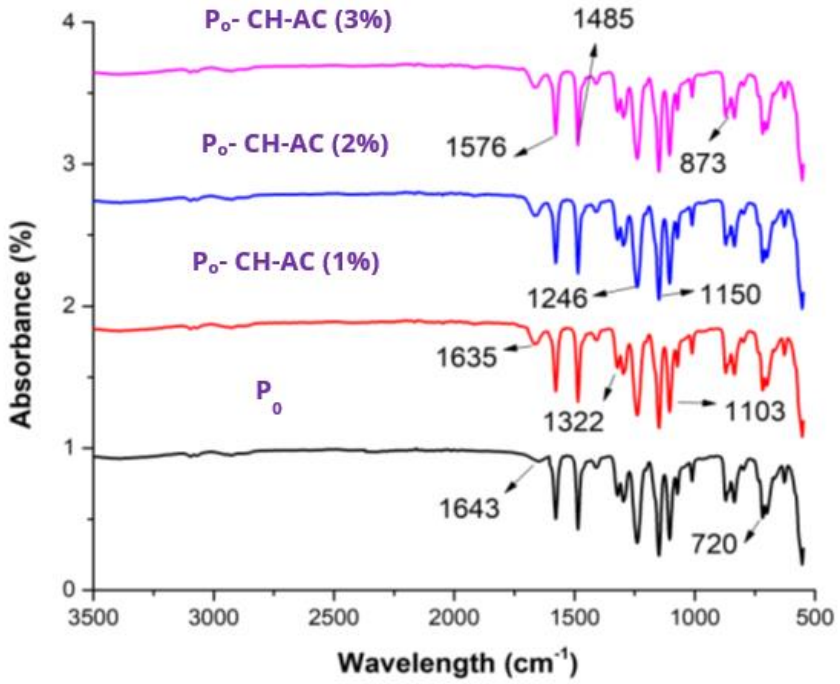


Figure 4.2 FTIR spectrum of PES different PES-Chitosan-AC composition membranes

4.2 Scanning Electron Microscopy

To comprehensively analyze the structure of the constructed membranes, SEM is utilized. SEM has clearly shown the surface morphology and cross-section view of the fabricated membranes. The asymmetric morphological structure of the manufactured membranes consists of a thickened top layer and a macroscopic framework at the bottom as depicted in Figure 4.3. Pristine PES membrane shows a dense top layer while P-CH-AC

morphological structure is visible an agglomeration at the top layer. Figure 4.4 shows the micrographs on the transverse sections of the membrane skin [69]. Asymmetrical structure is quite evident in these figures whereas thickness of the upper layer is also quite visible. Channels which are shown as finger like structures, and it improves the permeability. Beneath the upper layer there is a sponge like mesoporous structure which is due to the presence of chitosan and activated carbon. They increase the viscosity of the solution and the reduction on the development of macro voids. Enhancement of the porosity is due to the increased concentrations of chitosan and activated carbon but on the other hand it also increases the roughness. Porosity of the membranes usually increases by the addition of chitosan and activated carbon [70]. The hydrophilicity of the PES, chitosan and AC results in the fillers which are equally distributed finger like framework and have fewer macro voids. Furthermore, hydrophilicity of these membranes results in accelerated solvent and nonsolvent (NMP) interactions during the transformation of phases. These morphological structures are depicted in below figures:

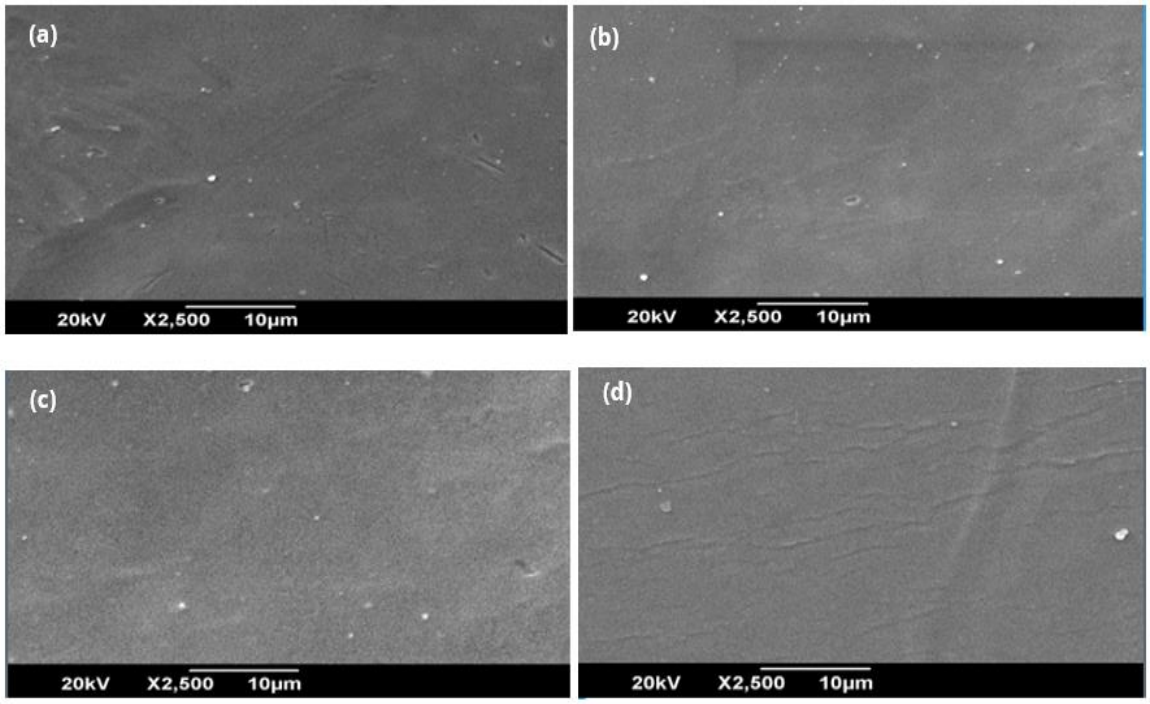


Figure 4.3 Topographical view of (a) P_o, (b) P_o-CH-AC (1%), (c) P_o-CH-AC (2%) and (d) P_o-CH-AC (3%)

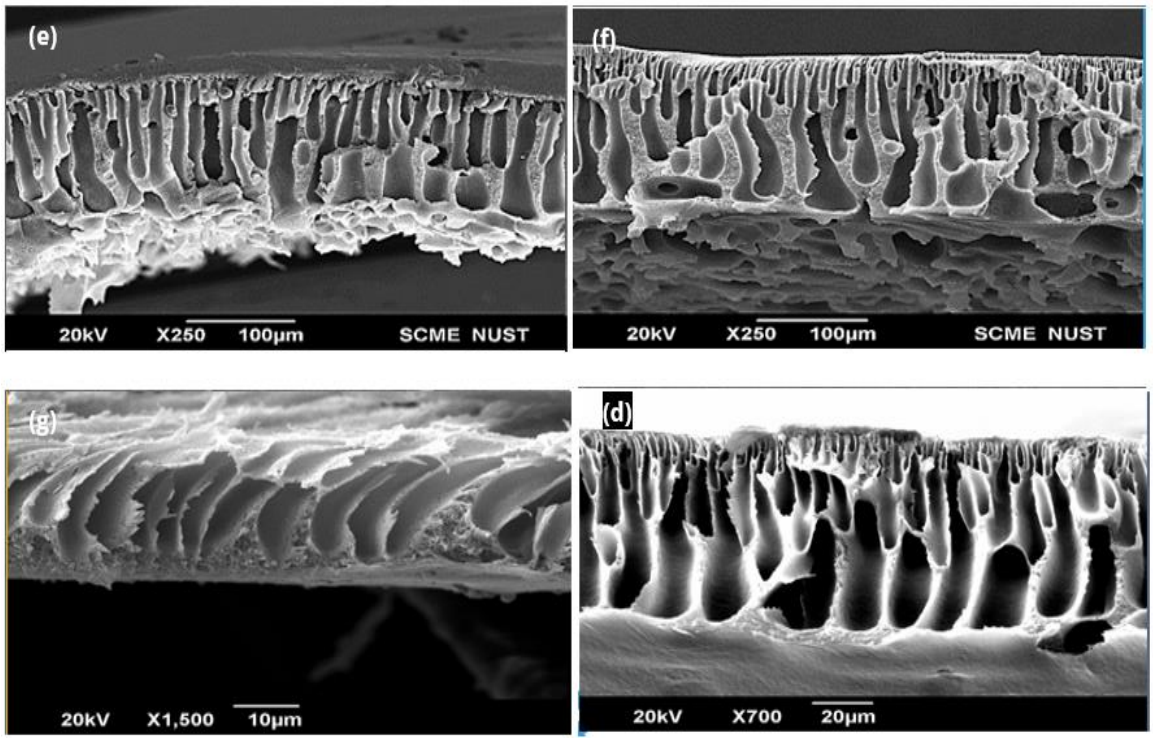


Figure 4.4 Cross-sectional view of (e) P_o, (f) P_o-CH-AC (1%), (g) P_o-CH-AC (2%) and (h) P_o-CH-AC (3%)

4.3 Water Contact Angle

The purpose of the addition of the AC and Chitosan composites in the PES structure was to enhance its chemical properties as well as hydrophilicity [71]. This result is vindicated from contact angle measurements as it dropped from 66.74^o to 50.13^o as shown in Figure 4.5.

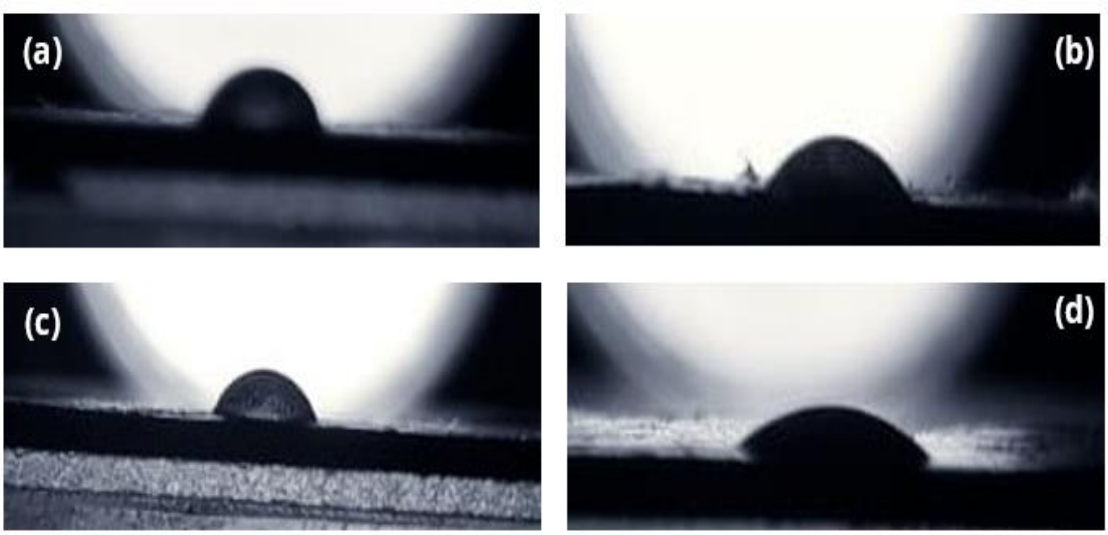


Figure 4.5 Average contact angles of (a) P_o, (b) P_o-CH-AC (1%), (c) P_o-CH-AC (2%) & (d) P_o-CH-AC (3%)

It is quite clear from the figure that introduction of chitosan and AC in the PES matrix has considerably decreased the contact angle therefore increasing hydrophilicity of the membrane. These results are further elaborated in Table 4.1.

Table 4.1 Average Contact Angles for Membranes

Membrane	**Average Contact Angle (θ)**
P_o	66.74±
P_o-CH-AC (1%)	57.426±
P_o-CH-AC (2%)	54.264±
P_o-CH-AC (3%)	50.127±

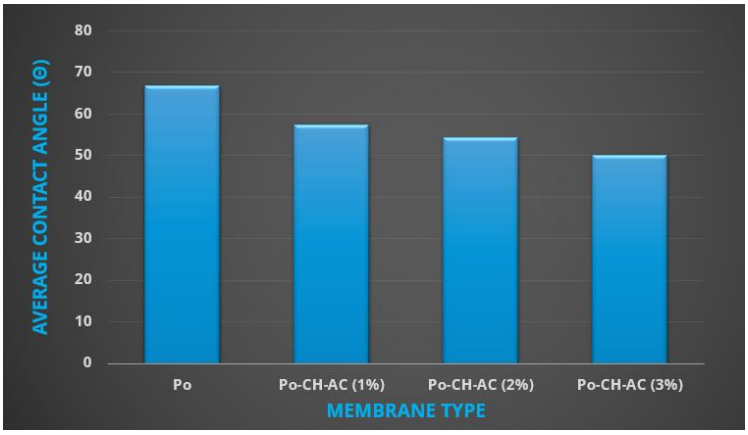


Figure 4.6 Bar Graph of Membrane's Average Contact Angle

4.4 Swelling ratio

Hydrophobicity decreases water retention, that's why PES membranes had the lowest water retention levels as opposed to other membranes [72]. This effect is presented in the form of bar graph in Figure 4.7.

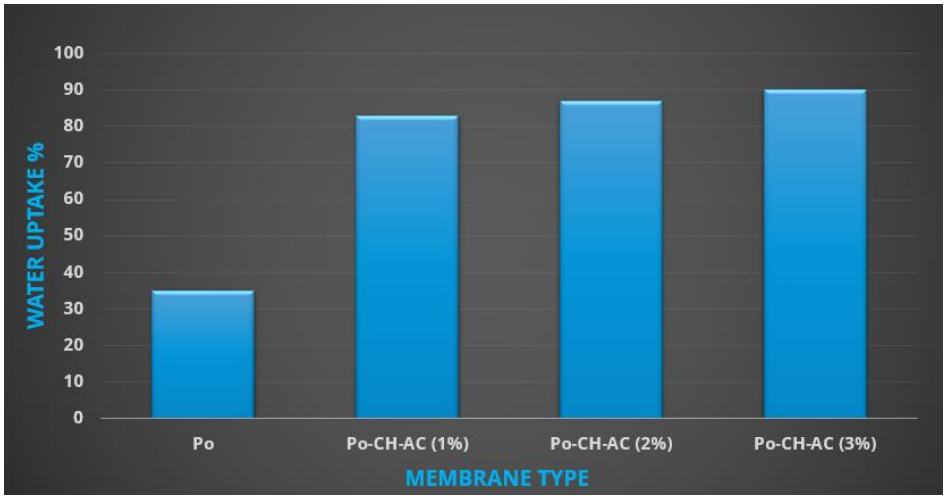


Figure 4.7 Water Retention Rate of Fabricated Membranes

Pristine membranes had asymmetrical top layers and were less dense due to the presence of fillers as depicted in SEM images. These fillers are the reason for lower water uptake. PES-CH-AC (3%) shows that it has the best water retention rate of 90%. The findings of this study validate the claim that higher levels of hydrophilicity of the membranes have higher water retention rates. It also enhances the porosity of the membranes as it can be derived from Table 4.2.

Table 4.2 Water Retention Rate of Membranes

Membrane	Water Uptake (%)
P_o	35±
P_o-CH-AC (1%)	83±
P_o-CH-AC (2%)	87±
P_o-CH-AC (3%)	90±

4.5 Porosity

Membranes permeability, adsorption rate and anti-fouling characteristic are tied to the porosity of membranes. The higher porosity that is more pores in membranes, higher the

penetration flux and vice versa [73]. The porosity of membranes is governed by hydrophilic fillers. Porosity of the fabricated membranes of this study is represented in the form of bar graph below:

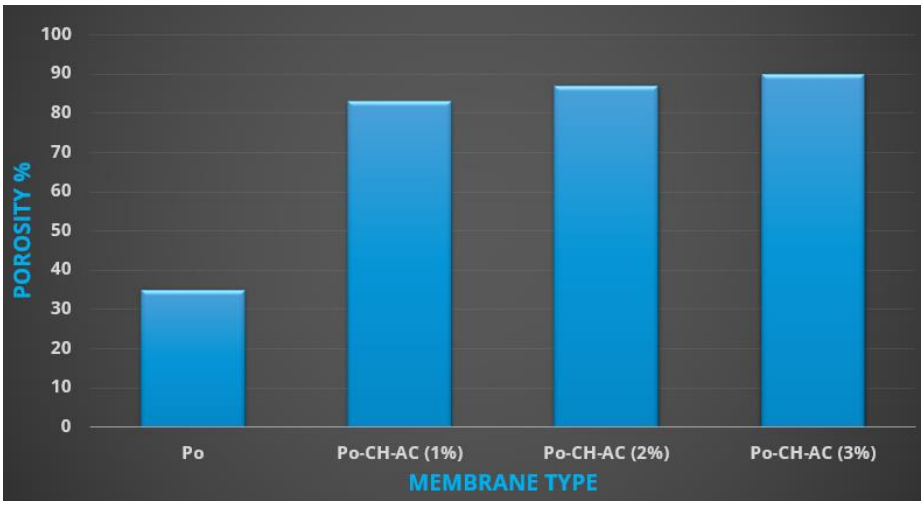


Figure 4.8 Bar graph of Percentage Porosity of Fabricated Membranes

The manufactured P_o-CH-AC (3%) composite membranes had the highest porosity level of 91% whereas pristine PES membrane had the lowest 36% of them all. These values are written in Table 4.3.

Table 4.3 Porosity percentage of Proposed Membranes

Membrane	**Porosity (%)**
P_o	36±
P_o-CH-AC (1%)	78±
P_o-CH-AC (2%)	83±
P_o-CH-AC (3%)	91±

4.6 Mechanical Testing

Mechanical strength is a vital part of membrane that can be enhanced using various composites such as AC and chitosan. Cracking sites in the structure of membranes can be reduced by the introduction of polymer. P_o-Ch-AC (3%) shows significantly more strength than other membranes as shown in Figure 4.9. This is since chitosan is more soluble in water than others thus giving it more mechanical strength. This causes voids to appear in the material where the element existed [74]. These spaces cause the fracture to spread leading to membrane tearing.

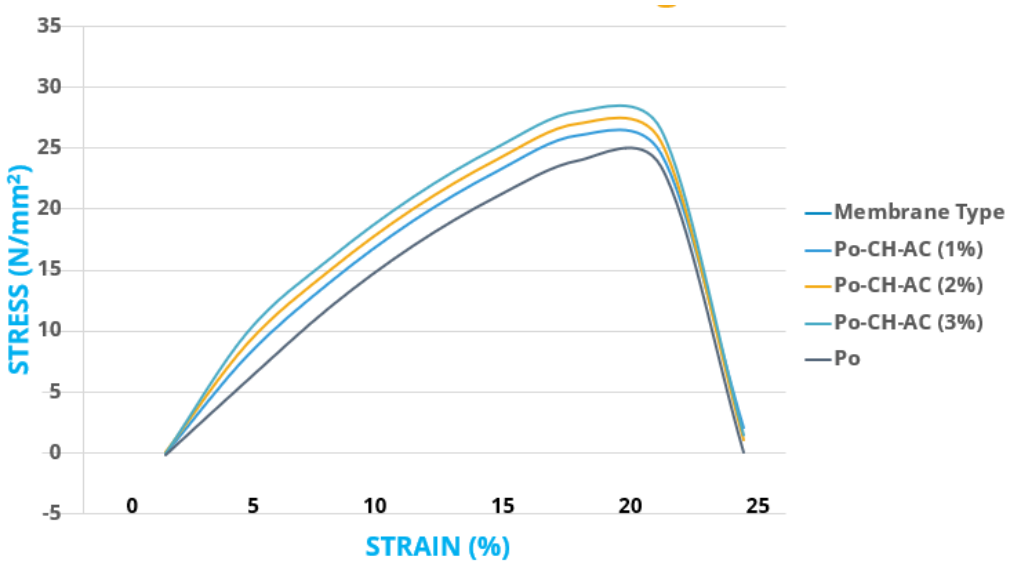


Figure 4.9 Stress vs Strain Graph of Fabricated Membranes

The resulting high mechanical strength of AC and chitosan-based membranes is due to high aspect ratio, effective dispersion, alignment, and interfacial stress propagation [75]. When these membranes are subjected to mechanical stress, it is transmitted to carbon particles that makes the membrane strength superior. This effect is deduced from Table 4.4.

Table 4.4 EM and UTS of Membranes

Membrane	EM (MPa)	UTS (MPa)
P_o	5.4	43.34
P_o-CH-AC (1%)	5.8	45.49
P_o-CH-AC (2%)	6.125	48.33
P_o-CH-AC (3%)	6.4	50.76

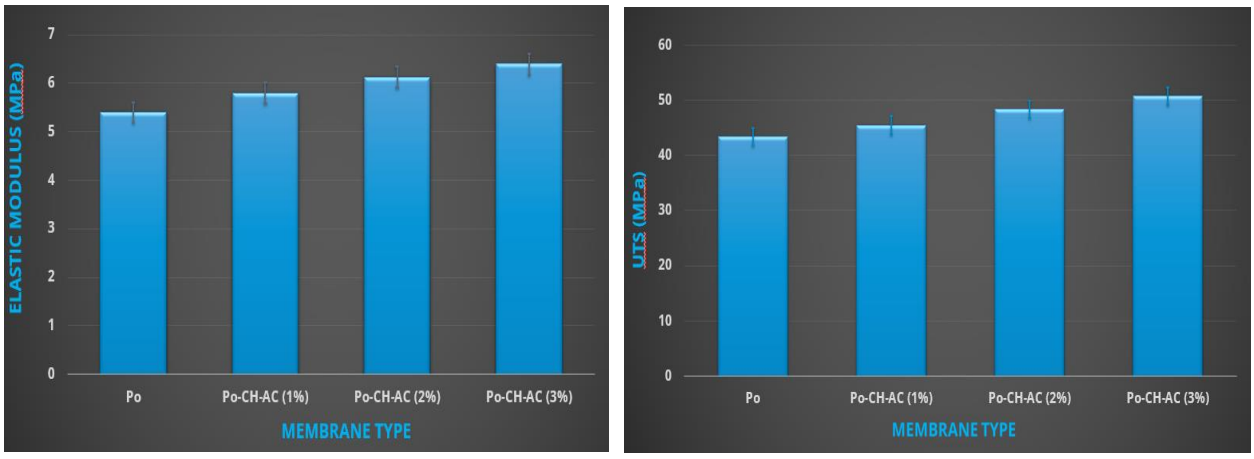


Figure 4.10 Bar Graphs Showing Elastic Modulus and UTS of Fabricated Membranes

4.7 Optical Profilometry

Fouling is one of the major reasons that membranes are subjected to various characterizations to access their features. One such parameter is surface roughness that needs to be measured to enhance membrane features. For this purpose, an optical profilometry test is conducted to extract its surface features [76]. According to the profilometry results, the chitosan and activated carbon particles increased their mitigation towards surface increases thus by increasing roughness of the membranes. These results are depicted in below figures and table:

Table 4.5 Surface Roughness of Membranes

Membrane	**S_r (NM)**
P_o	680
P_o-CH-AC (1%)	750
P_o-CH-AC (2%)	810
P_o-CH-AC (3%)	870

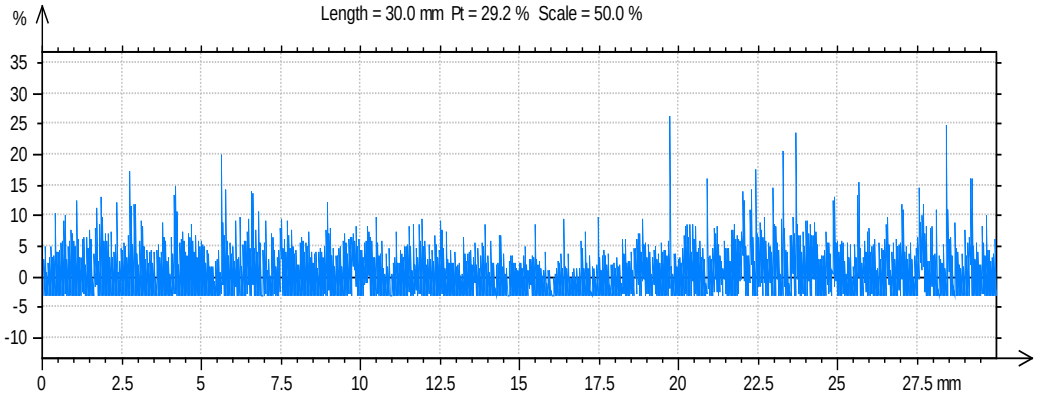


Figure 4.11 (a) Surface Roughness of PES Membrane

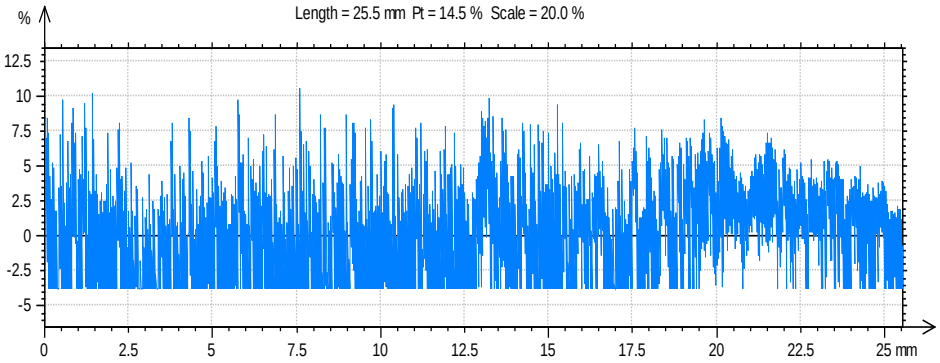


Figure 4.11 (b) Surface Roughness of P_o-CH-AC (1%) Membrane

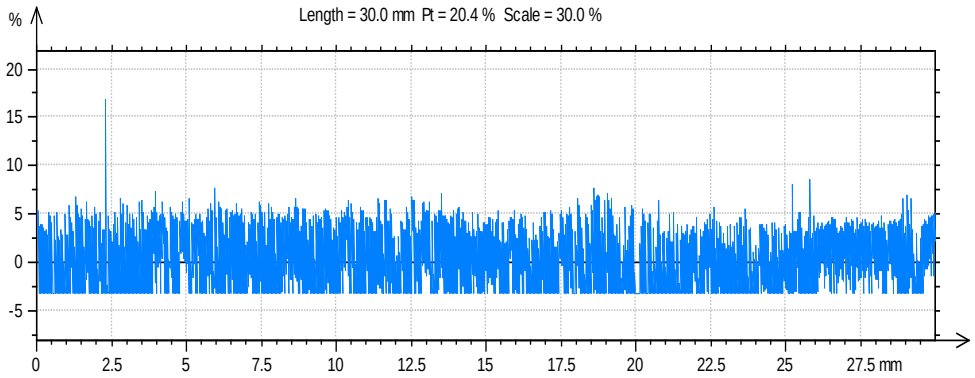


Figure 4.11 (c) Surface Roughness of P_o-CH-AC (2%) Membrane

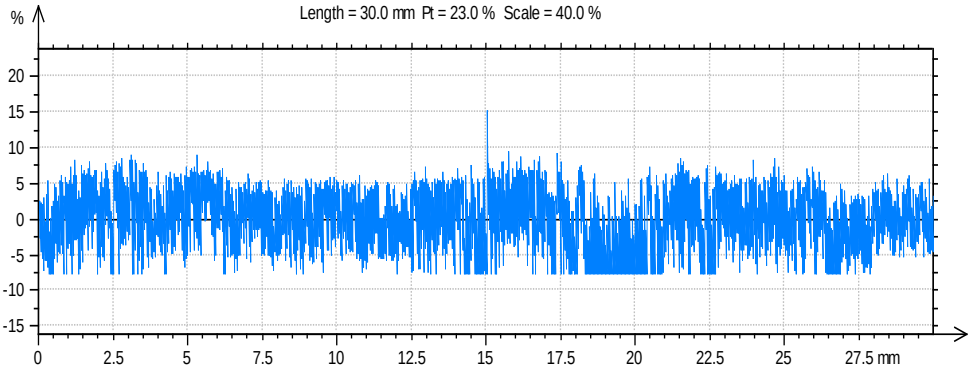


Figure 4.11 (d) Surface Roughness of P_o-CH-AC (3%) Membrane

Above figures showed the surface of individual samples whereas Figure 4.12 represents surface roughness in bar graph form.

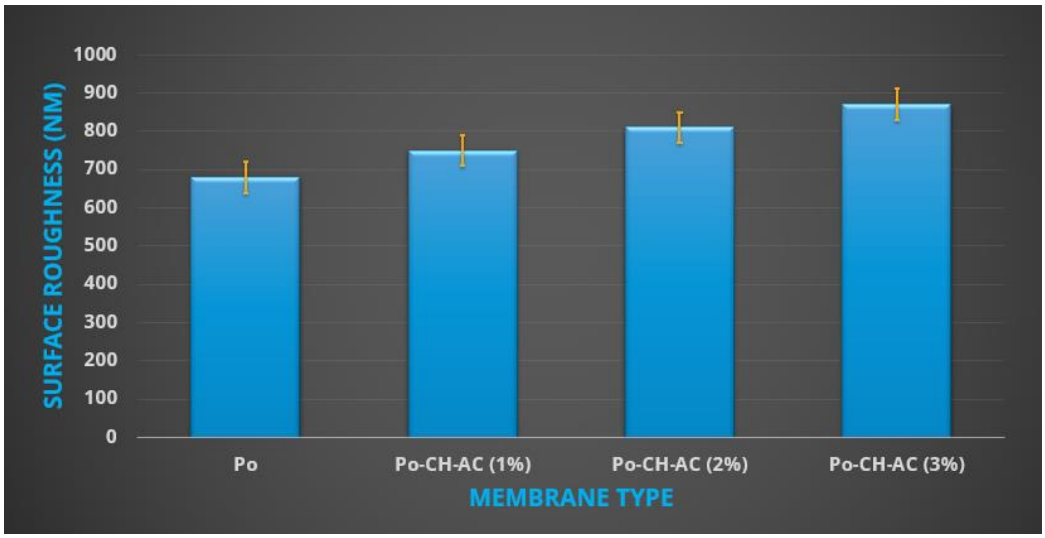


Figure 4.12 Surface roughness of the proposed membranes

4.8 Membrane Filtration Performance Test

Membrane filtration test is the ultimate performance analysis of a material. In this test permeability of the membranes is recorded against distilled water. This study was done in this research by synthesizing membranes at 60 cm Hg. With the increase in chitosan and AC in the manufactured membranes, permeation flux of the membranes also increases [77]. These values are illustrated in Figure 4.13 and Table 4.6 below:

Table 4.6 Water Flux of Membranes

Membrane	Water flux ($mL.cm^{-2}.h^{-1}$)
P_o	4.56
P_o-CH-AC (1%)	12
P_o-CH-AC (2%)	15.45
P_o-CH-AC (3%)	17.5

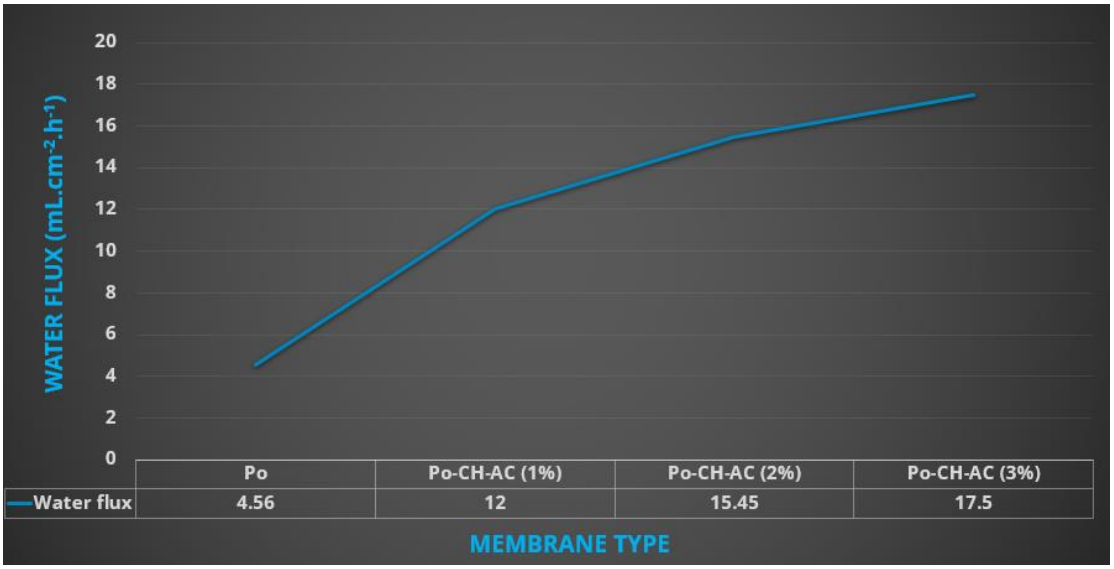


Figure 4.13 Permeability Flux of all Fabricated Membranes

These values show that pristine PES membrane had lowest flux value while as the concentration of chitosan and AC increases, increase in water flux is quite visible. This is since pristine PES membrane unorganized structure and small pores whereas addition of composites increases the flux and pore size as well [78]. These values are also in accordance with the contact angle of membranes.

4.9 Salt Rejection

The salt rejection values of all membranes consequently increase as the water flux increases. This result is presented in Figure 4.14 and Table 4.7:

Table 4.7 Salt Rejection Percentage of Membranes

Membrane	Salt Rejection (%)
P_o	68
P_o-CH-AC (1%)	78
P_o-CH-AC (2%)	95
P_o-CH-AC (3%)	97

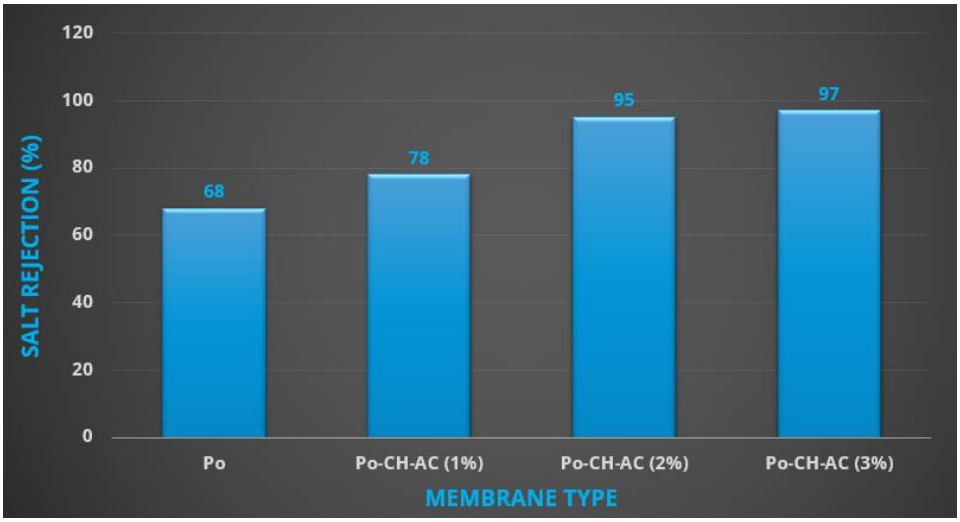


Figure 4.14 Salt Rejection Percentage of Fabricated Membranes

4.10 Antifouling Analysis

To test the membranes against foulant behavior, they needed to be exposed to bacteria that create this foulness in the AMD water. This reason demanded that they needed to be exposed to two illustrative bacteria, that is E. coli and S. aureus through disk diffusion methodology [79]. This technique involves measuring the diameter of the inhibition zone. The bacterial residuals that are prone to antiseptics show greater area of contact while others are relatively smaller. This phenomenon is depicted in Figure 4.15 and 4.16.

Figure 4.15 Antibacterial Testing Process

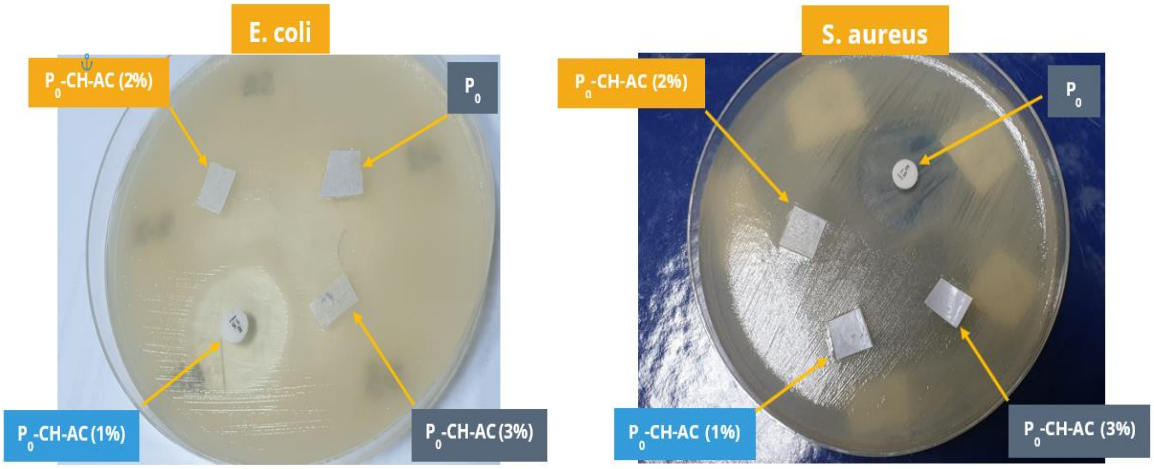


Figure 4.16 E. coli and S. aureus Antibacterial Test

A smaller diameter inhibition zone was recorded in the pristine PES membrane as opposed to the P_o-Ch-AC (3%) disk that shows the impregnation of PES with chitosan and AC effect on the antibacterial activity [80]. So, by the increment of concentration in chitosan and AC, antibacterial activity against E. coli and S. aureus increases, which validates the proposed claim. This is due to the hydrophilic nature of the membranes that causes oxidative stress and bacterial cell loss is caused by the induction of cell lysis. S. Typhi cells reduce when subjected to higher concentrations of chitosan and AC [81]. To further validate the results, these membranes were put into aqueous solution to study their effect against these bacteria

through shaking incubation method. Results tabulated in Figures and tables clearly shows this claim:

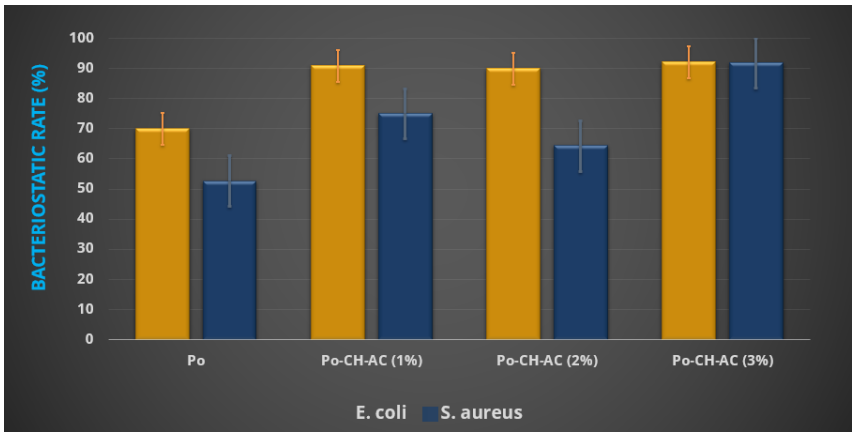


Figure 4.17 Bacteriostatic Rate (%) of Fabricated Membranes

Table 4.8 Bacteriostatic Rate (%) of Membranes

Membrane	**E. coli**	**S. aureus**
P_o	70	52.63
P_o-CH-AC (1%)	90.9	75
P_o-CH-AC (2%)	90	64.2
P_o-CH-AC (3%)	92	91.67

Table 4.9 Summary of the Performance of each Fabricated Membrane

Performance Parameter		**P_o**	**P_o-CH-AC (1%)**	**P_o-CH-AC (2%)**	**P_o-CH-AC (3%)**
Bacteriostatic Rate (%)	E. coli	70	90.9	90	92
	S. aureus	52.63	75	64.2	91.67
Salt Rejection (%)		68	78	95	97
Water flux ($mL.cm^{-2}.h^{-1}$)		4.56	12	15.45	17.5
S_r (NM)		680	750	810	870
Mechanical Strength	EM (MPa)	5.4	5.8	6.125	6.4
	UTS (MPa)	43.34	45.49	48.33	50.76
Porosity (%)		36±	78±	83±	91±
Water Uptake (%)		35±	83±	87±	90±
Average Contact Angle (θ)		66.74±	57.426±	54.264±	50.127±

Conclusions

In this research fabrication of polymer membranes was conducted using the phase inversion method. Fabricated membranes were made antifoulant using composites such as chitosan and activated carbon. These membranes have been characterized by various techniques such as SEM, FTIR, porosity, contact angle, mechanical strength, water uptake, bacteriostatic rate, and others. These membranes have been subjected to model water made of nitrites to study its resistance against it. The results have clearly indicated the increase amount of porosity channels of the membranes having chitosan/AC nanotubes that explicitly demonstrates higher permeability. The effect of various temperatures, concentration and pH levels examined clearly indicates the efficacy of the proposed methodology. Model water using nitrates as fouling agent was tested and the results indicated an increase in water flux from ±4.56 $mL.cm^{-2}.h^{-1}$ to ±17.5 $mL.cm^{-2}.h^{-1}$. This rush in the values and decrease in contact angle ±66.74° to ±50.127°. These results clearly demonstrate that membranes became hydrophilic in character. Nitrates in the acid mine water were absorbed by these hydrogels within the polymeric matrix. High concentration of AC and chitosan helped to provide higher interactions within chitosan particles, hence strengthening mechanical properties. These results promise economical clean drinking water by effectively removing nitrates and optimizing the pH (7) with effluent concentration of 48 mg/L and contact time of 50 minutes. Similarly, removal capacity for phosphate (99.99%) nitrate (99.80%) and ammonia (66.5%) contaminants were yielded. SEM results indicated differences in the morphologies of the acid mine and treated water. Membranes with AC and chitosan demonstrated huge finger-like pores and with high water flux. Tensile strength for PES membranes embedded AC and chitosan showed 4 times more strength as well. Bacteriostatic rate for E. coli and S. aureus bacteria has increased from 52.63 to 90.67. All these results indicate the efficacy of the fabricated membranes as well as the proposed methodology. In future other techniques and functional groups will be incorporated to yield more optimized results.

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