Highly Hydrophilic and Antifouling Ultrafiltration Membranes Incorporated with Water Dispersible Composite Activated Carbon/Chitosan and Activated Carbon/Thiolated Chitosan

By

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Dedication

This thesis is dedicated to my family and friends.

Acknowledgements

"In the name of Allah the most Beneficent and most merciful"

Abstract

A rapid increase in population worldwide is giving rise to many issues, safe drinking water availability being the most important one. There is a need to find ways that are effective and economical to be able to meet this challenge. For this purpose, membrane technology has shown a lot of promise but face the biggest challenge of fouling that reduces its life time. Fouling is the continuous buildup of materials that are deposited on membrane surfaces clogging the pores resulting ultimately in membrane failure. Chitosan and activated carbon have been proved to add value to the polymer membranes. Chitosan not only improves membranes hydrophilicity but also increases its anti-fouling properties. Activated carbon maintains taste and odor of the water and also acts as excellent adsorbent that also helps in reduction of fouling. Ultrafiltration polyethersulfone membranes were synthesized in two different concentrations i.e. 16 % wt. and 20 % wt. Chitosan, activated carbon and thiolated chitosan were incorporated individually in both the concentrations to see their effect on polyethersulfone membranes. The membranes were then incorporated with chitosan/activated carbon and thiolated chitosan/activated carbon to evaluate the changes in property by introducing modified chitosan having thiol groups. The membranes were then analyzed using ATR-FTIR, SEM, Optical profilometry, Mechanical Testing and Contact angle. Gravimetric analysis was done to gauge the effect on mean pore size. Water uptake and permeability rate was done to investigate flux rate. BSA (Bovine serum Albumin) was performed to assess the antifouling activity with change in fillers. The results show a general improvement in the membranes properties with the addition of chitosan/activated carbon and thiolated chitosan/activated carbon composites. The results showed increased hydrophilicity, mean pore size and water retention abilities. SEM micrographs also showed better channels for permeability with the addition of composites. Surface roughness for thiolated chitosan/Activated carbon composite was observed at 20 % wt. The mechanical properties for thiolated chitosan/activated carbon incorporated PES membranes showed decrease in mechanical properties which may be because of its solubility in water and high hydrophilicity. There was a significant increase in flux rate and BSA flux. Apart from membranes incorporated with only chitosan, the best BSA flux was shown by 20 % wt. thiolated chitosan/activated carbon composite membrane.

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List of Abbreviations and Symbols

PES   Polyethersulfone

PVP   Polyvinylpyrrolidone

WHO   World Health Organization

ATR-FTIR   Attenuated Total Reflection Fourier Transform Infrared

SEM   Scanning Electron Microscopy

^{1}H NMR   Proton Nuclear Magnetic Resonance

µm   Micrometer

P_o Pristine Polyethersulfone

PP   Polyethersulfone Membranes with Polyvinylpyrrolidone

PPC   PES membranes with PVP and Chitosan

PPAC   PES membranes with PVP and Activated Carbon

PPCAC   PES membranes with PVP, Chitosan and Activated Carbon

                  (Composite Membrane)

PPTCAC   PES membranes with PVP, Thiolated Chitosan and Activated

                  Carbon (Composite Membrane)

Chapter 1: Introduction

1.1. Background

Water is a resource that is continuously required and consumed by billions of people on a daily basis. It is one of the most basic and crucial resource required for not only human survival but also for the survival of almost every living being. Even though it is the most abundantly available resource naturally, its accessibility is denied to billions of people [1]. A common notion is that Earth is comprised of 70 % water and 30 % land and its scarcity is not an issue. Though water is abundant, the usable water percentage is very low. 97% of the total water is salt water that is unusable for now. The life sustainability needs access to fresh water (having dissolved salts less than 500 to 1000 ppm) which is approximately 3% of the total water reservoir of the whole planet, and even from that approximately two third water is frozen in the form of polar caps and glaciers [2]. Fig 1.1 shows the available sources of water [3].
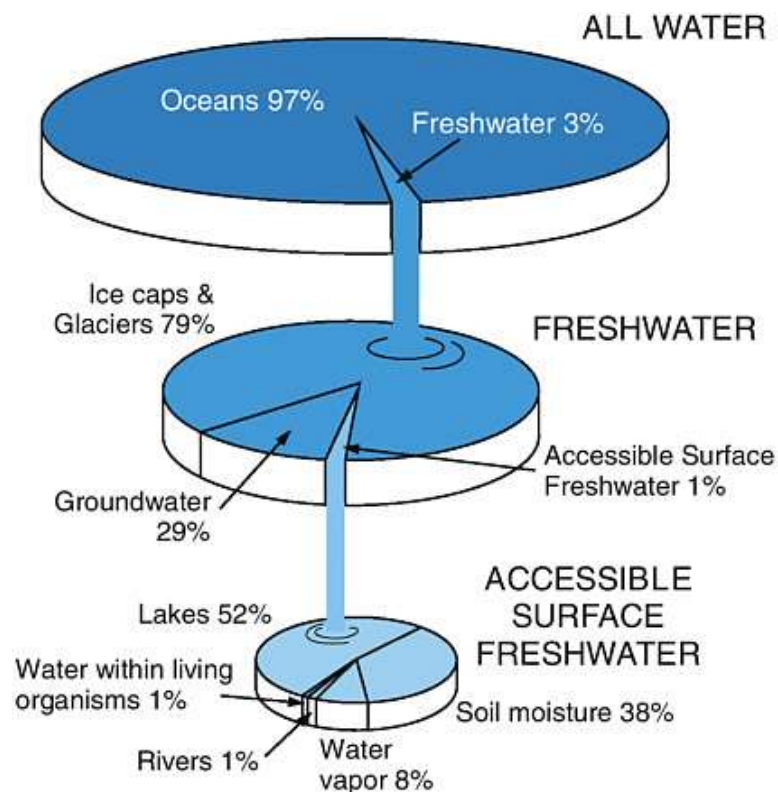
Figure 1.1. Water sources available on Earth [3].

For a large number of population, water that is safe for drinking purposes is inaccessible [4]. According to the UNICEF 2021 report, 450 million children meaning

one in five children worldwide do not get enough water for daily use. In the same report, it was predicted that by 2040, this ratio will come down to 1 in 4 children globally having little to none access to water for sanitation or drinking purpose [5]. With the increase in world population, there is also an increase in water scarcity. The reason being increase in construction, climate change, waste water and other waste discharge in water, industrial and urban development to name a few. Apart from basic hygiene and drinking water problems, other crises are also taking place including agricultural crisis as more water is being consumed by industries and households resulting in reduced accessibility for irrigation [6]. Another one is environmental crisis as on one hand the usable water is getting scarce and on the other hand there is an alarming rise in waste water. This waste water emanating from households, industries and other sources is disposed of into water streams endangering aquatic life and disrupting the ecosystem. It may also cause tensions among two groups (national or international) that share a single source of water.

Millions of deaths globally are a direct result of unsafe and contaminated water consumption. The pathogenic presence in consumed water is the one of the culprits leading to waterborne diseases and ultimately to death. Most of the victims are children below the age of 5 [7]. The usable reservoirs are limited, which necessitates means that can help in salvaging of the used water along with steps to reduce excess water usage so that more and more water can be saved and recycled. According to WHO Reports, in low income countries, only 8% of the waste water from municipality and industries is treated in any way, and in lower middles income countries this percentage only surmounts up to 28% [8]. Globally, approximately 80% of the waste water re-enters the environment without any treatment resulting in increase in water contamination [9]. The report highlights the following facts:

- Around 844 million population is unable to access basic drinking water service.
- Around the globe, approximately 1.8 billion people use water that is polluted with faeces [8].
- Polluted water is one of the main reasons of transmission of diseases such as cholera, polio, diarrhea, typhoid and dysentery. Among these diseases, diarrhea alone causes 502000 deaths per year.

- By 2050, a number of 2.3 billion will be added to the already alarming number that has little to no access to water for either sanitation or drinking purposes [10].

Water is the basic foundation for life on earth, just like a human body has vital signs to show presence of life, the existence of life on earth is dependent upon water. The basis for division of the water on earth is the amount of total dissolved solids also known as TDS. The TDS shows the presence of inorganic salts (calcium, magnesium, sodium etc.) and organic matter in the water. Water based on its TDS content is classified in four groups: Fresh water, Brine water, Brackish water and Saline water. TDS levels for seawater go up to 3000 mg/L to 4000 mg/L [11]. It means that the contamination is so high that consumption of even a few liters can result in death by over burdening your kidneys with large amount of salt. Introduction of more salt than your body's capability to process and excrete results in quick dehydration leading to death making it impractical to use. The only usage of seawater can be to flush toilets. Almost all the life on earth needs freshwater to survive. An adult human body is composed of almost 60 % water. According to numerous scientific data, one of the strongest solvents is water. Our body uses water as a carrier for transport of minerals and nutrients. Water not only keeps the balance of the human body but is also acts as temperature regulator for the body [11].

Water purification is one of the main fields that is addressing the issue of scarcity of drinking water worldwide. There must be emphasis on improved technologies for waste water treatment along with the regulation of waste water disposal. Better and improved technologies need to be encouraged that are also economical so that countries with lower or lower middle income can also afford those technologies as they are the ones suffering from water crisis the most [12]. Even though a lot of work has been done on waste water treatment, it still needs to be heavily researched as there is still a lot of scope for environment friendly and economical ways for water purification that have better efficiency.

1.2.   Water Crisis in Pakistan

Pakistan being one of the developing countries is facing major crisis regarding water. Pakistan, having 207 million inhabitants, is a populated country that requires good

resource distribution management and access to water. According to reports, around 27.2 million people are not able to get water that is safe enough to drink and 52.7 million people do not have access to water for sanitation [13,14]. One of the main reasons for Pakistan's stunted economic growth is water shortage as water is needed for all kinds of industries, factories, construction without which development is not possible. One of the biggest challenges is water pollution in Pakistan. In the absence of proper framework or regulations, there is almost no system for treatment of the contaminated water stemming from industries, construction sites and municipalities. This water is directly adding to water resources that may have been usable otherwise [15]. The death rate for water borne diseases (typhoid, diarrhea, cholera) in Pakistan is approximately 250,000. Textile industries discharge their dye contaminated waste water into rivers and streams polluting even more water. The discharge from other industries and municipalities faces the same fate. According to data, Pakistan has lost around 4260 m^3 per capita in 65 years. By 2025, the surface water available may decrease further from 1000 m^3 (2016) to 860 m^3 which will make the situation graver [16]. These statistics show the need for a viable mechanism for water purification.

1.3. Polymeric Membranes and Fouling

In chemical technology, membranes are one of the most exploited area of application that is being worked upon in recent times. Membranes are mostly used in separation technology that aims towards the separation of one component present in the mixture from the other one by hindering its permeation [17]. One of the key properties that make membranes an important tool in separation technology is the capability to regulate the permeation through the membranes.

Conventional methods used for water treatment include boiling, chlorination or other chemical but these processes have their disadvantages. Boiling is not entirely effective as it does not completely remove all the chemicals or heavy metals etc. from the water. It is also time consuming and non-economical as it requires use of either electricity or gas. Boiling also results in loss of water in the form of evaporation. Chlorination, although widely used, is also not a harmless process. Firstly, it effects water's taste and odor and produces hazardous by products. It also is ineffective against some microbes making it a less than perfect candidate for water purification [18].

Recently, there has been a surge in membrane technology usage. Membranes are a very effective way to treat water as they need less energy to operate. These are also environment friendly and can be bio degradable [19]. Another factor that makes membranes a really good alternate is the ability to functionalize the membranes. For example if a membrane is needed for a specific purpose, there are way to functionalize it to only serve that purpose, which also makes its efficiency percentage greater [20]. Although the membrane technology holds a number of advantages over the conventional methods, it too has some shortcomings. Usually, the polymers used are hydrophobic which presents a problem during water treatment. Also with time, the membranes experience fouling that results in less flux [21]. In water treatment, the processing conditions along with the condition of water to be treated are usually always changing. This change also has its effect on the membrane structure and efficiency i.e. it may not be able to filter out microscopic species after some time. For this purpose, ultrafiltration and polymeric membranes are being continuously explored. Ultrafiltration membranes are moderately inexpensive and need lower pressure and energy when compared to nanofiltration or reverse osmosis making it more economical. It is also a process to disinfect water as it removes out a number of viruses and bacteria. As for polymeric membranes, although polymers especially the ones containing sulfones contain a range of properties having remarkable thermal and hydrolytic stability, they suffer in mechanical strength. One big drawback of both ultrafiltration and polymeric membranes is their tendency for fouling [22].

Polymeric membranes have been used for effective water therapy including the treatment of olive mill wastewater which is a huge agro food by product [23]. These membranes have also found their applications in petroleum industry and withdrawal of contaminants from water [24]. There are four pressure driven membranes that are being explored as promising candidates for waste water treatment namely Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF) and Reverse osmosis (RO). Every membrane has its pros and cons [25].

Two major reasons for excessive use of polymeric membranes are low cost and ease of production[25]. The biggest challenge that these membranes present is to develop a system or a mechanism that can help in reduction of the fouling process happening in the membranes so that the life span of membranes can be increased. For this purpose, scores of research has been carried out and is still on going.

1.4. Problem Statement

In Pakistan, hazardous water supply is resulting in a death rate of approximately 250,000 per year because of water borne diseases (typhoid, diarrhea, cholera). The lower and lower middle income family systems suffer mostly because of lack of potable water. Around 27.2 million people are not able to get water that is safe enough to drink and 52.7 million don't have access to sanitation facilities resulting in severe health issues [14]. Membrane technology is a process that has been showing some promise to improve the water condition globally. But their biggest disadvantage is fouling that renders membranes useless after some time. Mechanisms or methods should be explored to help in reduction of fouling so that the flux rate remains unaffected for prolonged period of usage. A membrane having good flux rate and antifouling activity along with good mechanical properties is the need of this time and is crucial to produce water that is safe for use.

1.5. Research Framework

The research has been carried out in two major phases.

1.5.1. Phase I

Phase I includes successful synthesis of thiolated chitosan and membranes having different concentrations and additives. The polymer used is Polyether sulfone (PES) and two concentrations opted are 16 % wt. and 20 % wt. Activated carbon, PVP, chitosan and thiolated chitosan have been added as enhancers. The membranes were synthesized using these additives both separately and combined so that the effect of each additive can be understood better.

1.5.2. Phase II

In the second phase, different characterization techniques have been performed to investigate the outcome of additives on various properties. SEM, ATR-FTIR, Contact angle, UTS, Optical profilometry, Water and BSA flux, water retention and gravimetric analysis were done.

1.6. Aims and Objectives

The principal of the current study was to synthesize highly hydrophilic and antifouling ultrafiltration membranes incorporated with water dispersible composite activated carbon/chitosan and activated carbon/thiolated chitosan. This was achieved through the development of membranes incorporated with novel thiolated chitosan and activated carbon composite. Thiolated chitosan was synthesized, characterized and was subsequently used in water filtration polyethersulfone membranes. These membranes were then characterized and evaluated for their hydrophilicity by measuring contact angle and water retention test, morphological and functional group analysis was done using scanning electron microscopy and ATR-FTIR respectively, water and bovine serum albumin flux was performed to calculate water permeability and anti-fouling of the membrane. Mean pore radius was calculated using gravimetric method. Optical profilometry and mechanical testing was performed to gauge surface roughness of the membrane and ultimate tensile strength respectively.

To the best of our knowledge, thiolated chitosan was employed to fabricate polymeric membranes for water treatment and it was used as a novelty as there is no previous reported study available for thiolated chitosan incorporated polymeric membranes. Novel thiolated chitosan/activated carbon composite was employed in the polymeric membranes for achievement of high hydrophilicity and antifouling properties.

Chapter 2: Literature Review

2.1. Membranes

Quintessentially, a membrane is a distinct and thin interface which functions as a regulator that modulates the penetration or movement of chemical species that come into contact with it. The interface can be of many types i.e. it can either be a molecularly homogenous interface having uniform composition and assembly or it can be heterogeneous (chemically or physically) having defects or different pore shapes and sizes and in some cases formation of some other irregular formation in the membrane structure [26].

There are different factors that can be tuned for different permeation rates i.e. pore size can be either enlarged or minimized so that bigger or smaller particles respectively can pass through it [27]. Another factor is the surface treatment of the membranes to either make it chemically selective towards oncoming chemical species or make the surface charged to attract or repel the species. Normally, this definition of the membrane is applicable on filters but conventionally structures or membranes that help in separation of particle sizes that are bigger than 1-10 µm in a suspension are termed as filters.

2.2. Types of Membranes

There are different factors on the basis of which the membranes are divided into groups. Depending on the physical and chemical properties and structures, membranes can be of the following types [28]:
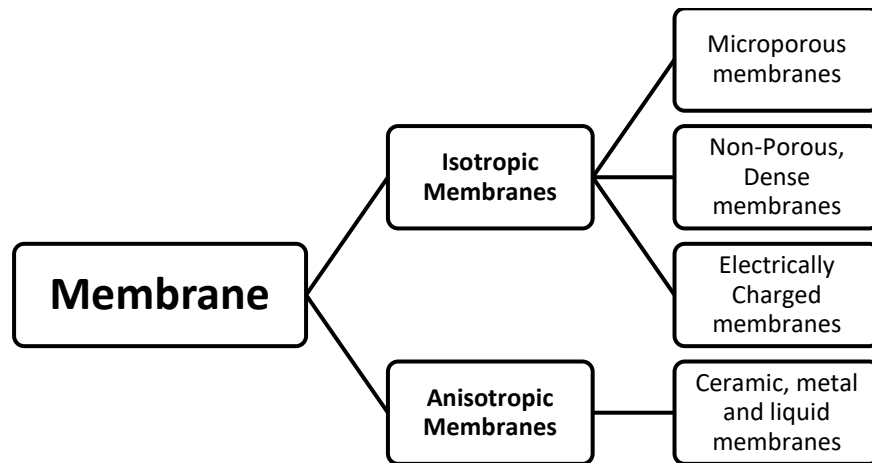
Figure 2.1. Types of Membranes.

Isotropic Membranes

2.2.1.1.   Microporous Membranes

A conventional filter has a lot of similarity with a microporous membrane with respect to functions and structure. They both have a rigid structure that has a high number of voids that are distributed randomly and have interconnected pores [29]. Although they both have the same structure more or less, they also have their differences. A microporous membrane has pores that are tremendously small having size on the order of 0.01 to 10 µm as opposed to that of conventional membranes. It rejects the particles completely that have sizes larger than the biggest pores present, but allows the particles that have smaller size range as compared to the pore size to pass, which makes it primarily a system that depends first on molecular size and second on pore size distribution. Generally, molecules differing only in size can be alienated by the microporous membrane system i.e. ultrafiltration membrane and nanofiltration membrane that differ in only pore size range [30].

2.2.1.2.   Nonporous, Dense Membranes

Another subtype of membranes is a nonporous membrane that has a dense membrane type. This membrane type works under certain driving forces that include concentration, pressure or electrical potential gradient that permit the transportation of permeants by diffusion. Different components have different solubility and diffusivity

and their separation process is determined by these properties. Within the membrane, there lies a direct relation between the separation of different components and their transport rate [31]. This type of membrane structure is used in most of the RO (reverse osmosis), gas separation and pervaporation processed. To improve the flux, these membranes are usually induced with an anisotropic structure.

2.2.1.3. Electrically Charged Membranes

Another subtype is an electrically charged membrane that usually has very fine micropores but is sometimes dense too. The charge on the membranes enables the pores to separate permeants based on their fixed charges i.e. positive or negative [32]. Based on charge there are two types of membranes, one is an anion exchange membrane having fixed ions that are positively charged and the other one is a cation exchange membrane having fixed ions that are charged negatively. The anion exchange membrane is the one that bind anions from the fluid. This kind of membranes work by excluding ions having similar charge as that of ions in the membrane. Another factor that plays its part is pore size but it has marginally less effect as compared to the charges [33]. The process of separation is also impacted by some other factors such as ion concentration in the solution e.g. divalent ions are separated more effectively than the monovalent ions. These membranes find their application in selectively permeable membranes and electrodialysis [34].

2.2.2. Anisotropic Membranes

There exists an inverse relationship between the thickness of the membrane and the species' rate of transport. These membranes are comprised of surface layers stacked on a substrate that is porous and thick but the surface layers themselves are particularly very thin [35]. The substrate is a substructure that supports the membrane mechanically and plays no part in determining the flux rate of the membrane. The separation process solely depends on surface layers and its thickness and permeability. In membrane technology, a major advancement in the past 30 years, was the fabrication of anisotropic membranes using new production techniques. Economically, it's better to have great transport rates so thin membranes are more desirable for separation processes [36]. For a membrane to be defect free and robust mechanically, the existing manufacturing process is limited. It fabricates membranes that are 20 μm

thick. Commercially, anisotropic membranes are the most used membranes because of their high flux rates.

2.2.2.1. Ceramic, Metal and Liquid Membranes

Up until some years back, most commercially used membranes have been organic and polymer based but recently a change in interest has taken place by diverting the focus towards membranes that are fabricated from materials that are less conventional. There are certain types of inorganic membranes that are now being used for different purposes and applications. One of them is a microporous membrane that is composed of ceramic materials [37]. In the processes where thermal as well as solvent resistance is required such as UF and MF, this special class of membranes is used. Since 1980, it has become a rapidly developing process and is now able to produce membranes that are defect free [38]. Fig 2.2 shows types of membranes [26].
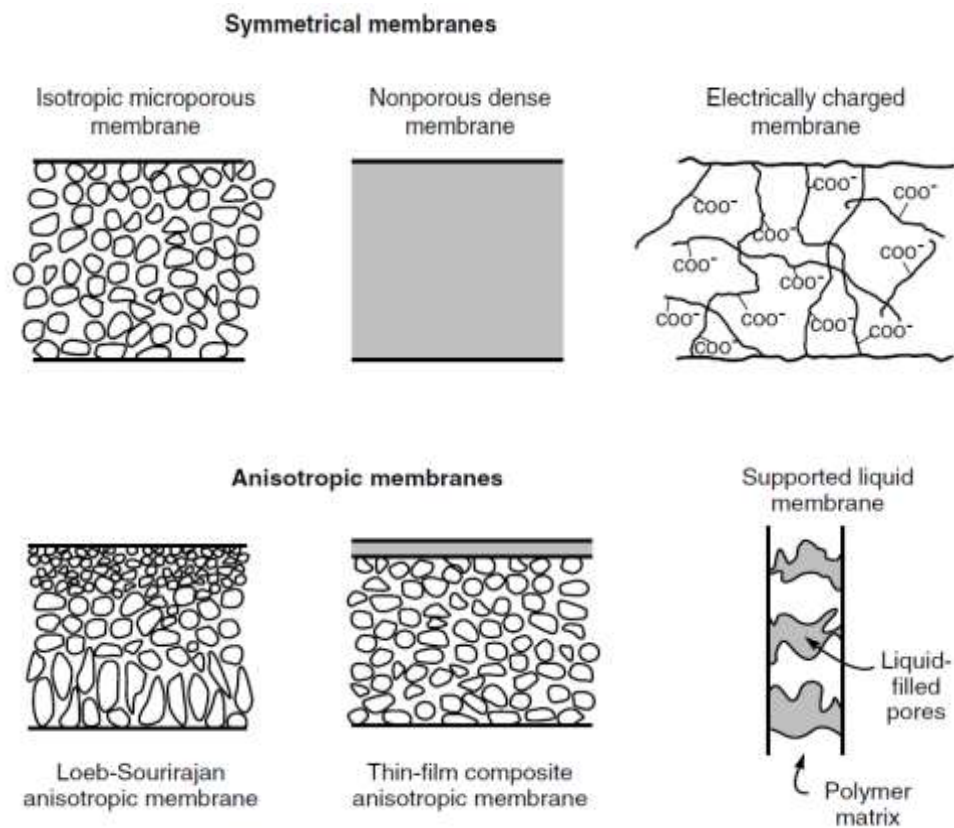
Figure 2.2. Types of membranes based on structure [27].

2.3. Membrane Processes

Water and surplus water produced as a by-product from several industries are further purified using membrane processes. Currently, due to shortage of water, advanced membrane processes are developed to substitute or complement conventional cleaning approaches. There are four membrane separation processes that are developed industrially[39], which includes:

- Ultrafiltration (UF)
- Microfiltration (MF)
- Reverse osmosis (RO)
- Nanofiltration (NF)

MF and UF are pre-filtration processes which are carried out first to remove particles with larger particle size. Then inorganic pollutants, ions and pathogens are removed using RO. Further NF also proves efficient in removing heavy metals or dissolved organics in the water.

2.3.1. Reverse Osmosis

Reverse Osmosis is a process which utilizes green technology. In this process ground water, wastewater and feed water is treated. This process is widely used for water treatment, but still it has limitation for sea water with high osmotic pressure and wastewater with high Total Dissolved Solid (TDS). The principle of reverse osmosis is based on the rate at which the impure/contaminated water is projected through the membrane. This rate must be faster than that of dissolved solids. As a result of this, water is separated from the contaminations (solute) giving clean water at the end. Osmotic pressure is exerted on the membrane by the natural motion of clean water to the impure water side. To avoid this, the impure water is subjected to an external hydraulic pressure causing the pure water to easily pass from the membrane leaving behind the salts. Membrane used for this process have a pore size diameter in a range of 0.1 nm (1 Å). This small size pores helps to remove dissolved salts, colloidal particles, microorganisms and sediments from the contaminated water. Reverse Osmosis operates under 10 – 50 bar pressure range, resulting in 20 – 50 L/m^{2}h flux rate.

Particles that are filtered out in reverse osmosis have molecular weight of greater than 50 Daltons. This includes almost all dissolved contaminants and TDS, bacteria,

viruses, heavy metals and organic pollutants. Trihalomethanes (THM's) like chloroform, dibromochloromethane, bromoform, and volatile organic compounds (VOC's) are also extracted. Thin film membranes composed of cellulose acetate are commercially used [38].

This process filters out all the impurities in a single step and also provides a low operating cost and high production capacity for water filtration. But the presence of strong acids and bases in contaminated water can most of the times damage the membranes. Free chlorine is also a damaging agent. These membranes are bound to become fouled more rapidly because of organic and inorganic pollutants. Biological constituents along with metal oxides also fasten the fouling process.

2.3.2. Nanofiltration (NF):

Nano-filtration is an advanced pressure process which filters dissolved contaminants using a nano-porous membrane which is semi permeable. It has a pore size ranging from 1 – 10 nm. This pore size helps in separating on the basis of molecular weight. It lets the elements with the molecular weight (300 – 500 g/mole) to pass. Pressure range 5 – 21 bar is used resulting in a flux rate of 20 – 200 L/m^2h. Nanofiltration works on the mechanism similar to Reverse Osmosis. In this process a pressure gradient is created to transport the clean water through the membrane leaving behind the TDS, hardness, color, turbidity and dissolved organics [40].

For NF applications spiral wound modules are presently used, which is likely to be replace by hollow fiber geometry in the future as it is cost effective [41]. The applications of NF include purification of ground water using intermediate total dissolved solids (range up to 800 ppm), as a substituent for the process of lime softening for reduction in hardness by removal of multivalent ions, preprocessing by removing mineral components from sea water, treatment of discharge or waste material from textile and dairy industry and heavy metal separation from dissolved solutions [42]. Following are some major advantages of Nanofiltration:

- NF offers a lesser energy consumption process in comparison with Reverse osmosis, as it utilizes lower pressure values. Hence it is a good replacement of Reverse osmosis [43].

- Molecular sieving or charge based exclusion is used as a separation technique, in which NaCl a monovalent salt passes out through the membrane whereas $CaCO_3$ a bivalent salt experience extreme withholding.

2.3.3. Ultrafiltration (UF)

Ultrafiltration, though a pressure driven process, finds its difference in pore size and separation on the basis of molecular weight of the solutes. It has pore size ranging from 0.005 to 0.02 µm. This pore size results in successful extraction of macromolecules from the solution. It also can take out colloidal substances and solute that have high molecular weight [44]. The pressure range for ultrafiltration operation ranges from 1 to 10 bar. This pressure requirement may change slightly depending on the molar masses of the solutes to be isolated e.g., for solutes with 1 to 300 kDa, the pressure required will be higher than 1 MPa. In this case, when all the required conditions are fulfilled, the solutes with lower molar mass than 300 kDa can be allowed to pass through and the ones with greater molecular weight will be rejected. Most often, composite membranes are used in ultrafiltration [45]. Dissolved solids present in the feed solution cannot be filtered out using ultrafiltration but most of the microbial structures can be. Although the major application for UF is making water safe enough to drink it also finds its applications in some other industries e.g. food refinement (juices etc,), protein adsorption from food and dairy [46]. In biotechnology, cell or protein (liposome or lysosome) harvesting is also an application of ultrafiltration. Recovery of critical toxins can also be a benefit of this process. Ultrafiltration is also used as a pretreatment process for nanofiltration and reverse osmosis [38].

2.3.4. Microfiltration (MF)

Microfiltration is a water cleaning process which operates under 0 – 2 bar pressure range to filter out bacteria, suspended particles and large colloids from the feed solution. Microfiltration process contain symmetric or asymmetric structured porous membranes with 0.05–10 µm ranged pore size and 10 – 150 µm thickness respectively [47].

Ceramics or synthetic polymers are used for the preparation of microfiltration membranes. Some examples include nylon, polypropylene (PP), polytetrafluoroethylene (PTFE), and polysulfone (PSf) materials are used for the

preparation of MF membranes. Hollow fiber, tubular, plate and frame modules are widely used. In industries such as semiconductor and pharmaceutical, ultrapure water is used that is obtained by using microfiltration process. Microfiltration can be used for lessening chemical dosage. Machine footprint is lower in comparison. The removal capability of microfiltration has a wide range [48]. It can remove not only large clusters along with bacteria, but also suspended and colloidal particles. An important application of microfiltration is its use in membrane bioreactors. A membrane bioreactor is used in waste water treatment that removes chemical oxygen demand and biomass. Biological treatment in waste water can also be done via microfiltration as it helps in removal of bacteria also. Microfiltration helps in reduction of fouling of membranes with smaller pore sizes i.e., ultrafiltration, nanofiltration and RO following removal of colloidal particles during pretreatment and preventing clogging the smaller pores. Although microfiltration is an excellent separation process and is one of the most used pretreatment technologies but it also has a drawback. Microfiltration is restricted as a pretreatment technology because of a number of reasons, one being its inability to removed dissolved species, nitrates and heavy metals. Another one being an impossibility to remove or reduce hardness from the waste water [49]. Apart from limited functionality, cost of microfiltration is more than other available treatments. Different filtration types are categorized in Fig 2.3.
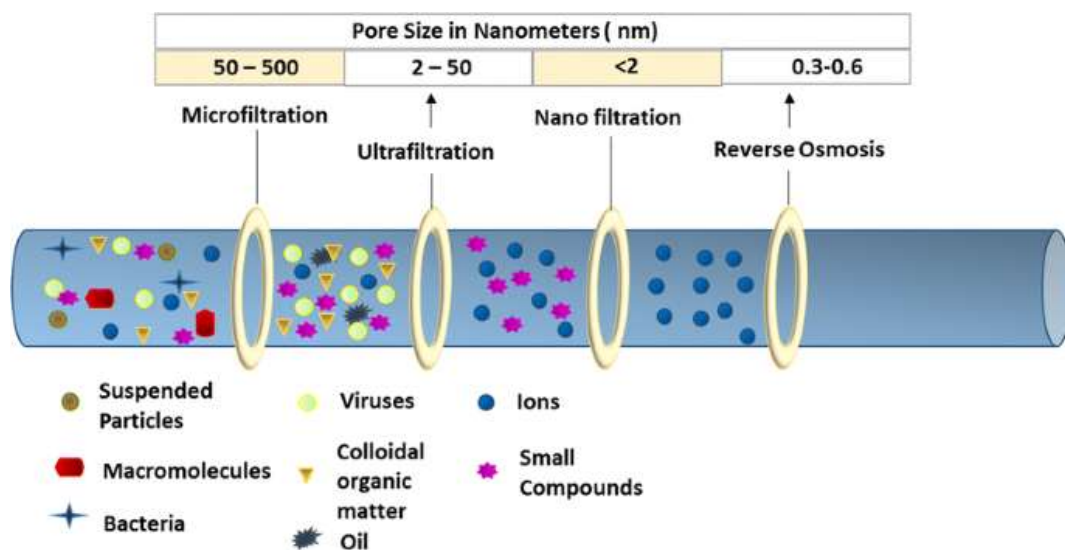
Figure 2.3. Membrane Filtration Types [51].

2.4. Polyethersulfone (PES)

The chemical name for Polyethersulfone is Poly(oxy-1,4-phenylenesulfonyl-1,4-phenylene). And the molecular formula for Polyethersulfone is $(C_{12}H_8O_3S)_n$. Polyethersulfone is a modified form of polysulfone and is synthesized by undergoing the process of polysulfonation or polyester synthesis. It is composed of aromatic rings (phenyl and biphenyl groups) that are linked alternatively by ether and sulfone groups as shown in Fig 2.4.
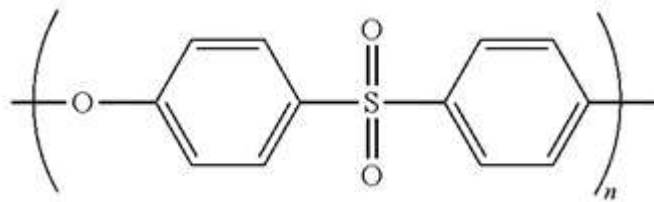
Figure 2.4. Chemical structure of Polyethersulfone [52].

Polyethersulfone is a thermoplastic that can be engineered on high temperature which gives it an advantage over other polymers [52]. It is a flame-resistant material along with being one of a fewest smoke emitting material. They are also used as flame retardants.

Polyethersulfone is an amorphous polymer which is preferred in a lot of applications over other polymers because of a number of its properties. The bonds present in polyethersulfone have a very high value of heat resistance and oxidative stability that gives it an edge over other polymers. Due to the presence of sulfone groups, polyethersulfones have elevated temperature performance[53]. Apart from sulfone groups, ether linkages are also a part of PES structure which allows the polymer chain mobility during the process of melting. In comparison to polysulfones, polyethersulfones display a greater impact strength and also superior chemical resistance [54]. The glass transition temperature T_g for polyethersulfone is around 225^0 C which makes it a dimensionally stable material over a broad spectrum of temperature. Its creep resistance is long term and exceptional and can uphold it to temperatures up to 150^0 C which makes it better than polycarbonate, polysulfones or phenylene oxide-based resins as far as creep is concerned [55]. The processing of polyether sulfone is an easy method and it is also a biocompatible material showing

low mold shrinkage. PES exhibits resistance to aliphatic hydrocarbons, alkalis and oily substances [56]. It is also sturdy against acids and alcohols.

Due to its versatile properties, PES has a number of market applications including but not limited to electrical, automotive and medical industries.

2.4.1. Automobile industry

The major properties that make polyethersulfone applicable in automotive industry is its resistance to gas and high-temperature oil [57]. These properties allow PES to be used where other plastics do not fulfil the performance requirements. As discussed earlier, polyether sulfone itself is not a very strong material, it needs reinforcement. The reinforcements used for applications in automobile industry are either carbon fibers or glass. The modified version of polyethersulfone has even switched places with metals and other materials such as thermosets in this industry. It can help reducing the overall weight of the machinery by replacing high weight materials with light weight polyether sulfone materials [58]. It is mainly used in exterior and body of the machine resulting in reduction of the overall weight of an automobile.

2.4.2. Electrical applications

The main attribute that makes polyether sulfone a good candidate for use in electronics is its dimensional stability along with its strength and stiffness. These properties allow its use in a number of applications including socket connectors, coil formers, transparent switch and signal lamp covers, sensors, power circuit components, parts for TV, as a component in ovens, fans, power contactors, hairdryers and projectors. It also finds its application in battery seals, chip trays and carriers, injection molded printed circuit boards, heat shields etc.

2.4.3. Industrial applications

As discussed earlier, PES have properties that are lacking in most of the other polymers. It is used where other engineering plastics are unable to meet the performance requirements. Polyether sulfone possesses a set of properties that makes it desirable in multiple industries. Those set of properties include better mechanical strength, a better range of operating temperatures and rigidity etc. These extraordinary characteristics make it a better alternative to metals, ceramics and thermosets as it also helps in reducing weight, being a light weight material itself, in addition to providing better mechanical and chemical properties [59].

Pumps and valves are manufactured for industrial markets by using polyether sulfone to use in chemical industry. These components are also used in process equipment. In mechanical field, polyether sulfone is used in a lot of applications for instance as a component for pumps, dispensers, heat exchanges etc., in sensors that detect oil level and as idlers in conveyer belts along with other applications.

2.4.4. Medical applications

Due to its mechanical strength, PES has the capability for repeated sterilization endurance. This ability makes it useful to be used in numerous medical applications. PES shows endurance towards germicides and sterilants along with gamma and electron beam radiation [34]. The prospect of repeated sterilization at a very high temperature makes parts that are prepared by PES very desirable and economical for use in medical industry. According to data, the polymer retains most of its properties even after a hundred sterilization cycles and does not lose its transparency [60]. Nevertheless, it does experience decline in tensile strength and ultimate elongation due to high energy radiation exposure. Some of the medical applications that use PES include reusable syringes, membranes for dialyzers, sterilizing boxes etc.

2.5. Membranes Made from Polyethersulfone

One of the very common polymers used for membrane fabrication commercially is polyethersulfone. Its key properties include strength and high temperature resistance compared to other polymers which enable the formation of asymmetric membranes that are strong and have microporous structure [61]. During general filtration process, the removal of particulates is done efficiently using these membranes. These membranes are also used for drug recovery that are used in chemotherapy and I.V. along with surgeries. Polyether sulfone membranes are also being continuously modified by different methods to improve their properties. These methods include either functional groups or addition of different additives etc. Sometimes these modifications are specific to a certain application and sometimes they are for the general improvement of the membrane that might include permeability, strength or lifetime. These modifications are also done to introduce new property such as antifouling etc. The examples include SPES membranes that have sulfonic group attachments on the ether, chitosan membranes that have chitosan as an additive to the

membrane matrix, membranes that have graphene as an additive helping in antifouling and a lot more.

To achieve optimum functions of the membrane, chemical design and as well as physical construction are important factors to be considered. Advance materials, surface modification and membrane processing methods are critical for the fabrication of high-performance membranes.

Membrane materials are selected on the basis of structure property relation in polymer, novel materials which enhance membranes permeability and selectivity are explored. Moreover, membrane material should withstand permeation conditions which include factors like temperature, pressure and pH. Robustness and ease of preparation are also to be considered while selecting material. Membrane material can be synthesized and modified by polymer blending, copolymerization, cross linking and by formation of hydrogen bonds in the polymer chains. Further chemical and physical treatments are also used as modification techniques. Chemical treatment is associated with contact of the membrane with a chemical agent, solvent, surface active agent, coupling agent or any other additives. While physical treatment techniques involve ultraviolet and plasma irradiation and sputtering.

Variety of polymers can be used for preparation of casting solution and membrane preparation. The selection criteria cater hydrophobicity, hydrophilicity, heat resistance and inertness to chemicals.

Polymer and its concentration in the casting solution determine the density of membranes. Casting solvent also effects the entanglement and distribution of polymer chains and subsequently the density of final fabricated membrane. Casting solvent can also be used in combination that is, as a mixture of organic solvents. One of the two solvents have lower boiling point while the other one has higher boiling point [62]. Permeability of membrane for liquids depends on the structure of membranes and its pore size, which is determined by the nature of casting solution. Therefore, it is crucial to explore all the possibilities and choose the most viable.

2.6. Membrane Fouling

One of the biggest reasons for membranes failure is fouling. Fouling is an accumulation of materials on the membrane surface. These materials contain particles which when deposited on the surface create layers upon layers and finally result in gel formation that clogs the pores completely. The particles instead of filtering out are either trapped into the pores or deposited on the surface of the membrane leading to membrane failure. The material is either adhered on the walls of the membrane or deposited in the mouths of the pores, or indeed a mixture of both. Fouling is one of the biggest problems that is being faced by the membrane technology.

This accumulation gives rise to a resistance against flux. Lower flux rate means lesser flux rate than the theoretically calculated flux keeping in mind the operating conditions. This resistance then requires more pressure and more energy to operate [63].

There are certain factors that play a huge part in the fouling of the membranes: (i) The type of the membrane (ii) Surface properties of the membrane and the material it is composed of, (iii) Fluid dynamics of the membrane, (iv) the amount and nature of solutes and solvents. In general, there are four distinguished foulants:

   i.   Organic foulants
  ii.   Particulates
 iii.   Precipitation
  iv.   Microbes

Different types of fouling have different effects on the membranes. Some partially handicap the membrane while others completely render the membranes useless. The mechanisms that lead to fouling are:

2.6.1. Adsorbent

When the membranes surface and the solutes particles undergo special interactions, the adsorption process starts. In this form, the solute particles settle themselves on the surface and inside the pores of the membrane by adsorbing themselves to the membrane [64]. In this way a layer starts to form on the surface effecting the performance of the membrane.

2.6.2. Pore blocking

The solute particles while filtering can get trapped into the pores owing to a number of factors which slowly clogs the pores. This reduction in pore availability has adverse effects on permeation flux [65].

2.6.3. Deposition

The deposition of solute particles on and in the pores is a reason for reduced flux. The particles when continue to deposit start forming a layer. Due to this, pore on the membrane surface is mostly blocked.

2.6.4. Cake formation

As the layers on the membrane surface keep growing, they form multiple layers on the surface. These multiple layers are the reason for hydraulic resistance and consequently membrane failure.
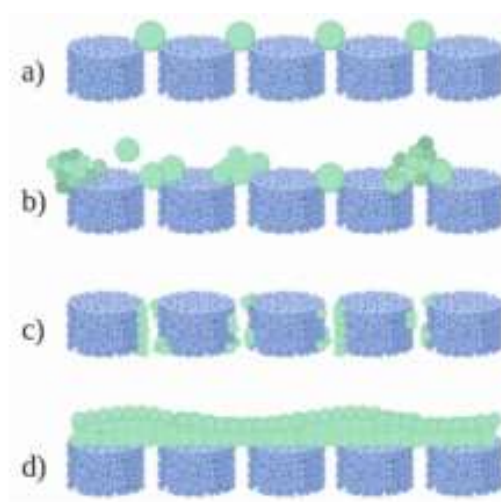
Figure 2.5. a) Adsorption, (b) Pore blocking, (c) Deposition

and (d) Cake formation [65].

2.7. Anti-Fouling Membranes

Anti-Fouling is a specialized category of coatings applied to enhance the properties of surface which helps in slow growth of inadmissible particles or facilitate detachment of such particles. Anti-fouling membranes are formed as functionalities and structure can easily be modifies thus allowing the tuning of the surface properties that is antifouling properties. This helps in making the surface of membrane less favorable

for foulant attachment by using white side's rule, thus making surface hydrophilic, which includes hydrogen bond donors and acceptors and by making interaction of charge of surface and of foulant, overall neutral. Three strategies for antifouling membranes includes the modification of surface chemistry, surface topography and architecture [66]. The approaches for the prevention and reduction of the influence of fouling on membranes are separated into two major groups i.e., direct, and indirect methods.

Initially, many antifouling coatings included metals, these coatings itself are considered to be harmful to the environment, thus the focus was shifted to tributyline also known as TBT, it was the most successful coating but it was found toxic, harming organ system, thus was banned around the world [67]. Thus an interest has generated in identifying compounds which can be used as antifouling but must include certain properties like a mechanism that is non-toxic, a non-toxic mode of action, ability to breakdown toxic materials into non-toxic materials and should be effective against a wide range of organisms that lead to biofouling. Table 2.1 describes some processes for fouling prevention.

Table 2.1. Steps for Membrane fouling Prevention.

Turbulence promoters (e.g., modified membrane spacers)	Pretreatment by filtration
Pulsed or reverse flow	Treatment of the membrane surface
Rotating or vibrating membranes	Preparation of more hydrophilic membranes
Stirred cells with rotating blades close to the membrane	Selection of appropriate operating mode
Ultrasonic enhancement	Selection of optimum operating conditions
Periodic maintenance cleaning • Chemical cleaning. • Hydraulic cleaning. • Mechanical cleaning	
Periodic backwash with permeate or gas	
Generation of a dynamic membrane layer	

2.8. Activated Carbon

Activated carbon has diverse structural properties. It not only has a porous structure but also has chemical properties. Its high adsorption property is due to its porosity but it has heteroatoms that are covalently bonded that also play an important role. Although the structure is roughly similar to graphite but there is a difference in crystalline structure. The interlayer spacing in activated carbon is greater than that of graphite.
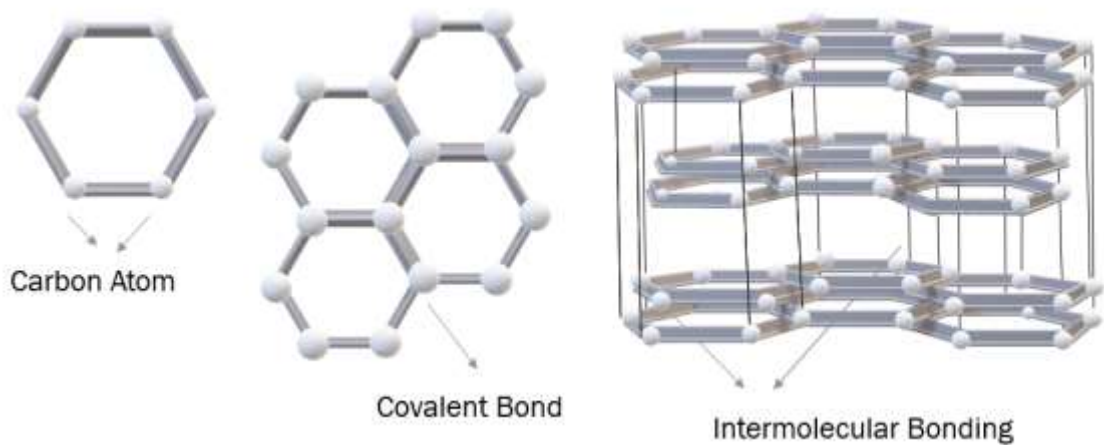
Figure 2.6. Structure of activated carbon [68].

Activated carbon has been increasingly used in membranes for a number of reasons. Activated carbons possess a number of functional groups including hydroxyl, epoxy, silane, alkene. It may have more groups based on the source it is derived from or the method used. In water treatment, activated carbon is mostly used as an adsorbent. Apart from the presence of enhanced active sites, the presence of van der waal's forces also play a role in the physisorption [69]. These forces attract the pollutant from out of the solution and onto the porous surface of the activated carbon. It also maintains the taste and smell of the processed water. Due to its high porous structure, the active sites are abundant for activated carbon for adsorption [70].
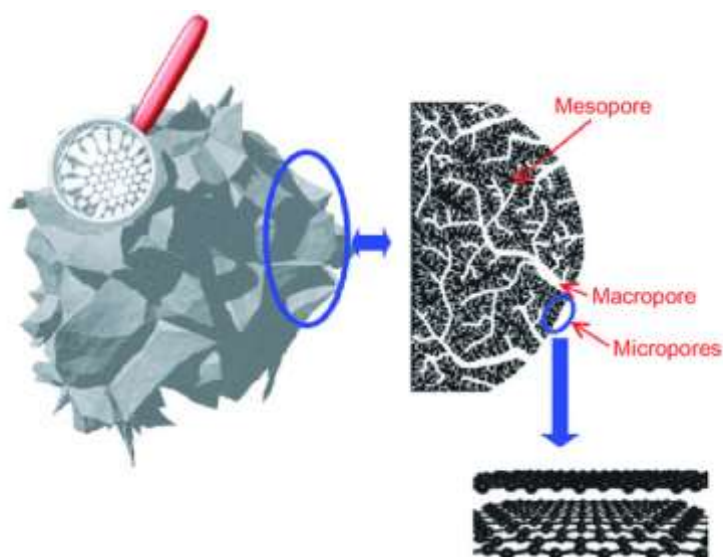
Figure 2.7. Crumpled Paper Model by Oberlin 1989 [71]. ·

This figure shows the loose stacking of aromatic carbon sheets. This leads to macro and micropores along with a mesoporous structure.

2.9. Chitosan

One of the most commonly found polysaccharides in nature is chitin and its deacetylation results in the formation of chitosan. It consists of glucosidic bonds that link N-acetyl-D-glucosamine and D-glucosamine together as shown in Fig 2.8.
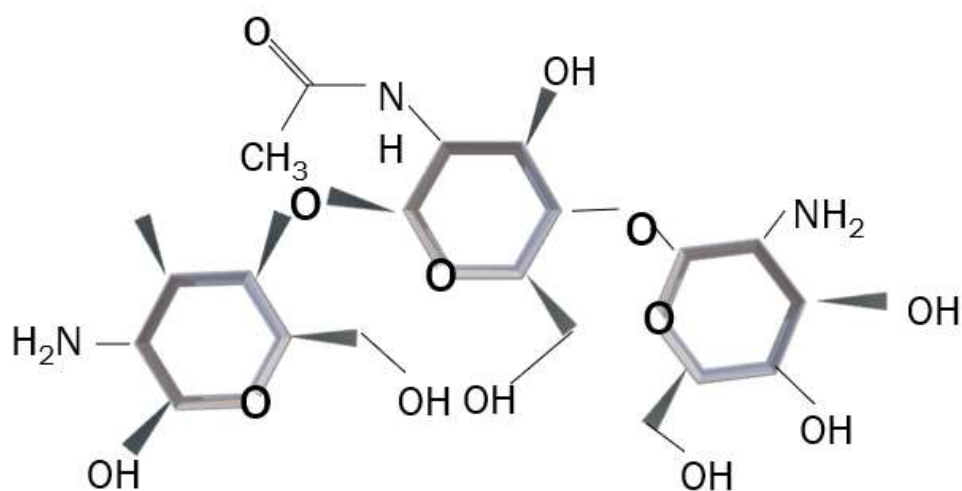
Figure 2.8. Structure of Chitosan.

Chitosan has received enormous attention due to its wide range of properties. Chitosan is used for immune stimulation, as an anticoagulant and has showed great antimicrobial activity. It is widely being used in pharmaceutical industries. Its key properties are that its almost nontoxic, biocompatible and biodegradable [72]. The role of chitosan has also been investigated in membranes. The structure of chitosan is similar to cellulose. But instead of –OH group of cellulose, chitosan has –NH$_2$ repeating unit making it a hydrophilic polymer [73]. It is not only used to enhance the surface wettability but also to increase adsorption in water treatment. Chitosan acts as a flocculent resulting in agglomeration of colloids making their extraction easy [74]. Chitosan membranes find their applications more useful in UF and RO. In ultrafiltration, the surface characteristics of membranes lead to a significant role. Addition of chitosan increases the wettability property of the membrane hence enhancing its efficiency by absorbing less protein and reducing the flux loss. This helps in reduction of membrane fouling. The exact mechanism of antibacterial property of chitosan has not been conclusively deducted. There are certain theories that explain to some extent the probable mechanism. One theory in particular is rampant that states that due to the positive charges present on chitosan surface, it binds to the cell wall of the bacteria which is negatively charged. This binding disrupts the cell causing change in the permeability of the membranes. It then attaches to the DNA and inhibits its replication process leading to the death of the cell [75]. There is one other theory that has gained popularity. It finds its basis on the chelating properties of the chitosan stating that this ability enables chitosan to bind with metal components that are present in trace amounts and cause production of toxins which in turn inhibits the growth of microbes [76].
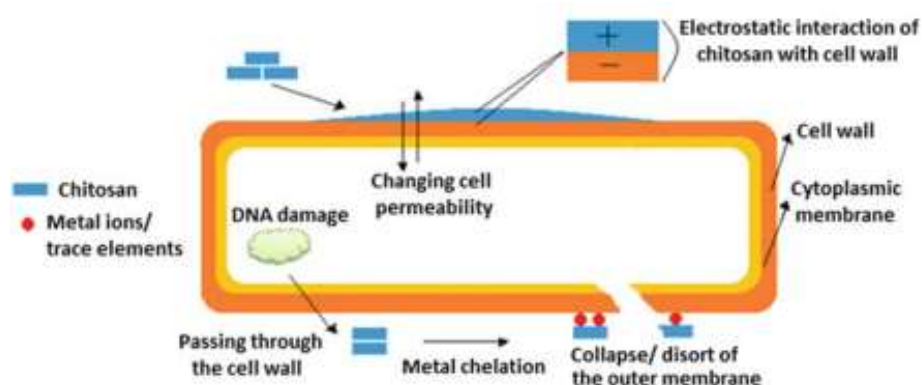
Figure 2.9. Proposed Mechanisms For Antibacterial Activity Of Chitosan [76].

2.10. Thiolated Chitosan

Due to the versatility of chitosan, a lot of work has been and is being done on modification of chitosan. One of the most used process is the addition of functional groups onto the chitosan to either enhance its properties or make chitosan an application specific derivative. One such derivative is Thiolated chitosan that has –SH groups covalently attached to primary amino and hydroxyl groups of the chitosan polymer [77]. These were discovered in 1998 and have proven to be substantially better assets than simple chitosan. Fig 2.10 shows the structure for chitosan.
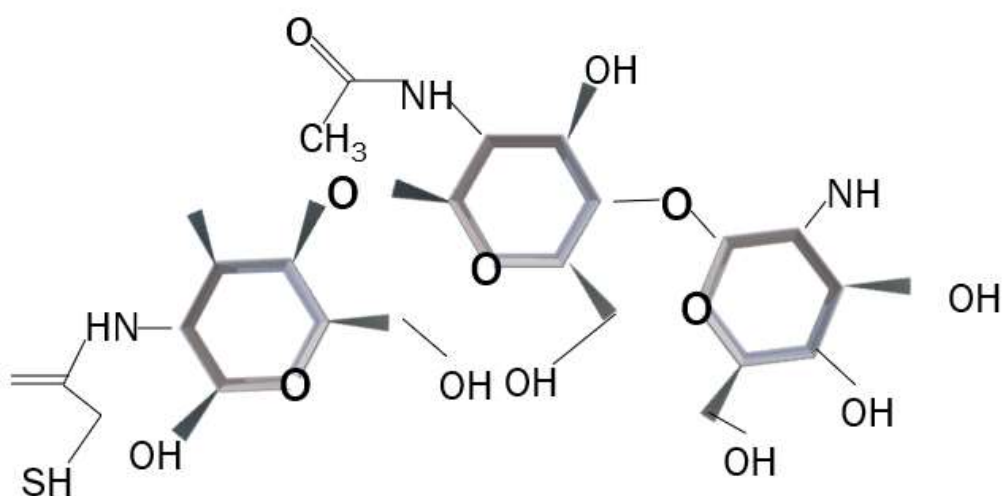
Figure 2.10. Structure of Thiolated Chitosan.

The unmodified chitosan is treated with thioglycolic acid in the presence of EDAC (1-ethyl-3-(3-(dimethyl amino) propyl) carbodiimide). The addition of thiol group not only increases the adhesive properties of the chitosan but also gelling properties. The introduction of –SH group also impacts the swelling properties of the chitosan [78]. The rate of swelling is less in modified chitosan comparatively making it a suitable material in biomedical applications such as wound healing and controlled drug discharge. The use of thiolated chitosan in biological environments has results in increased permeation flux and cellular uptake. It has shown to inhibit certain enzymes and its positively charged amino groups have the ability to interact electrostatically [79]. The presence of thiol groups has also shown inhibition of Poly-glycoprotein. Chitosan treated with thioglycolic acid also has ability to form complexes with metal ions. Due to the presence of –SH group on the polymer, binding ability increases. It

showed 40% strong binding ability for Ni_{2+} than chitosan where chitosan beads were incorporated with Thiolated chitosan and adsorption properties were examined [80]. It has also proven to be a promising sorbent for arsenic removal from ground water [81].

The induction of thiol groups also results in antioxidation property. It enables them to create disulfide bonds allowing them to incapacitate hazardous radicals [82]. It has also been explored as an E. Coli immunosensor [83]. These reports show that there is definitely a lot of potential in chitosan thiomers which needs to be explored. Its sorption and binding abilities can help greatly in waste water treatment. It also adds value to this polymer that it also has shown inhibition to certain enzymes which can be manipulated in membranes to increase anti-fouling and anti-bacterial activities [84]. The sulfhydryl group also has a hydrophilic nature making it more practical for use in membranes.

Chapter 3: Experimental Work and Characterization Techniques

The materials required for the experimental procedure are given below.

3.1. Materials

Analytical grade chemicals were used during the whole experimentation. Distilled water was used during membrane casting and other processes. Polyethersulfone (58000 M_w) was aquired from Ultrasone, Germany. N, N-Dimethyl acetamide (DMAc) with molecular weight 87.12 was used as a solvent and obtained from Fisher Scientific, UK. Polyvinylpyrrolidone (PVP, M_w 40,000 g/mol) was purchased from Merck, Germany. Activated Carbon was obtained from PIEAS, Islamabad. Both Thioglycolic acid and 1-Ethyle-3-(3-dimethylaminopropyl)carbodiimide) for synthesis of thiolated chitosan were acquired from Sigma-Aldrich, USA.

3.2. Thiolated Chitosan Synthesis and Membrane Fabrication

The experimental procedure involved formation of membranes with two different weight percentages of PES (16% wt. and 20% wt.) incorporated with chitosan/activated carbon and thiolated chitosan/activated carbon. A polyester fabric sheet was used as a support for membrane casting.

3.2.1. Synthesis of Thiolated Chitosan

Thiolated chitosan was synthesized in collaboration with Quaid E Azam University. For the fabrication process, 1 % wt. chitosan was dissolved in 1 % wt solution of acetic acid. After the hydration process, 500 mg of thioglycolic acid (TGA) was added to the solution. A coupling reagent 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDAC) was introduced so that the carboxylic acid group of thioglycolic acid can be activated. 10 M NaOH was used to attune the reaction pH to 5.5. The mixtures were then put on stirring for 3.5 hours under incubation.

A dialysis membrane tube was used having molecular weight cut off in the range of 12 to 14kDa to dialyze the resultant solution for a total of five times under the maintained temperature of 10°C so that the excess sulfhydryl groups that did not attach themselves to the chitosan were isolated. This process was done for three days and the solution was shielded from light. The process of dialysis was repeated using 5mM HCl. The functionalized polymer was again dialyzed by using 1 % wt. NaCl two times.

As chitosan is positively charged and the sulfhydryl group brings with a negative charge, there is bound to be ionic interaction between these two parts. The dialysis with NaCl was done to remove any such interaction. In the end, the resulting solution went through dialysis using 1 mM HCl for pH adjustment. Freeze drying was done on the end product. The polymer was then preserved at the low temperature of 4°C.
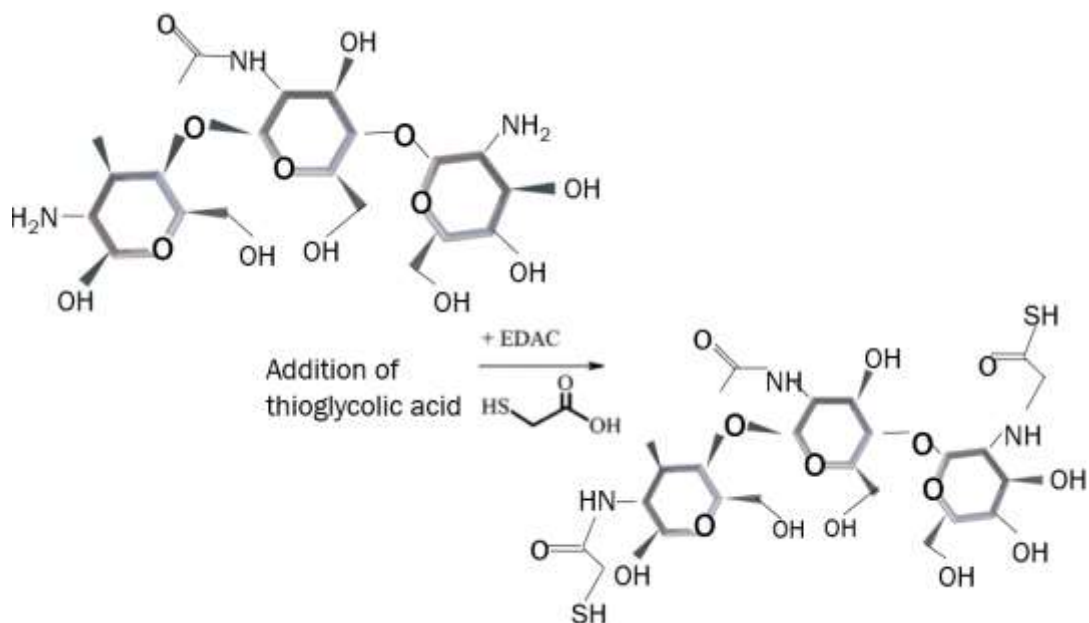
Figure 3.1. The Process of Chitosan Modification to Thiolated Chitosan.

3.2.2. Membrane Fabrication

Phase inversion method was used to synthesize membranes. Two batches of membranes were synthesized using 16 % wt. and 20 % wt. PES. For the first batch (16 % wt.), five membranes were fabricated. Pristine PES membrane, PES membrane with PVP, PES membranes with the additives and PES membrane with composite were all fabricated following the same procedure. PES was added in the DMAc solvent while continuously stirring in a media bottle to create a casting solution. The solution was stirred for 24 hours to ensure homogenous mixing at room temperature. The casting solutions were composed of different combinations of PES, PVP as a pore former, chitosan and activated carbon. The details for casting solutions are given below in table 3.1. and 3.2. For Batch 2, the same process was done with 20 % wt. polymer. The additives included in this batch were PVP, chitosan, activated carbon and Thiolated chitosan. The table 3.2 shows details for 20 % wt. casting solutions.

Table 3.1. Composition of Membranes with 16 % wt. PES and fillers.

Sample	PES (%)	PVP (%)	Chitosan (%)	Activated Carbon (%)
P_0	16	-	-	-
PP	16	1	-	-
PPC	16	1	1.25	-
PPAC	16	1	-	1.25
PPCAC	16	1	1.25	1.25

Table 3.2. Composition of Membranes with 20 % wt. PES and fillers.

Sample	PES (%)	PVP (%)	Chitosan (%)	Activated Carbon (%)	Thiolated Chitosan (%)
P_0	20	-	-	-	-
PP	20	1	-	-	-
PPC	20	1	1.25	-	-
PPAC	20	1	-	1.25	-
PPCAC	20	1	1.25	1.25	-
PPTCAC	20	1	-	1.25	1.25

A polyethylene/propylene support was fixed firmly onto a glass slide on which these mixtures were then casted using Filmograph elcometer which is an automatic film applicator with a speed of 20 mms^{-1} on room temperature. The thickness of the membranes was maintained at 250 µm. After the membrane solution was spread uniformly onto the fabric, the glass slide was then dipped into cold water (5° C) immediately and was left into the water for 15 minutes so that the membrane is casted completely and no solution form is left. The immersion in water makes sure the coagulation of the polymer. Membranes were then washed with distilled water. Two ways were adopted to preserve the membranes. One was to wrap in filter paper for drying for 24 hours and then save the dried membrane in polyethene bags. The other was to preserve the membranes in water having small amounts of glycerol as glycerol during the time where the membrane is not operational. Glycerol has antimicrobial properties and helps in preserving the membranes for much longer than pure water.
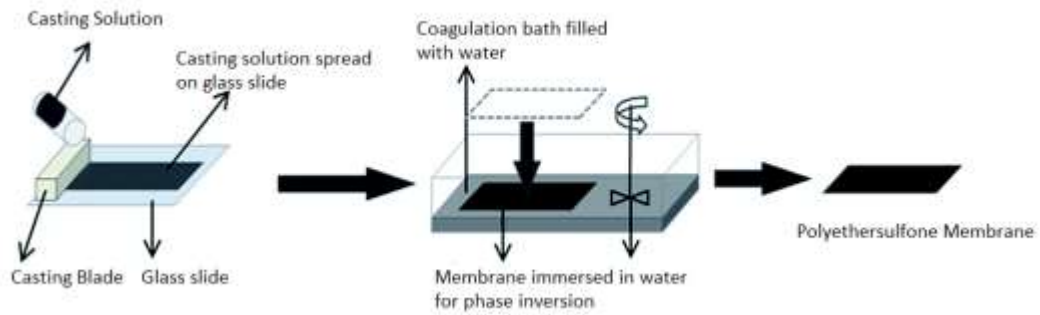
Figure 3.2. Process adopted for Membrane Fabrication.

3.3. Characterization Techniques

Different characterization tools were used for the characterization and testing of the samples the details of which are given below.

3.3.1. Scanning Electron Microscopy

For membranes, topographical and structural examination was done. Membranes were also investigated for cross-sectional morphology[85]. The SEM analysis was done using JEOL-JSM- 6490LA) which had the working distance of about 10 mm, operating voltage 10-20 kV and 35-60 spot size. The membranes were cut into 1 cm^2 pieces and were placed into liquid nitrogen for drying and clean breaking into small pieces so that cross section is not disturbed. The obtained samples were then mounted on steel stud blocks and treated with gold sputtering to create conduction. The membrane samples were then analyzed in high vacuum.

3.3.2. ATR-FTIR

This technique not only gives information about functional groups but also about polymers chemical structure [86]. The dried membranes were cut into 0.5 x 0.5 cm^2 dimensions for ATR-FTIR. The spectral range was between 500 to 3500 cm^{-1} and the resolution was about 2 cm^{-1}. The practice was done on a BRUKER model: ALPHA II of FTIR spectrophotometer.

3.3.3. Optical Profilometry

Optical profilometry is a non-contact, non-destructive technique which is done to gauge the surface roughness of the membranes. For this purpose, 0.25 x 0.25 cm^2 pieces of membrane were cut and pasted on a glass slide. The slide was then placed onto the stage and using the profilometer, the surface is scanned. NANOVEA PS-50

optical profilometer was used for this purpose to measure the roughness of membrane samples.

3.3.4. Contact Angle

Contact angle is the measure of an angle between a liquid and solid interaction. It depicts a surface's wettability. The most common method for contact angle measurement is sessile drop method. The dried membrane sample of roughly 1 x 1 cm^2 was vaccinated with a deionized water droplet. The angle between the membrane surface and the droplet was determined at 3 random points for minimal error. The reported values are an average of three values. The equipment used for this purpose was a DSA-25 drop shape analyzer by KRUSS.

3.3.5. Water Flux

This process is done to evaluate permeation flux of the membranes which the amount of fluid   passing through a membrane under the influence of certain parameters that include time, area, volume etc. The membrane sample was place inside the filtration assembly which was attached to vacuum that maintained a 60cmHg pressure. Distilled water was made to flow through the membrane and time and volume was noted. The acquired values were then put into the equation given below.

$$J = \frac{V}{AT} \qquad \text{(i)}$$

Where J is the permeate flux calculated in $Lm^{-2}h^{-1}$, V is the water volume, A is the area of membrane and T is the time for permeation flux. For every membrane, three values were calculated for minimal error.

3.3.6. BSA Flux

Bovine serum albumin (BSA) flux was calculated to gauge the anti-fouling properties shown by the membranes. 1000 ppm solution of BSA was prepared by dissolving one gram in one liter water. This alkaline solution had a pH of 8.22. the ionic strength was calculated to be 0.1. This solution was projected through the synthesized membranes at a pressure of 0.1 MPa.

Using calibration curve, the concentration present in the permeate was calculated by measuring absorbance at 280 nm. This was done in agreement with Beer-Lambert's law. UV spectrophotometer was used for this purpose and the model was SHIMADZU, UV.

The BSA rejection was calculated by putting the required data into the following equation.

$$J = \frac{V}{AT} \qquad \text{(i)}$$

3.3.7. Water Retention Measurement:

Water Retention is done to measure the ability of the membrane to absorb water. This measurement is done by soaking 2 cm^2 pieces of the membrane in distilled water. After 24 hours, the samples were removed and excess water present on the surface was removed. The membranes were then weighed and this weight was termed as wet weight (W_h). The membranes were then dried for 3 hours at $40°C$ under vacuum. The membranes were weighed again and the weight was named as dry weight (W_{dry}). The values obtained were inserted into the equation given below to measure water retention WR.

$$WR = \frac{Wh - Wd}{Wh} \times 100 \qquad \text{(ii)}$$

3.3.8. Gravimetric Method

The procedure for gravimetric method to calculate porosity of the membranes is almost the same as water retention. Membranes were first dried at $50°C$ for 3 hours to remove any moisture. The membranes were then weighed. The weight of dry membranes is termed as Wd. These dried membranes are then soaked into water for 24 hours at room temperature. After 24 hours, the membranes were removed from water and excess water droplets are wiped off carefully. These membranes are now weighed to obtain wet weight Ww. The values obtained were applied to the equation. The method was repeated three times and average values were calculated.

$$\varepsilon = \frac{Ww - Wd}{Axlx\rho} \times 100\% \qquad \text{(iii)}$$

3.3.9. Mechanical Properties

This test is performed by using Universal Testing Machine UTS (Shamizdu AG-X Plus). Membrane samples were cut into specified sizes (2.4 cm long and 1.4 cm wide).

These samples were then placed into clamps so that both ends of the membrane were gripped tightly. Then the required data was fed into the computer such as the load, displacement rate etc. and the test was started. Gradually load was increased on the sample by pulling it in opposite directions until necking occurred and ultimately the sample broke. The data of the test was displayed on the screen on a graph of stress vs. Strain or force vs. Displacement. All other parameters can be found from the obtained graph.

3.3.10. Nuclear Magnetic Resonance

Proton NMR was done for confirmation of Thiolated chitosan synthesis. The model used was 500 MHz ^{1}H NMR by Varian Inc., USA. This process was done under deuterated dimethyl Sulfoxide.

Chapter 4: Results and Discussion

4.1. Thiolated Chitosan Analysis

4.1.1. FTIR

Chitosan and thiolated chitosan were analyzed using Fourier Transform Infrared (FTIR).
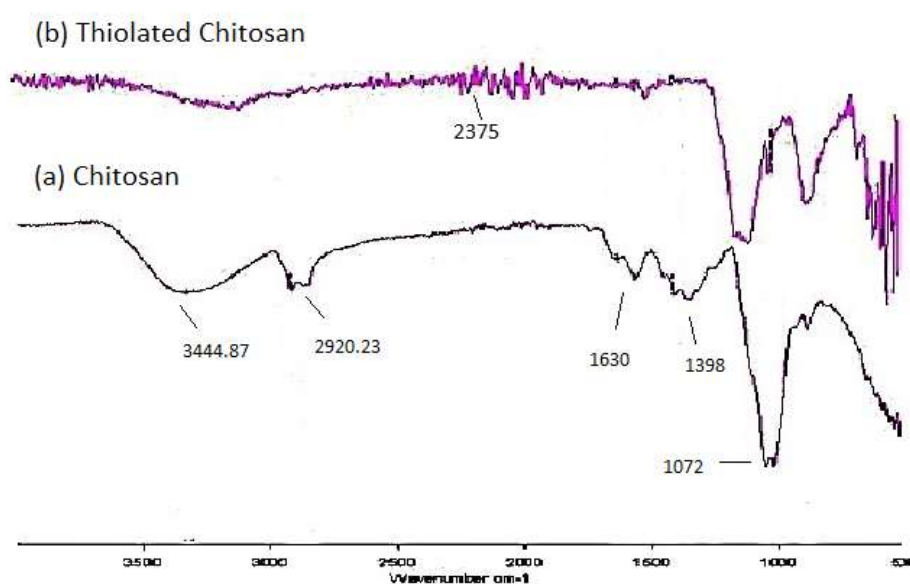
Figure 4.1. FTIR spectra for (a) Chitosan and (b) Thiolated Chitosan.

As can be seen in Fig 4.1., most of the peaks attributed with chitosan can be observed. From the spectra a bridge at 1156 cm^{-1} can be observed. At 1072 cm^{-1}, a vibrating pattern attributed to -COO can also be seen. This confirms presence of saccharin group in the chitosan polymer [87]. A difference between both the graphs can be observed. There is a peak present at 1630 cm^{-1} in chitosan representing amino groups but it is reduced greatly in the thiolated chitosan spectra. It may be because of the attachment of thiol groups present in thioglycolic acid onto the amino groups which strongly suggests the attachment of thiol groups [88]. For thiolated chitosan stretching peaks can be observed at 3352 cm^{-1} and 3207 cm^{-1} representing O-H and N-H. For chitosan and thiolated chitosan, bands at 1517 cm^{-1} are observed. These bands correspond to -NH$_{3+}$ for chitosan showing the presence of electrostatic interactions. Thiolated

chitosan shows additional bands near 2900 cm^{-1}. At around 1070-1090 cm^{-1}, peaks for hydroxyl group can be seen [89].

4.1.2.   NMR spectroscopy

Nuclear Magnetic resonance or NMR spectroscopy is a technique that uses magnetic field to observe and evaluate the resonance frequency of magnetic nuclei with the electromagnetic field. The NMR done to evaluate thiolated chitosan was the proton magnetic resonance denoted as ^{1}H-NMR. In this method, the field is applied to proton spins. Comparing FTIR spectra and Fig 15 and Fig 16 for chitosan and thiolated chitosan it can be deduced that the thiolation of the chitosan polymer was done successfully. In Fig 4.2. the NMR spectra shows some similarities between the unmodified chitosan and thiolated chitosan.
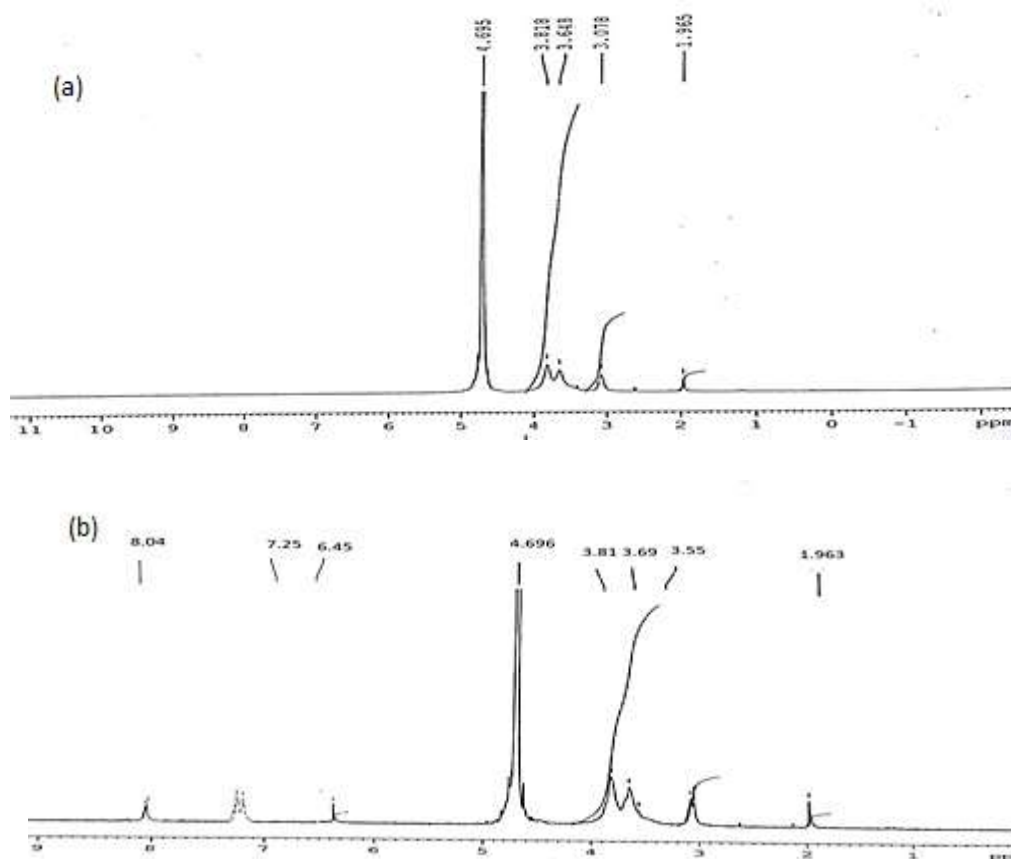

Figure 4.2. ^{1}H-NMR for (a) Chitosan and (b) Thiolated Chitosan.

Signals shown at 1.96 ppm confirm the presence of (NHCOCH$_3$). Peaks close to 3 confirm H$_1$ attributing to -CH protons. For thiolated chitosan, Signals are produced at 3.69 and 3.81 ppm showing presence of H$_2$, H$_3$, H$_4$ and H$_5$. These CH protons

correspond to glucosamide group [90]. Peak at 4.69 ppm is observed for H_7 and NH_2. Peaks shown at 2 ppm show new side chain attributed to CH protons. Spectra between 1 and 2 ppm show the presence of thiol group. The ^{1}H-NMR graph confirms the addition of mercaptopropionic acid to unmodified chitosan [91].

4.2. ATR-FTIR

The ATR FTIR spectra for 16 % wt. and 20 % wt. membranes show most of the characteristic peaks of PES polymer. For all membranes Fig 4.3., 4.4. and 4.5. show peaks at 1580 cm^{-1} (strong C=C bending intensity shows benzene ring) and 1480 cm^{-1} (C-C bond stretching) that correspond to polyethersulfone structure [92]. Bands shown at 1200 cm^{-1} confirm C-O stretching of ether and carboxylate structures. The C-O-C stretching was also strong at 1249 cm^{-1} due to the presence of an ether group in the membrane in the polyethersulfone structure. At 873, C-O and C-H vibrations show the presence of Activated Carbon. Peaks at 1578 can be attributed to conjugated hydrogen bonded carboxyl group [93].
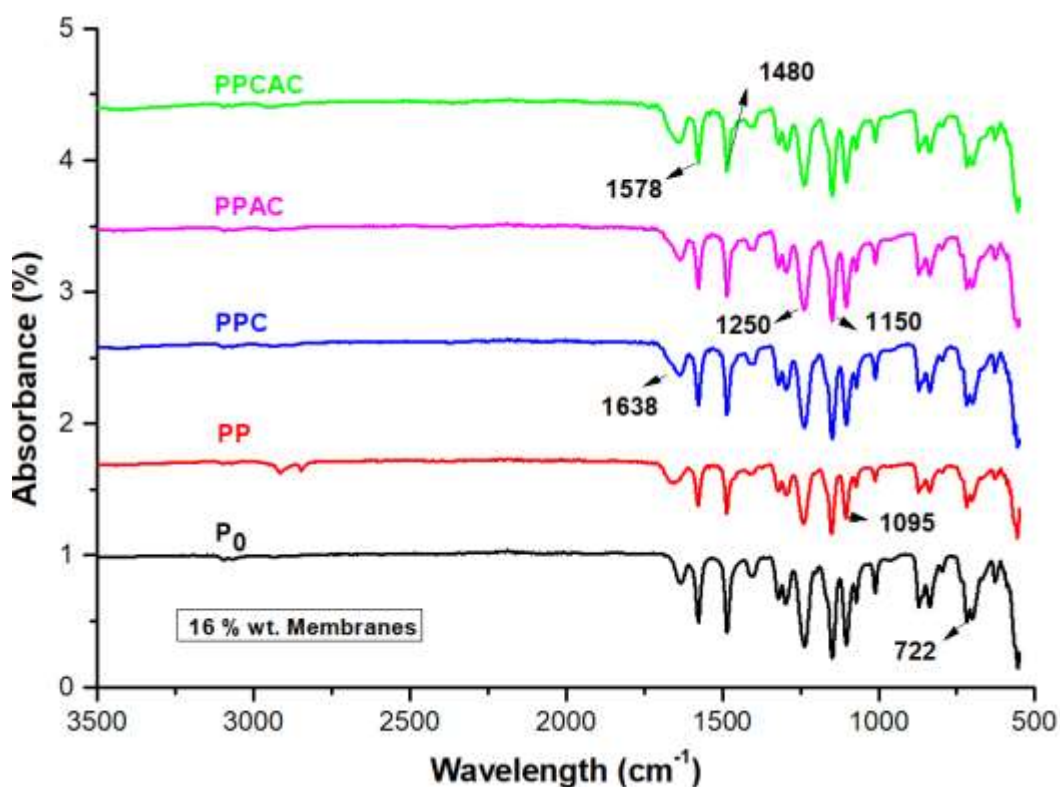

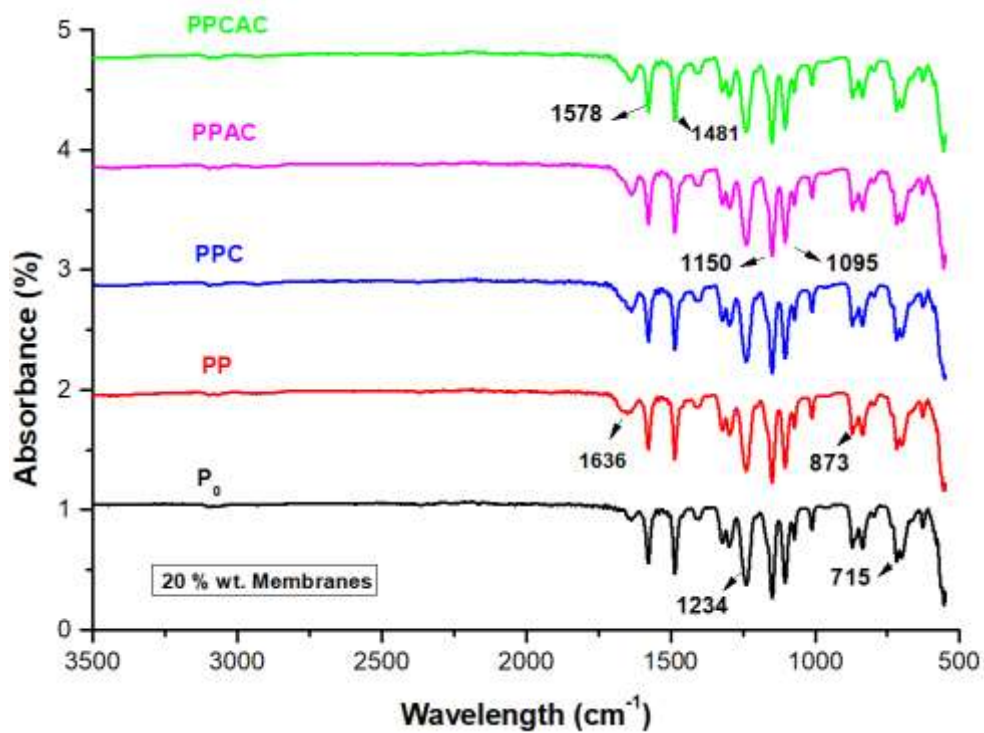Figure 4.3. ATR-FTIR spectra for 16 % wt. PES Membranes.

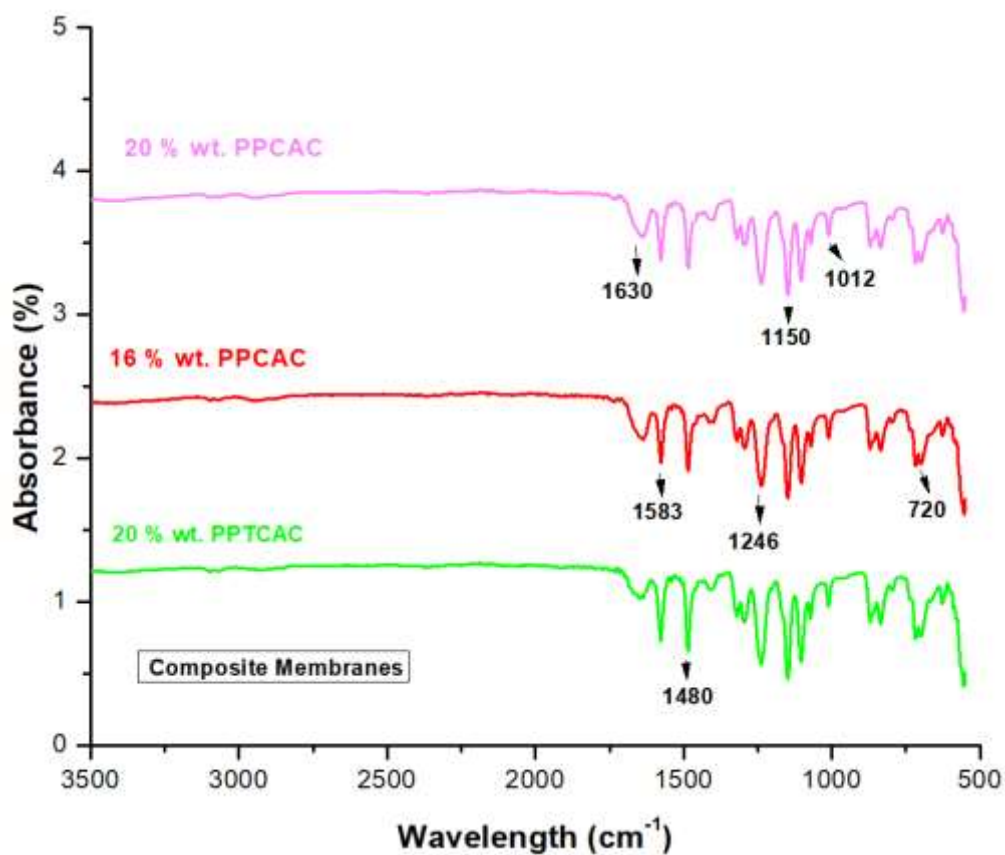Figure 4.4. ATR-FTIR spectra for 20 % wt. PES Membrane.

Figure 4.5. ATR-FTIR spectra for Composite Membranes.

4.3. Morphological Analysis

Scanning electron microscopy was used to investigate the morphology and cross section of the membranes. The micrographs shown in Fig 4.6 and Fig 4.7 show the cross sections of the membranes. These membranes are shown to have an asymmetrical assembly having a gradient like structure. A dense top layer can be observed in all the PES membranes. A porous sublayer consisting of finger-like structures that are also called as channels can also be observed. These channels are responsible for the permeability of the membrane. Better channels connectivity and more channel formation results in better permeability. Under this sublayer, a sponge-like mesoporous structure can also be found [22] . With the addition of additives such as PVP and chitosan, a slight change in the morphology can be observed. The addition of these fillers make the solution more viscous as both PVP and chitosan have high molecular weights favoring lesser macrovoids formation [85,86]. PVP, chitosan and thiolated chitosan are hydrophilic in nature [87,80]. The finger like structures are more evenly distributed and lesser macrovoids are observed in membranes incorporated with these fillers. This change in membrane structure can be attributed to the hydrophilicity of these fillers causing swift non solvent and solvent (DMAc) exchange throughout the phase inversion process. This rapid exchange gives birth to wider channels (finger-like structures).

In comparison, there is a difference in 16 % wt. and 20 % wt. membranes. Generally the increase in polymer concentration diminishes macrovoids and makes better finger like structures [97]. So, the membranes with increased polymer concentration show better channel structures as shown in Fig 4.7. There is a reduction in macrovoids and increase in the fingerlike cavities. The addition of fillers like PVP and chitosan have resulted in a denser top layer as compared to pristine PES membrane. With the introduction of activated carbon in the membranes, not only porosity increase but also the surface roughness. Usually with the addition of activated carbon, the pores widen/expand which results in increased membrane porosity [98]. In the case of pristine PES membrane, the active layer is on the top whereas there is also an uneven region below depicting the polyethylene/polypropylene fabric that was used as a support. Membranes incorporated with composite in both the concentrations show better channel formation. For 16 % wt. composite membranes there are more voids present (Fig 4.6.) as compared to 20 % wt. composite membranes. The reason maybe

as concentration of the polymer increases, the casting solution becomes more viscous resulting in formation of a membrane having lesser voids. The addition of thiolated chitosan also resulted in pronounced and smooth channel formation as shown in Fig 4.7.
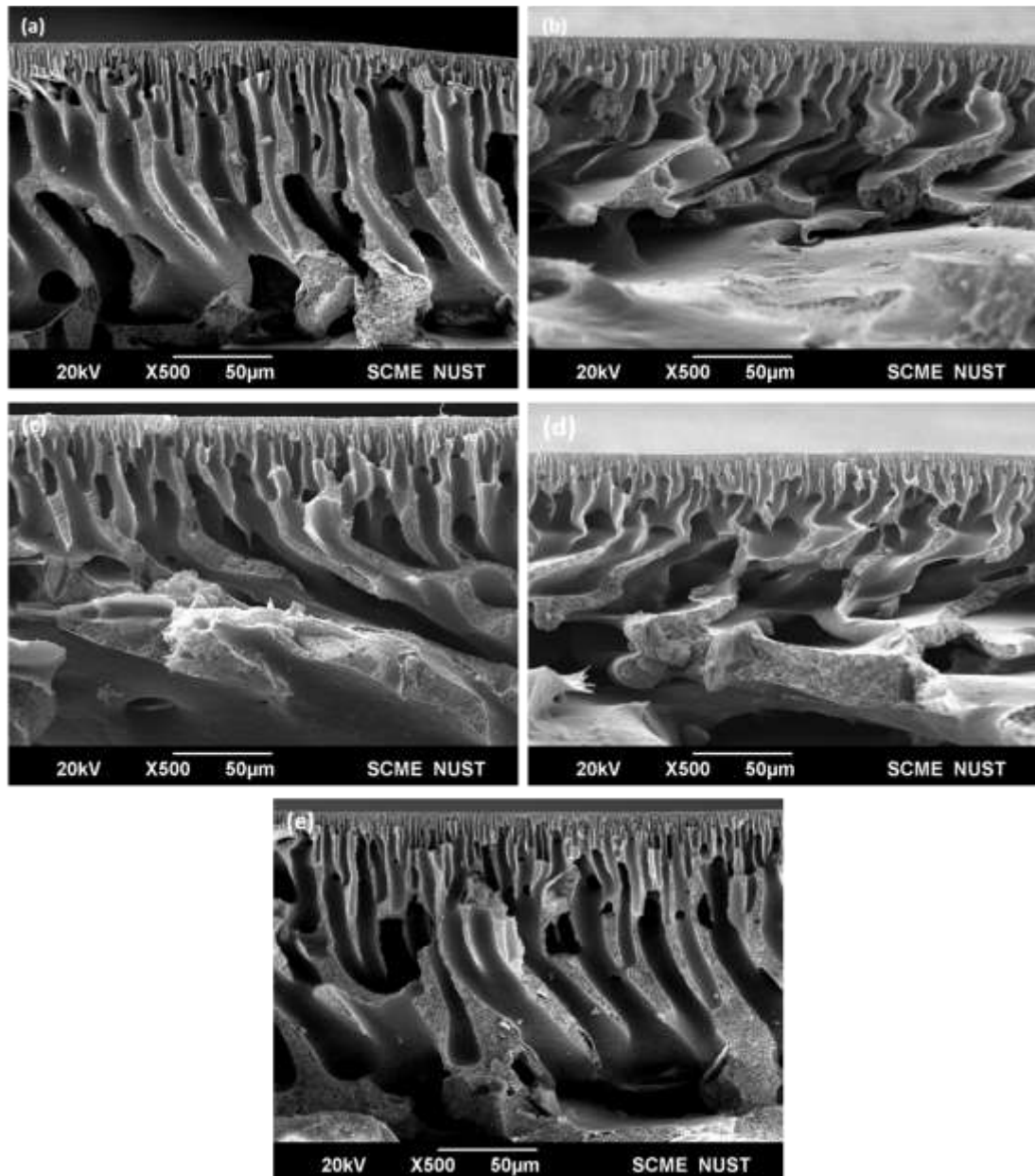
Figure 4.6. Cross Sectional SEM Micrographs for 16 % wt. membranes where P_0, (b) PP, (c) PPC, (d) PPAC (e) PPCAC and (f) PPTCAC.
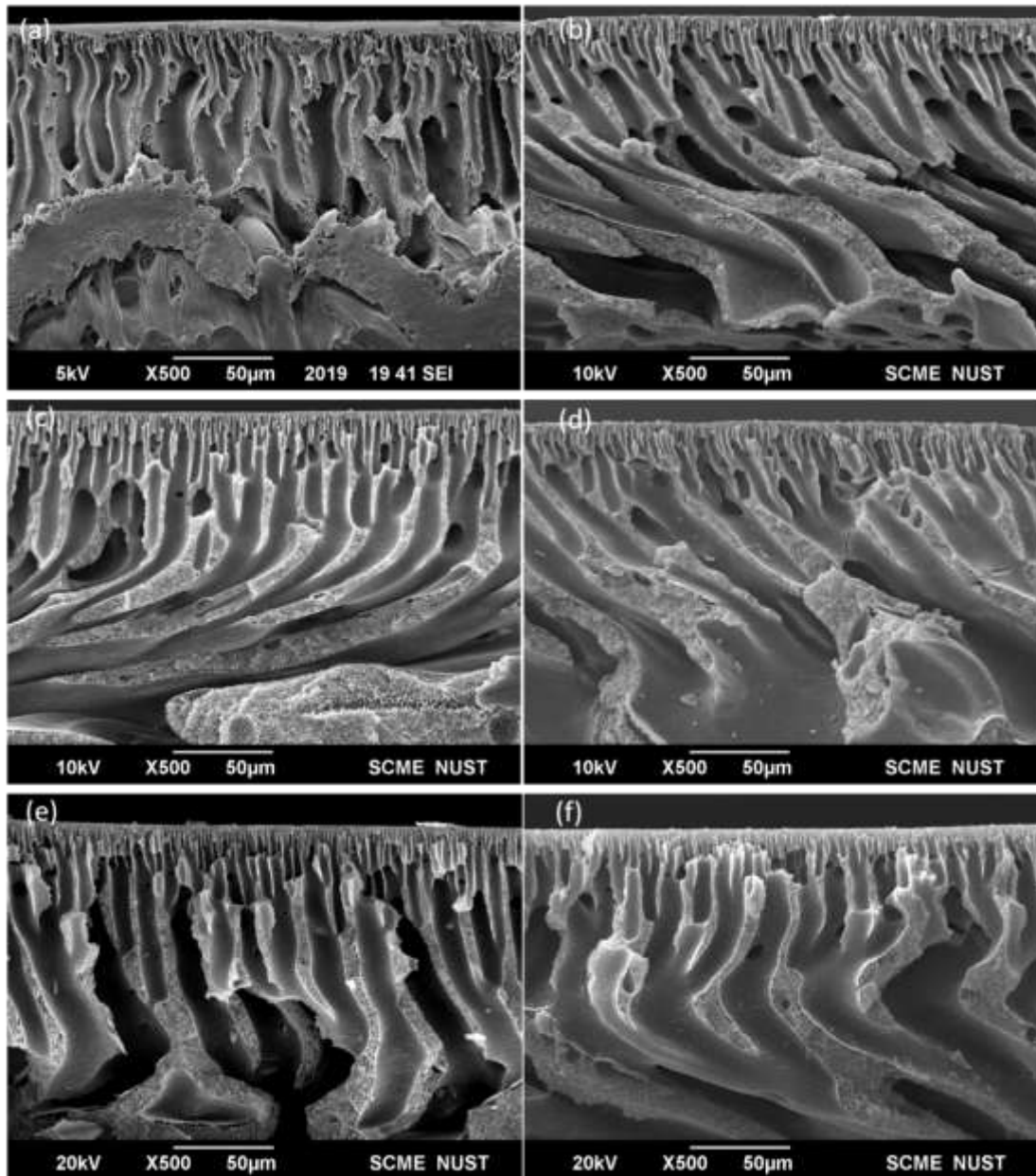
Figure 4.7. Cross Sectional SEM Micrographs for 20 % wt. membranes where (a) P_0,
(b) PP, (c) PPC, (d) PPAC (e) PPCAC and (f) PPTCAC.

The addition of composites has shown improvement in the finger like cavities. These cavities also termed as channels help in improvement of water flux. So, the membranes with better and wider channels (membranes with composites) show promise for increased flux rate and better membrane performance.

4.4.   Water Flux and Bovine Serum Albumin Flux

Water flux is the measure of the pure water passed through the membrane under a specific pressure and temperature whereas BSA flux is bovine serum albumin flux and

it shows the antifouling properties of the membrane by rejecting the protein. As can be seen in the Figure 4.8. for 16 % wt. PES membranes, the lowest water flux was shown by membranes incorporated with activated carbon. This may be due to the hydrophobic nature of the activated carbon [99]. Although it has porous structure and contains increased active sites, the water repelling ability of activated carbon may have hindered the flow of water through the membrane. With the induction of activated carbon, the surface of the membrane becomes somewhat more hydrophobic as compared to pristine PES membrane resulting in decrease of water permeated through the membrane. Both the PES and activated carbon are hydrophobic in nature and with only 1 % wt. PVP incorporated in the membrane, there is no significant effect on the hydrophobicity of the membrane. But this membrane shows the best BSA flux. This may be due to excellent adsorption properties of the activated carbon [99].

As shown in Fig 4.8. the best permeability rate was shown by membranes incorporated with chitosan and PVP as both these fillers are highly hydrophilic, thus affecting the performance of the membrane in a positive way. Membrane with the composite (containing both the fillers i.e., activated carbon and chitosan) show more permeability rate than the pristine PES membranes and membranes having AC but less than chitosan incorporated membranes. This may be due to the presence of activated carbon in the membrane as it lends its porosity and active sites to the membrane. The trend remains almost the same for the membranes with 20 % wt. PES concentration. There is a slight drop in the flux rate as compared to the 16 % wt. membranes. This slight drop can be because of increased amount of polyethersulfone as it is closer to the hydrophobic end of the spectrum and may be the reason for lesser flux comparatively [100].
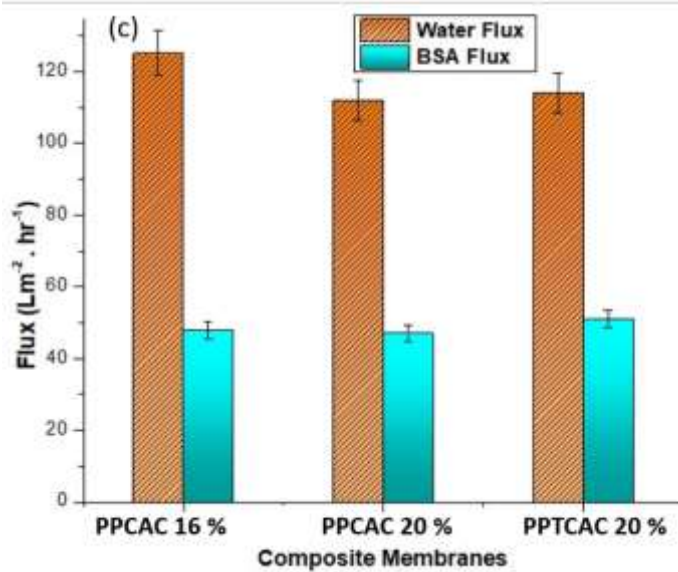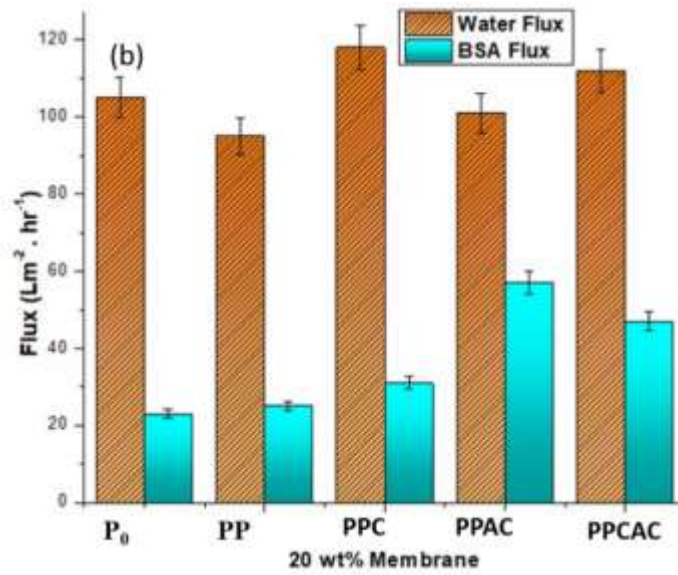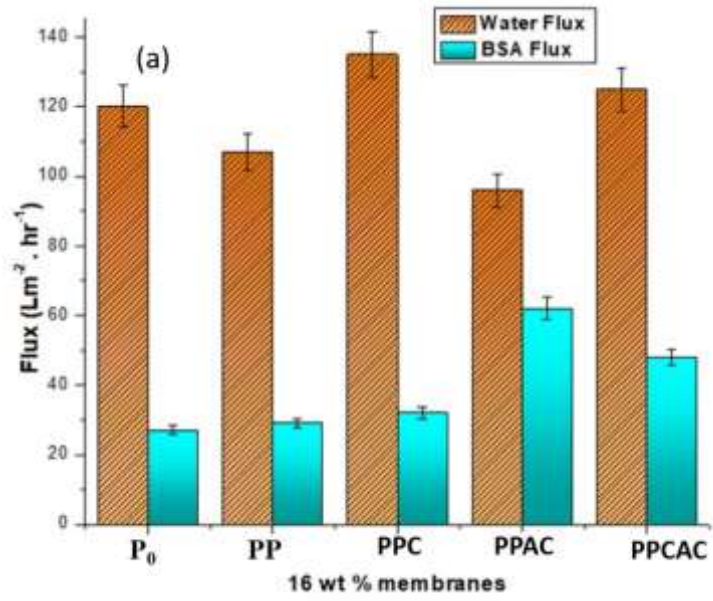
Figure 4.8. Water flux and BSA flux results for (a) 16 % wt. Membranes, b) 20 % wt. Membranes and (c) Composite Membranes.

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The greatest BSA flux is shown by membranes incorporated with activated carbon as a filler. The composite activated membranes also showed great BSA flux rate, only second to the AC incorporated membranes. This may be due to the highly porous nature of the activated carbon.

Due to its porosity the pores are expanded which may have been the reason that the protein could not clog the pores [98]. But the BSA flux was lower for membranes with PVP and chitosan as compared to the ones with activated carbon. This might be the result of hydrophilicity of the membrane. It is possible that some part of the albumin protein present in the feed solution was trapped in the pores and the flux rate was affected by it. The 20 % wt. membranes incorporated with thiolated chitosan and activated carbon also show reasonably well BSA flux compared to the other composite membranes. As thiolated chitosan and PVP both are hydrophilic and activated carbon is hydrophobic, a balance seems to have been reached resulting in good permeation rate and BSA flux

4.5. Contact Angle

The wettability of a membrane shows its hydrophobic or hydrophilic nature which is one of the most substantial information for a membrane. One of the major factors that govern permeability rate for membranes is their wettability. The more the wettability, the more hydrophilic character, the more enhanced flux rate and anti-fouling property[17]. The property is evaluated by the measurement of contact angle. Whereas surface energy can be defined as intermolecular force present on the material surface. It is the determinant for the extent of forces either repulsive or attractive that are exerted on the other surface. There exists an inverse relation between the contact angle and surface energy [101]. The graph plotted between these two values prove that with increase in contact angle, there is a decrease in surface tension and vice versa. For a surface to be hydrophilic, contact angle should be less than 90°. Similarly, the angles above 90° confirm the hydrophobicity of the surface. The values for contact angle are given in table 4.1. and 4.2.

Table 4.1. Average contact angle for 16 % wt. PES Membranes.

Sample (16 % wt.)	Average Contact Angle θ
P_0	65.2±2
PP	60.7±2
PPC	59±2
PPAC	73.6±2
PPCAC	52.2±2

Table 4.2. Average contact angle for 20 % wt. PES Membranes.

Sample (20 % wt.)	Average Contact Angle θ
P_0	64.5±2
PP	57.6±2
PPC	48.1±2
PPAC	70.7±2
PPCAC	59.5±2
PPTCAC	55.7±2

Fig 4.9. and 4.10. show that pristine PES membranes have a higher contact angle showing less wettability properties. With the addition of fillers like PVP and chitosan for both concentrations, there has been a drop in the contact angle values as both of these fillers are hydrophilic themselves. When these additives are added in the membrane solution, some part of them remains on the surface while casting. This presence on the surface of the membranes induces hydrophilic groups on the surface hence decreasing the contact angle and increasing the surface energy. For membranes incorporated with activated carbon, the increase in contact angle is more pronounced for both concentrations. This may be the result of presence of activated carbon on the membrane surface as activated carbon is highly hydrophobic.

Some reports also claim that decrease in contact angle results in better anti fouling activity [97]. As shown in Fig 4.11. for the composite incorporated membranes, the contact angle of 52.2 for 16 % wt. and 59.85 for 20 % wt. shows that the addition of both chitosan and activated carbon has resulted in a balance of hydrophilic and hydrophobic functional groups on the membranes' surfaces. The contact angle of 20

% wt. composite incorporated membrane is slightly more. This may be due to the higher concentration of PES as PES itself is hydrophobic. A decrease in contact angle can be seen for this membrane when unmodified chitosan is replaced with thiolated chitosan. The –SH group on chitosan thiomer seems to have better hydrophilic abilities than that of the chitosan. All in all the combination of these additives has somewhat achieved the desired aim to reduce the hydrophobicity of the membranes.
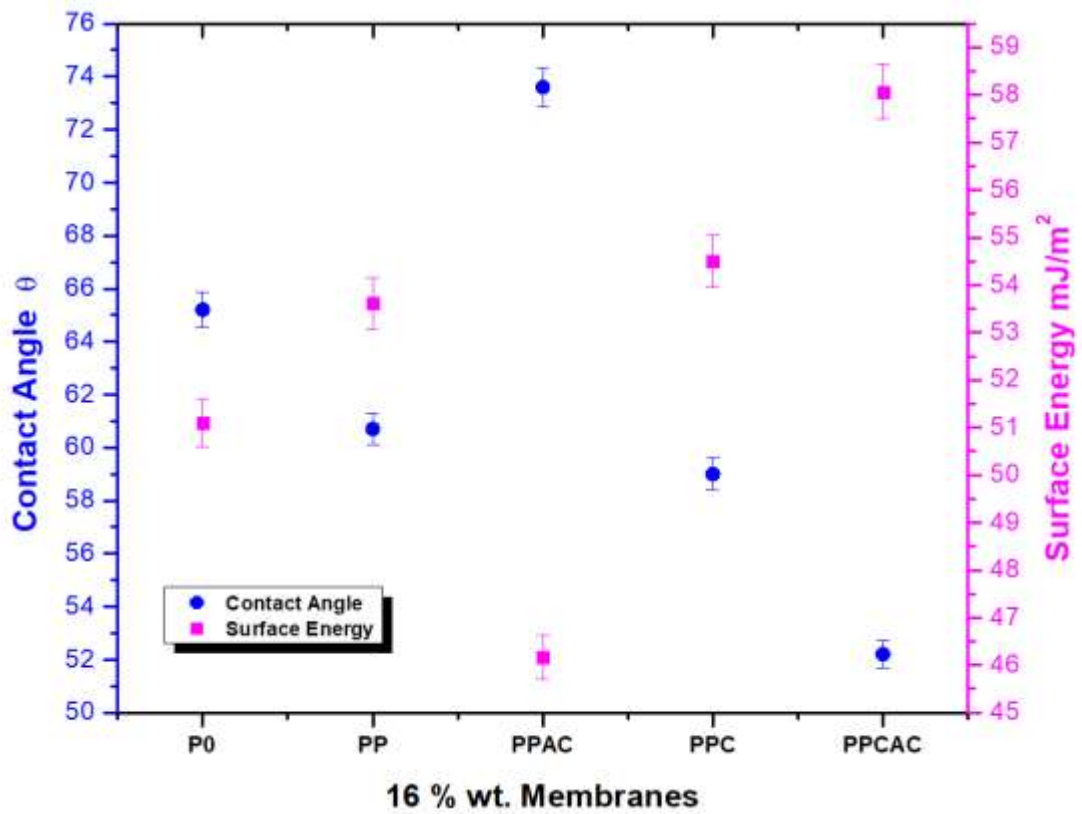

Figure 4.9. Contact Angle vs Surface energy for 16 % wt. Membranes.
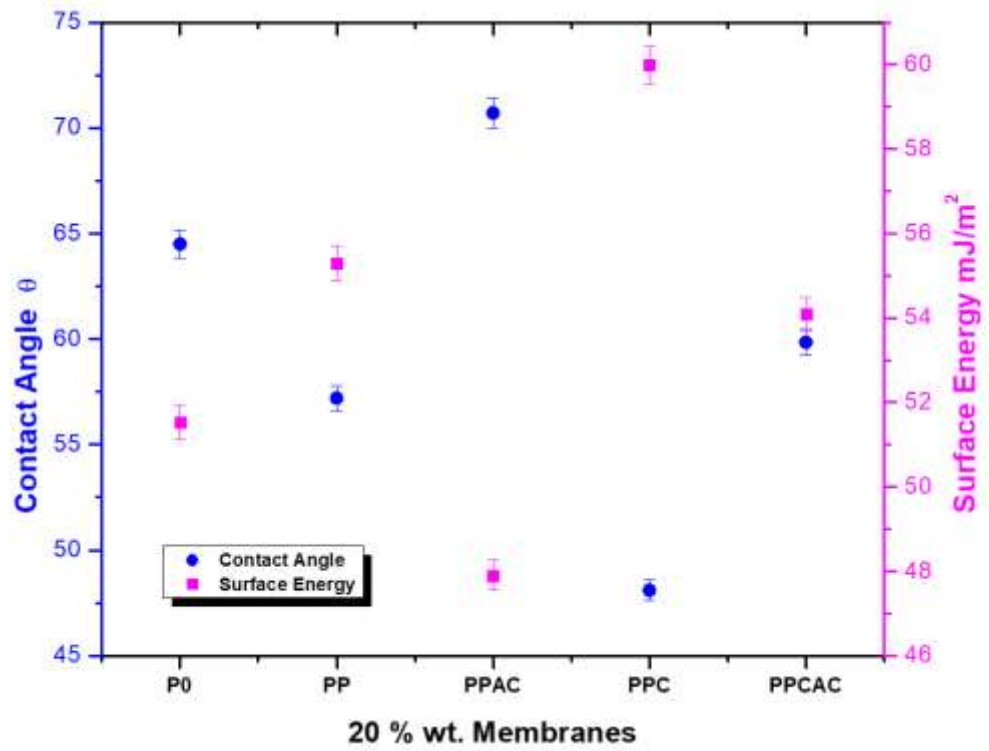
Figure 4.10. Contact Angle vs Surface energy for 20 % wt. Membranes.
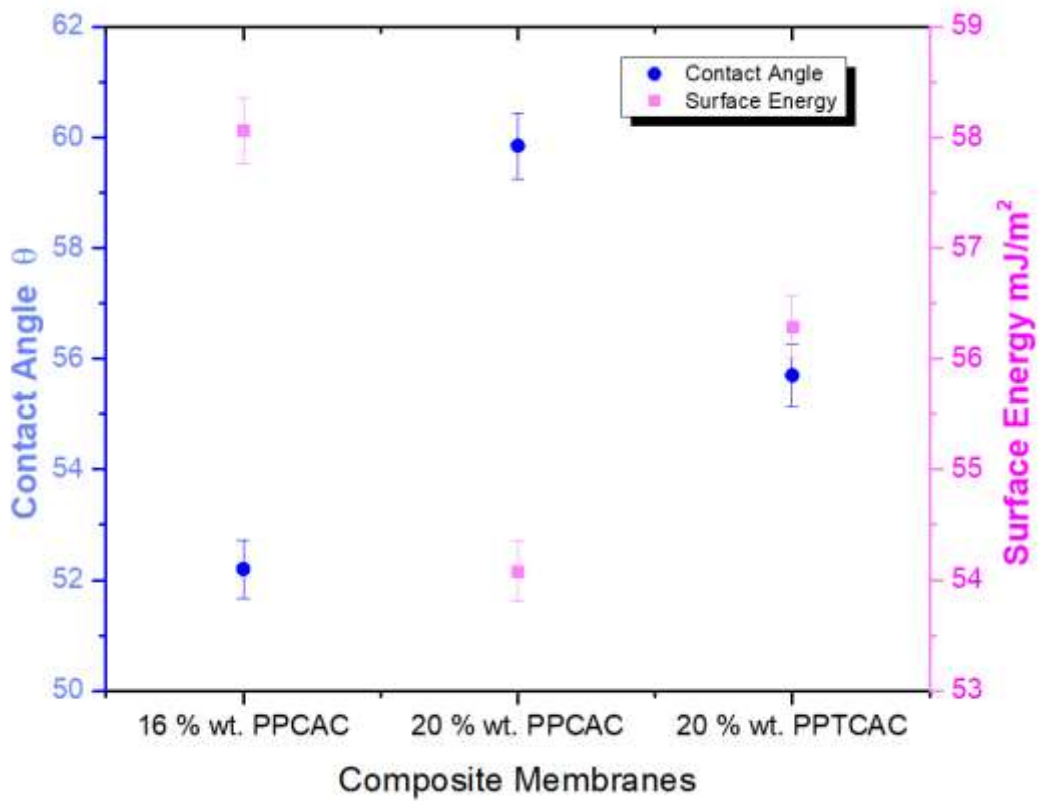
Figure 4.11. Contact Angle vs Surface energy Composite Membranes.

4.6. Optical Profilometry

The surface roughness of the membrane is also an important factor. The decrease in roughness of the membrane surface is responsible for reduction in fouling as it gives less active sites for the solute to settle in [102]. To investigate the effect of fillers on the membranes, optical profilometry was done. As shown in Fig 4.13, the highest surface roughness was observed for membranes incorporated with thiolated chitosan. This may be the effect of thiol group hydrophilicity. During phase inversion, increased hydrophilicity may impact the phase exchange process and accelerate it resulting in immigration of the thiolated chitosan particles on the surface. Membranes incorporated with activated carbon show increased surface roughness in Fig 4.12. This may be due to the presence of activated carbon particles on the surface. The porous activated carbon particles present on the surface may be the reason for it [103].

The lowest roughness was for 20 % wt. composite membrane. This may be due to polymer concentration. With increase in polymer concentration, less defects are formed [97]. The high surface roughness for PES/PVP/Activated carbon membrane may be due to the highly porous structure of the AC.
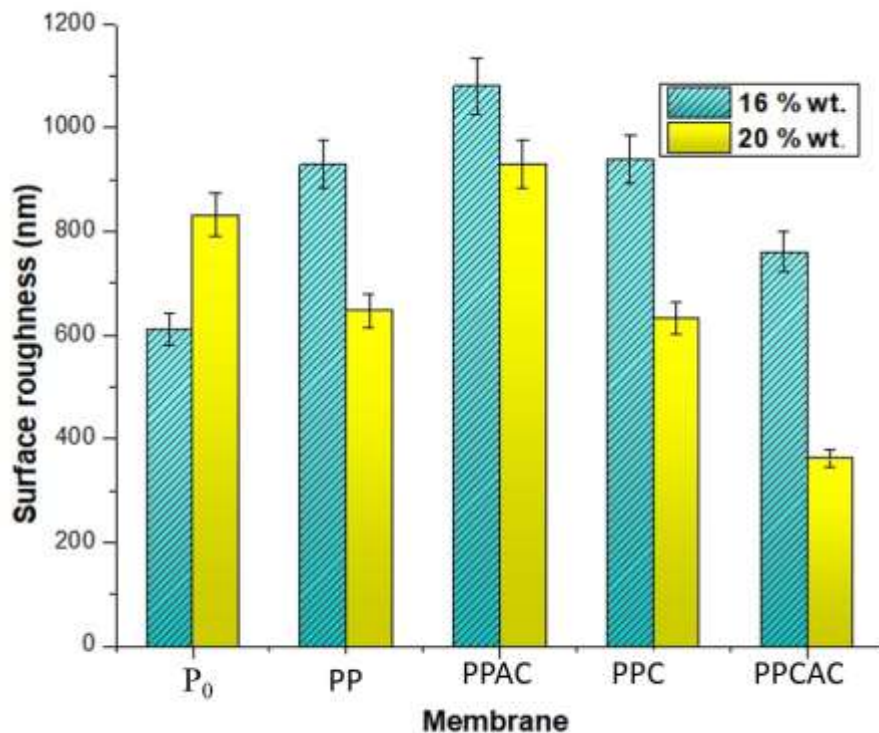
Figure 4.12. Surface Roughness Bar Graph for 16 and 20% PES Membranes.
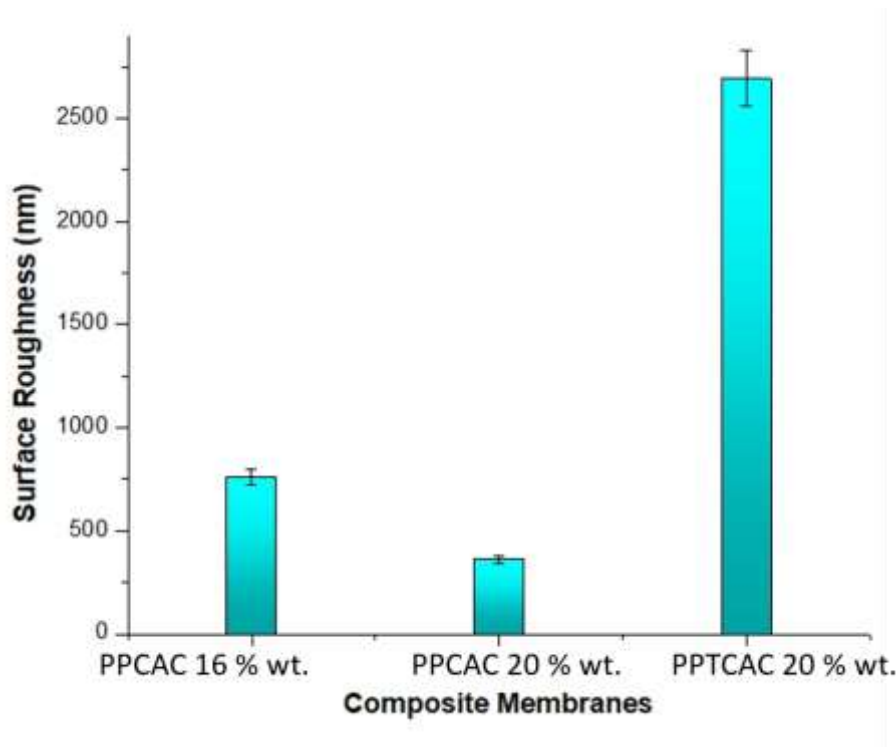
Figure 4.13. Surface Roughness Bar Graph for Composite PES Membranes.

4.7. Water Retention Test

Another important aspect for membranes to uphold is their water retention property. It is the ability to soak up moisture. Water retention shows the maximum ability of the membrane to absorb water. The membranes with hydrophobic content show less water uptake whereas the ones with hydrophilic property show more water uptake. Water uptake and contact angle are inversely related to each other. With decrease in contact angle, the hydrophilic property of the material increases resulting in increased water retention. As per Fig 4.14. and 4.15., in case of pristine PES, the percentage for water retention was lowest because of the hydrophobic nature of PES. The SEM micrographs too showed the asymmetric top layers for pristine PES membranes to be less dense than with the fillers which may also be a reason for lower water uptake. The highest water retention ability was shown by membrane with thiolated chitosan at 76.5 %. The results contribute to the fact that with increase in hydrophilicity, water retention abilities of the membranes are also increased [54]. As per Fig 4.15., all the composite membranes showed remarkably better performance than pristine PES membranes. Addition of activated carbon also seems to have a positive impact. Even though it is

hydrophobic, it has a highly porous structure. This increased porosity may have played a role in better water retention [53].
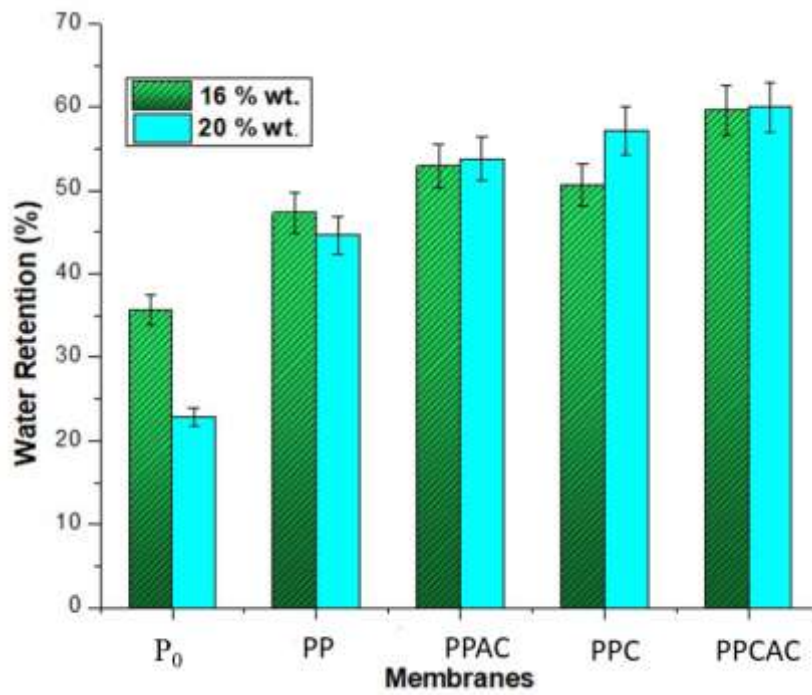
Figure 4.14. Water Retention Bar Graph for 16 % wt. and
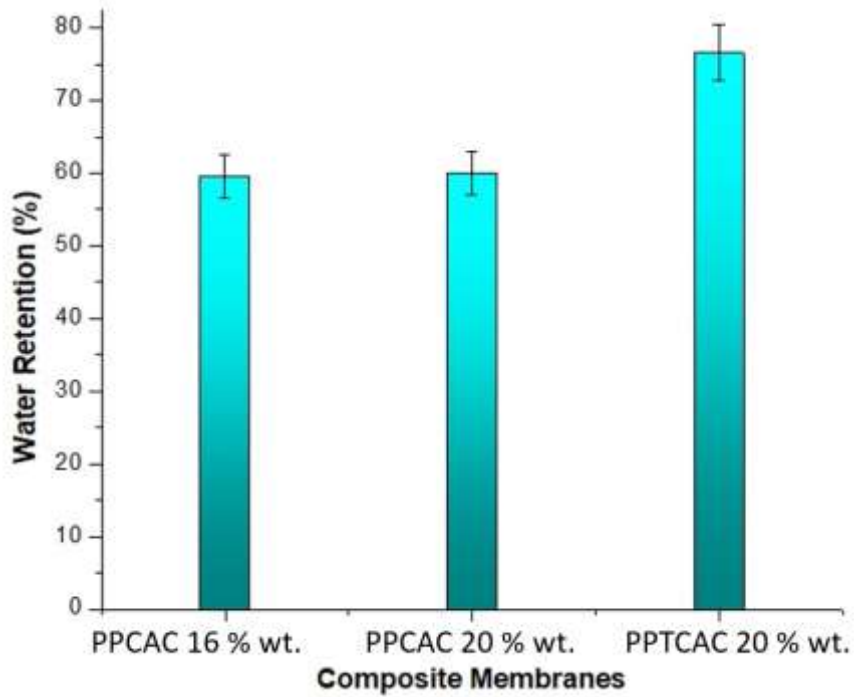
20 % wt. PES Membranes.

Figure 4.15. Water Retention bar graph for Composite Membranes.

In the table 4.3., the values obtained are given along with the water contents percentage.

Table 4.3. Results For Water Retention For 16 % Wt. PES Membranes.

Membrane Sample	Wet Weight (g)	Dry Weight (g)	Water Content (%)
P_0	0.300	0.193	35.6
PP	0.256	0.135	47.3
PPC	0.361	0.170	52.9
PPAC	0.339	0.167	50.7
PPCAC	0.532	0.215	59.6

Table 4.4. Results For Water Retention For 20 % Wt. PES Membranes.

Membrane Sample	Wet Weight (g)	Dry Weight (g)	Water Content (%)
P_0	0.302	0.233	22.84
PP	0.159	0.088	44.65
PPC	0.392	0.181	53.8
PPAC	0.815	0.349	57.2
PPCAC	0.534	0.212	60
PPTCAC	0.289	0.068	76.5

4.8.   Porosity

Porosity of a membrane is a very important factor. It plays its role in permeation ability, adsorption abilities and fouling properties of the membranes. The membranes should be porous enough for good permeation flux. Hydrophilic fillers can play an important role in porosity of the membranes [104]. According to Fig 4.16., in composites, the highest porosity percentage was observed in 16 % wt. composite membrane at 85% closely followed by 79% porosity of 20 % wt. thiolated chitosan induced membranes. 20 % wt. membranes with chitosan also showed good porosity percentage of 73 % but it is relatively low when compared to other two composite membranes as shown in Fig 4.17. This may have been a result of increased polymer

concentration resulting in more viscous casting solution, but the concentration of the pore former (PVP) was not increased. This leads to reduced mean pore radius.
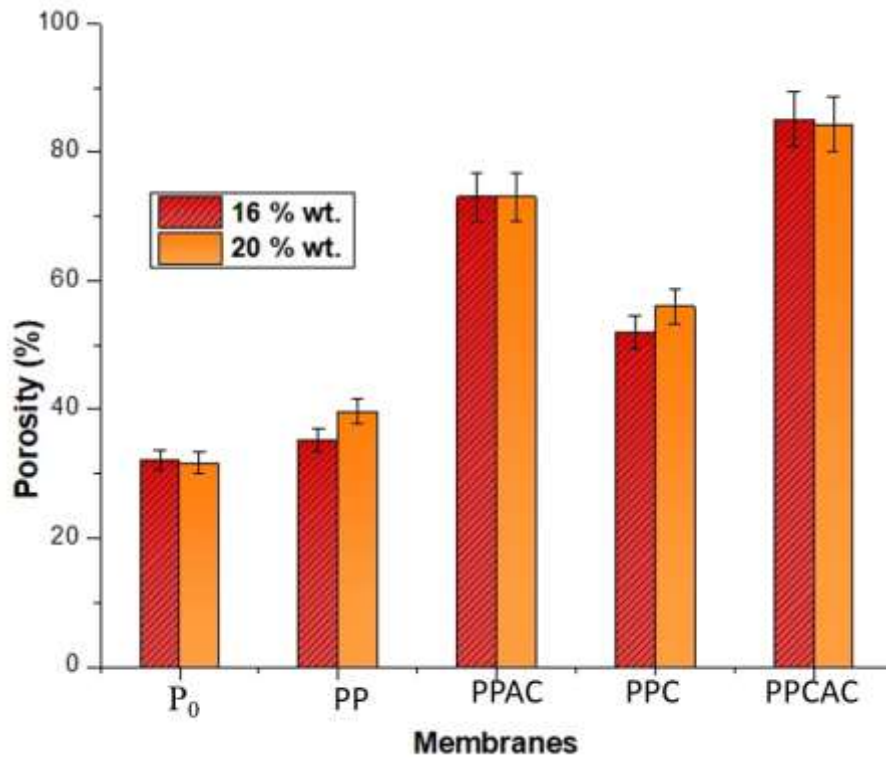
Figure 4.16. Porosity Bar graph for 16 % wt. and 20 % wt. PES Membranes.
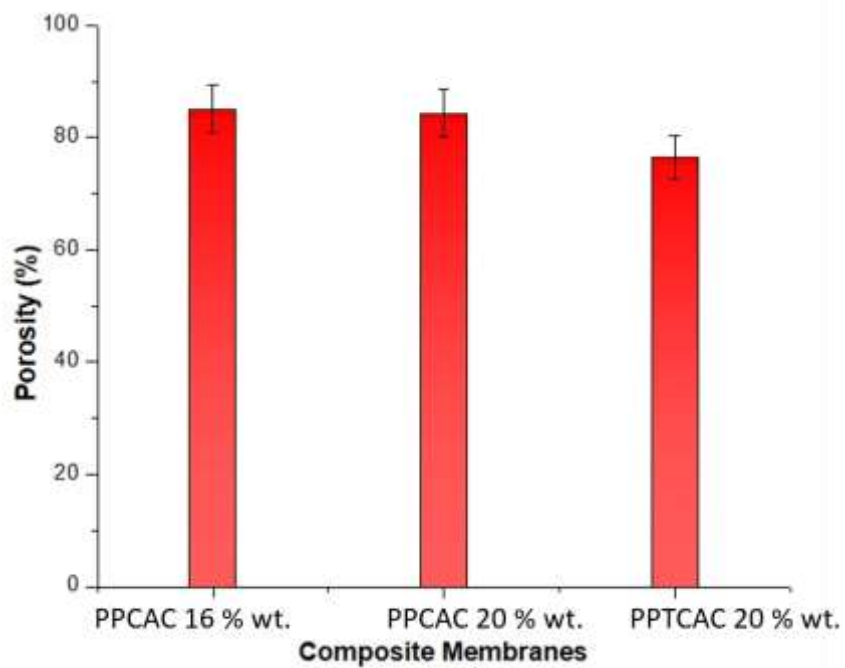
Figure 4.17. Porosity Bar graph for Composite PES Membranes.

Table 4.5. Results For Gravimetric Analysis For 20 % Wt. PES Membranes.

Membrane Sample	Dry Weight (g)	Wet Weight (g)	Area Of Membrane (m)	Porosity (%)
P$_0$	0.193	0.300	1.19	35.7
PP	0.136	0.256	1.49	32.15
PPC	0.166	0.339	1.32	52
PPAC	0.171	0.361	1.03	73
PPCAC	0.217	0.532	1.47	85

Table 4.6. Results For Gravimetric Analysis For 20 % Wt. PES Membranes.

Membrane Sample	Dry Weight (g)	Wet Weight (g)	Area Of Membrane (m)	Porosity (%)
P$_0$	0.202	0.332	1.64	31.7
PP	0.088	0.159	0.714	39.7
PPC	0.211	0.534	1.26	56
PPAC	0.181	0.392	1.15	73
PPCAC	0.348	0.615	2.27	84.3
PPTCAC	0.068	0.289	1.11	79

Table 4.5. and 4.6. show the values obtained by measuring the wet and dry weights of the membranes. These values were put in equation (i) Where ρ is the density of water which is assumed to be 1 g/cm^3 and thickness of the membrane was 250 µm.

As per Fig 4.16., Membranes incorporated with activated carbon also show a pronounced mean pore radius with 73% porosity for both the concentrations owing to highly porous structure of activated carbon. This may also be because of the expansion of the pores in the membrane because of activated carbon [98]. These widened pores are good for flux rate but in case of porosity, instead of increase in mean pore radius the existing pores are widened with addition of activated carbon.

Chitosan membranes have lower porosity because it is possess a very high molecular weight and the casting solution becomes very viscous with even 1.25% addition of chitosan. This may be the reason for lower pore size.

4.9.   Mechanical Testing

Membranes are employed under different operating conditions. Membranes with good mechanical strength are the need of this time where synthesis of multifunctional membranes is so prevalent. Membranes having high polymer concentration possess lesser voids and defects in their structure reducing the available sites for the cracks to initiate or propagate. So, membranes with greater concentration of polymer show better tensile strength as can be seen in Fig. 4.18.

Ultimate tensile strength is calculated by area under the stress-strain curve. The highest value for UTS was shown by 20 % wt. composite membrane at 41.39 MPa. The lowest value was observed in 20 % wt. membrane with thiolated chitosan at 15.11 MPa. The values for membranes with PVP pore former are also low compared to pristine PES membranes. This can be due to the solubility of PVP and thiolated chitosan as both of these are soluble in water [75,88]. Using fillers that are soluble in water may result in reduced mechanical properties as during immersion, these soluble molecules tend to increase macro void formation compromising the mechanical strength of the membranes. The materials with higher water solubility dissolve in water. This leads to the formation of voids where the material resided. These voids then provide the sites for the crack to propagate further resulting in membrane tear.
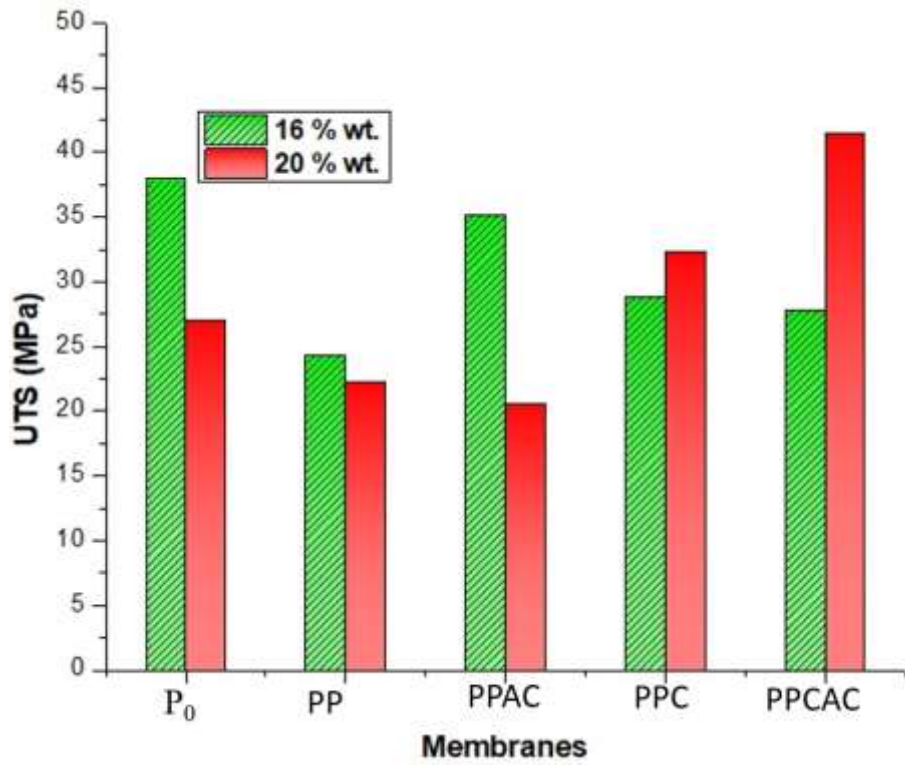
Figure 4.18. Ultimate tensile strength for 16 % and 20 % PES Membranes.
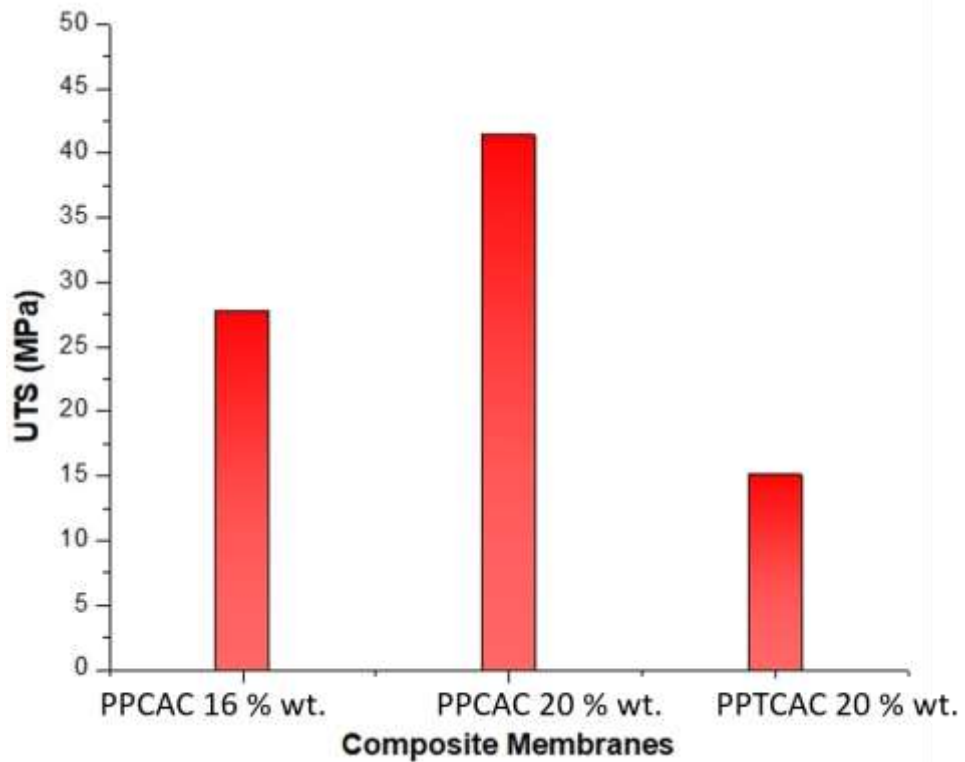
Figure 4.19. Ultimate tensile strength for Composite PES Membranes.
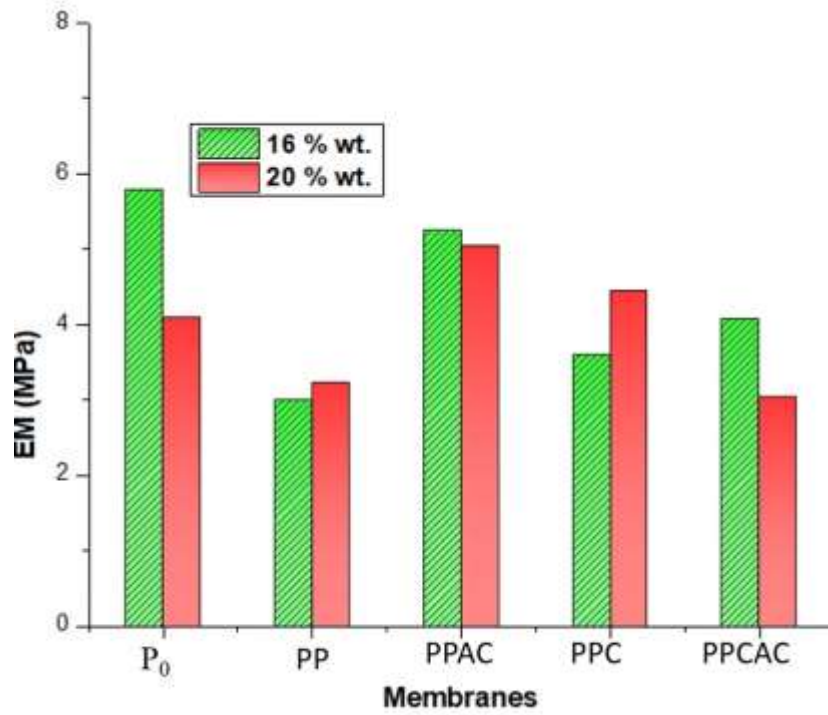
Figure 4.20. Elastic Modulus for 16 % wt. and 20 % wt. PES Membranes.
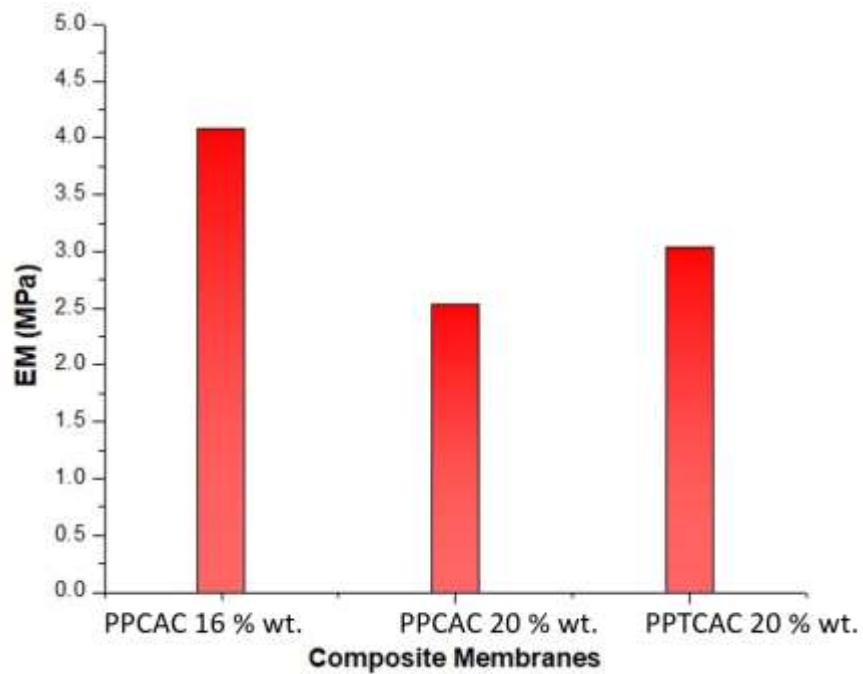
Figure 4.21. Elastic Modulus for Composite Membranes.
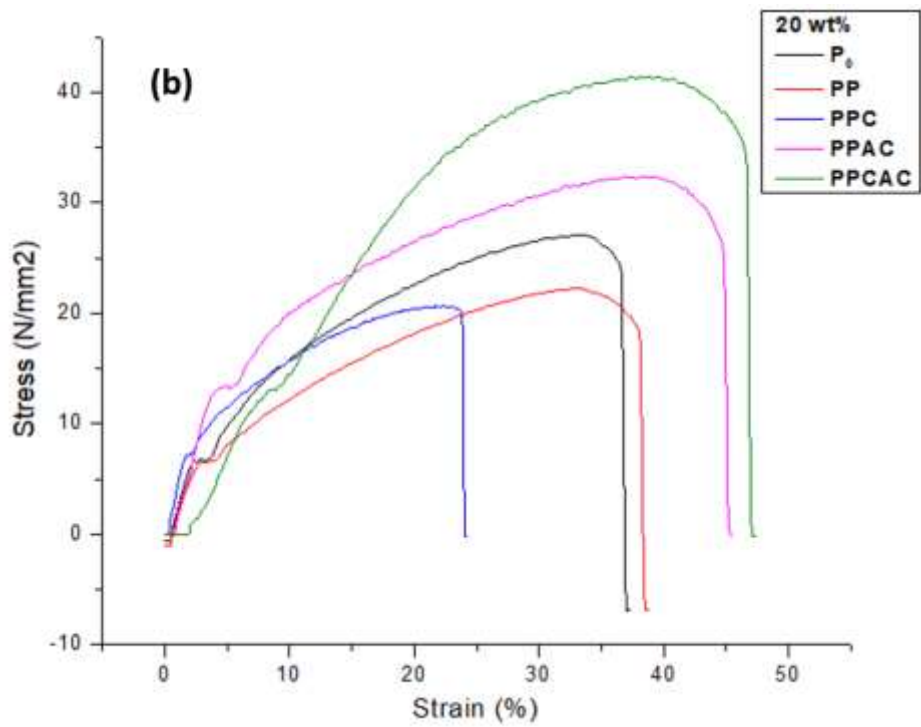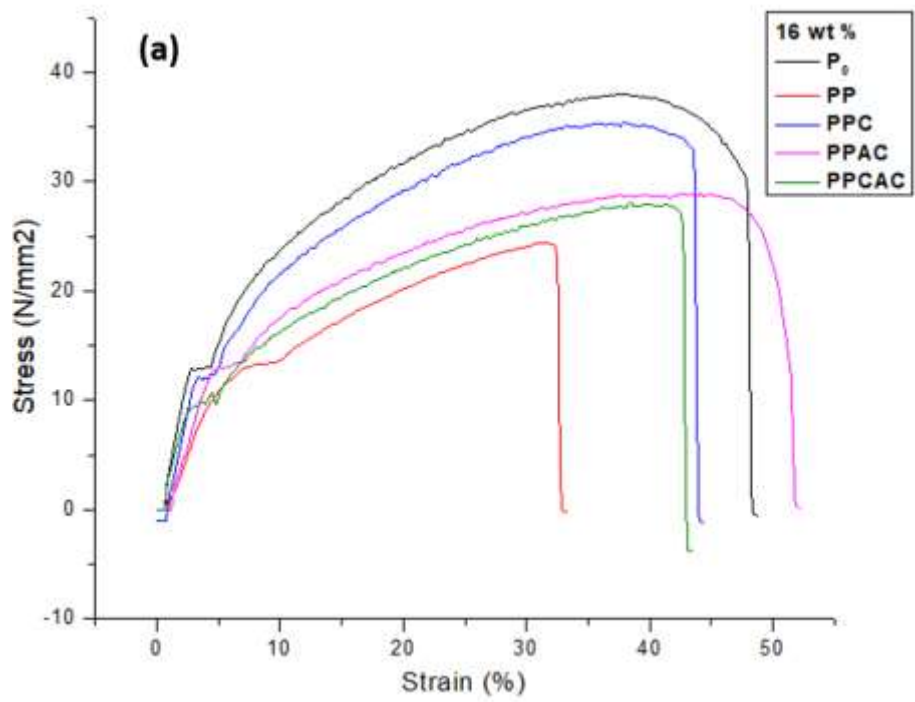
Figure 4.22. Stack Graphs for Mechanical Properties of (a) 16 % PES membranes

and (b) 20 % PES Membranes.
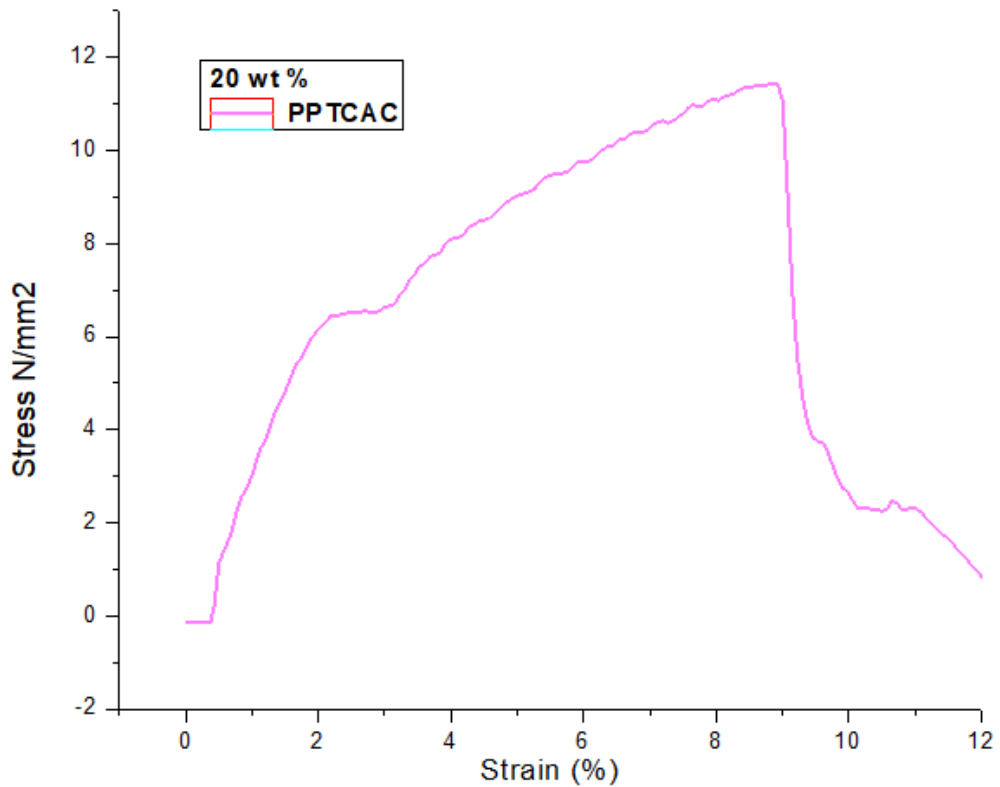
Figure 4.23. Graph for Mechanical Properties of 20 % wt. PES Membranes incorporated with Thiolated Chitosan.

Incorporation of activated carbon particles results in increased porosity of the membrane. As can be seen from Fig 4.20., addition of activated carbon resulted in lesser strength. Mechanical properties like elastic modulus also decreases with sudden increase in porosity because of a high molecular weight filler [106]. In the case of elastic modulus, activated carbon is not a polymer and its elastic region is very low as compared to the polymers. This reduced elastic region may be a reason for decrease in elastic modulus. For the evaluation of results, graphs given in Fig 4.22. and 4.23. were used to obtain the values.

Table 4.7. Summary of properties for 16 % wt. PES Membranes.

16 % wt. Properties	P0	PP	PPC	PPAC	PPCAC
Water Retention (%)	35.6	47.3	52.9	50.7	59.6
Gravimetric analysis (%)	35.7	32.15	52	73	85
Contact Angle θ	65.2± 2	60.7± 2	59± 2	73.6± 2	52.2± 2
Surface Roughness (nm)	612	929	1080	940	764
Young's Modulus (MPa)	5.79	3.00	5.25	3.6	4.08
Ultimate Tensile Strength (MPa)	37.9	24.35	35.2	28.79	27.8
Flux Rate ($Lm^{-2}h^{-1}$)	120	107	135	96	125
BSA Flux ($Lm^{-2}h^{-1}$)	23	29	32	62	48

Table 4.8. Summary of properties for 20 % wt. PES Membranes.

20 % wt. Properties	P_0	PP	PPC	PPAC	PPCAC	PPTCAC
Water Retention (%)	22.84	44.65	53.8	57.2	60	76.5
Gravimetric analysis (%)	31.7	39.7	56	73	84.3	79
Contact Angle θ	64.5±2	57.6±2	48.1±2	70.7±2	59.85±2	55.7±2
Surface Roughness (nm)	832	647	931	633	362	2690
Young's Modulus (MPa)	4.09	3.24	5.05	4.45	2.53	3.04
Ultimate Tensile Strength (MPa)	27	22.19	20.6	32.3	41.39	15.11
Flux Rate ($Lm^{-2}h^{-1}$)	105	95	118	101	112	114
BSA Flux ($Lm^{-2}h^{-1}$)	23	25	31	57	47	51

Conclusions

A novel Thiolated chitosan/Activated carbon composite was introduced in 20 % wt. polyether sulfone membrane to synthesize highly hydrophilic and antifouling ultrafiltration membrane. ATR-FTIR results confirm the functional groups for PES. The membranes incorporated with Thiolated chitosan/Activated carbon (PPTCAC) showed improved hydrophilic character than the Pristine PES membrane (P_0) which was considered to be a reference membrane. The contact angle for 20 % wt. PPTCAC was reduced to 55.7 from 65 of 20 % wt. P_0. The pure water flux increased from 105 L/m^{2}h of 20 % wt. P_0 to 114 L/m^{2}h for 20 % wt. PPTCAC. Remarkable increase in antifouling properties was also observed as BSA flux was calculated at 51 L/m^{2}h for 20 % wt. PPTCAC which was considerably higher when compared to 20 % wt. P_0 at 23 L/m^{2}h. The cross-section images of Scanning Electron Microscopy exhibited enhanced finger like structures for 20 % wt. PPTCAC which helped in better flux rate. Yield point decreased for 20 % wt. PPTCAC to 3.04 from 4.09 of 20 % wt. P_0 as it is water soluble and results in formation of macro voids leading to reduced mechanical strength. The Water Retention properties showed great improvement from 22.84 % of 20 % wt. P_0 to 76.5 % of 20 % wt. PPTCAC. Surface roughness saw an increase in case of 20 % wt. PPTCAC at 2690 nm whereas the surface roughness observed for the reference membrane was 832 nm. The composite incorporated membrane displayed substantial increase in mean porosity which was measured using gravimetric analysis. The porosity increased to 79% for the 20 % wt. PPTCAC from 31.7% of the reference membrane. These results demonstrate that novel thiolated chitosan/activated carbon composite shows significant potential in the field of membrane technology and as an anti-foulant.

Recommendations for Future

Membrane with Thiolated Chitosan/Activated carbon has shown promise specially as an anti-fouling agent. Membranes with thiolated chitosan can be further improved by addition of additives that can add to the mechanical strength of the membrane as that is one area which has suffered with the addition of thiolated chitosan. More additives are to be investigated to improve their mechanical properties. Some additives that have helped in increasing mechanical properties include PEG, GO, Nano clays, cellulose etc.

As chitosan itself is a good candidate for membranes being both a flocculant and an anti-fouling agent, more modifications of chitosan must be explored. Addition of functional groups that can improve the hydrophilicity of the membranes along with antifouling properties. Another option is to make composites of chitosan with such materials that bring better functional properties to the membranes. Graphene oxide is another good option which should be explored with chitosan. As GO is hydrophilic and already used in membranes.

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