

**Fabrication Of Nanofiltration
Membrane PES-Chitosan Incorporated
With Drug-Based Emulsion For High
Antifouling and Flux Property**



**By
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**School of Chemical and Materials Engineering
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Dedication

This thesis is dedicated to my husband whose tremendous support and cooperation led me to this wonderful accomplishment...

Acknowledgments

All the praises are attributed to the Almighty ALLAH the compassionate, the most merciful. He is the source of all knowledge and wisdom, which gave me strength to continue my work for this thesis.

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Regards,
Zainab Malik

Abstract

Growth in global population is causing a significant shortage of safe and clean drinking water, prompting the search for practical and cost-effective alternatives. Membrane filtration has demonstrated a lot of promises for the purpose of purifying water, but it confronts the difficulty of fouling, which reduces its lifetime. Currently, membrane technology is successfully used to treat water and is gaining popularity as a substitute for traditional methods of treating both water and wastewater. The membrane permeate flow directly affects these issues with the capital and operating expenses of membrane systems. Additionally, there are several ways to reduce fouling. Membrane-based water purification systems are most highly rated in pharmaceuticals, biotechnology, food industry, especially in the general water purification industry. Current study's objective is to create nanofiltration polyether sulfone membranes utilizing the phase inversion approach by combining chitosan and carbon nanotubes in an unique way to improve salt rejection. PES membrane containing chitosan, were created (0.75 wt. percent). To obtain antifouling capability, the goal is to successfully encapsulate a therapeutic drug. Considering the emulsion that is drug loaded and contain drug polycaprolactone (PCL) with cefotaxime was created utilizing nanotechnology, nano-precipitation method through the optimization of several process variables. The dip-coating of Chitosan membrane is done with the prepared PCL polycaprolactone With Polyvinyl alcohol surfactant. Further examinations of the coated membranes included functional group analyses with attenuated total (ATR-FTIR), morphology and cross-sectional views with (SEM), water retention for water uptake analysis, mechanical testing for membrane strength, roughness, flux and contact angle for water wettability. Two of the strains are used that are bacterial i-e E. coli, Gram-negative and Gram-positive S. aureus showed antifouling activity. The outcome of the studies show promising antifouling activity and provide the chance to treat water to get rid of contaminants and raise the standard of drinking water.

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List of Abbreviation

NMP	N-methyl-2-pyrrolidone PES Polyethersulfone
WHO	World Health Organization
UN	United Nations
SEM	Scanning electron microscopy
ATR- FTIR	Attenuated Total Reflection–Fourier-Transform Infrared spectroscopy
Nm	Nanometer
C	Celsius
ml	milliliter
μl	microliter
G	grams
Sec	Seconds
Rpm	Rotations per minute KBr
P	Membrane code for PES
PCH	Membrane code for PES incorporated with chitosan
AFM	Atomic Force Microscopy

Chapter 1

Introduction

1.1 Background

Water is the basic resources on earth as water is essential for utilization by all other life and hence, plays a major role in all aspects of human life[1]. Although a large proportion that is 72% of the Earth's surface is covered with water but only 3% is of fresh water [2]. The water abundance is shown in figure 1.1.

Water has economic value. Life cannot exist without water. It is a basic substance that occurs in solid, liquid, and gaseous states[3, 4]. Earth is probably the only planet with large amounts of water on its surface[1].

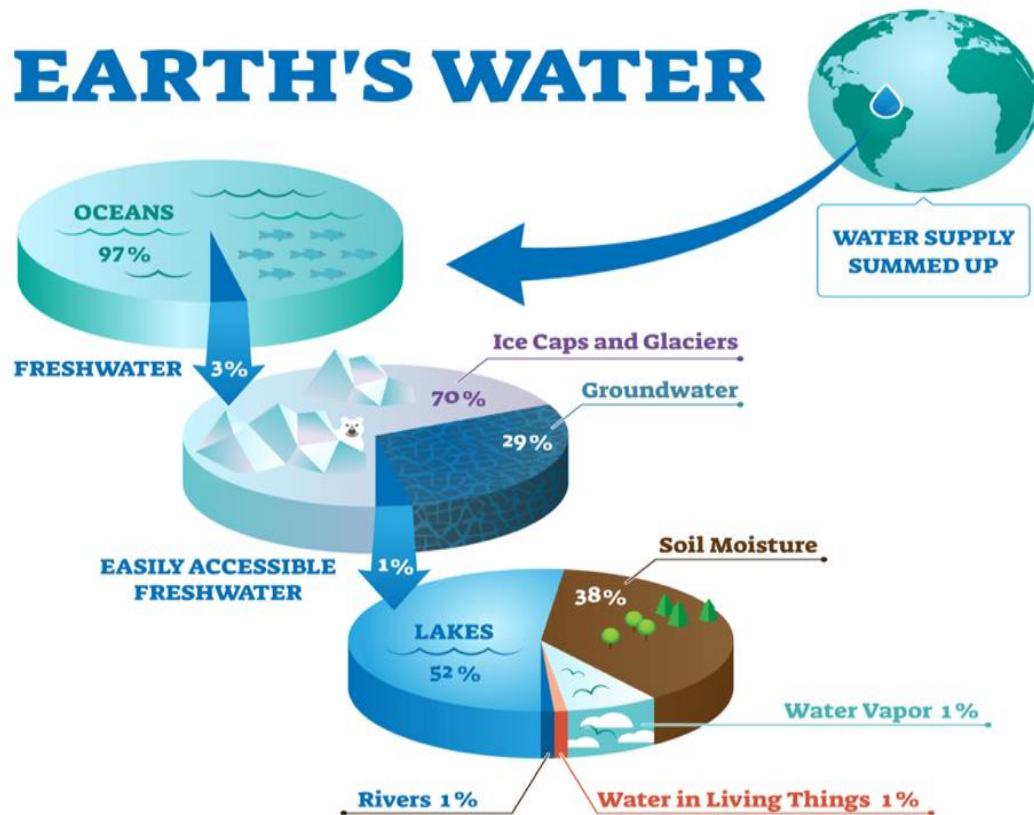


Figure 1. 1: Earth water's constitution

Due to the geography of water supply and consumption, which is complicated and continually changing, it is challenging to predict the future sufficiency of freshwater supplies. In defining the state of the world's water systems through 2025, rising water demands vastly outnumber greenhouse warming.[5]. Direct human effects on the world's water supply are still poorly understood but may be significant aspects of the wider subject of global change[1].

Every year, millions of deaths occur due to a lack of clean water and sanitation. To fulfil an ever demands for water, numerous options have been proposed, including better water resource management, water reuse, and desalination. Several more water cities access that have rain-hit around the world have access to saltwater, bacteria and groundwater. These may be converted into clean water to help with water demand[4].

1.2 Pakistan's Water Crisis

Water shortages has already become a critical situation in Pakistan. The country is placed 14th out of 17 countries in the world with 'very high-water risks', including hot and dry countries like Saudi Arabia. Pakistan faces a serious water crisis.[6] The country is rapidly moving from 'water stress' to 'water scarcity', with annual water availability falling below 1,000 cubic meters per her capita and already surpassing that threshold[7]

Pakistan's groundwater resources (a last resort for water supply) are in additament to surface water. significantly overexploited, primarily to provide water for irrigation. If things continue as they are, the country could face water shortages by 2025[8].

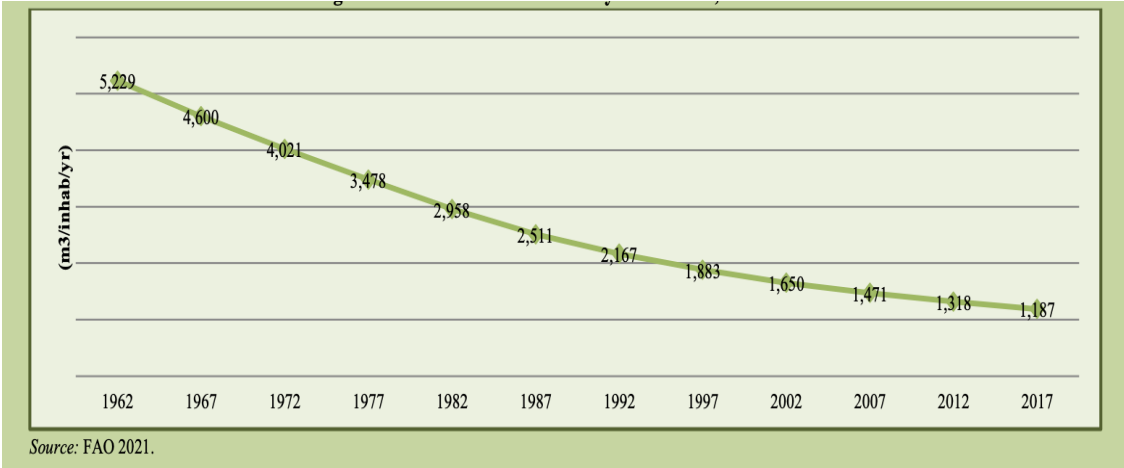


Figure 1. 2 Trend of water availability in Pakistan from 1962 to 2017

1.3 Polymeric Membranes: The Ultimate Solution

In the water sector, membrane filtration is used to clean the water for use, reuse, or discharge into the environment [7]. Membranes can remove contaminants ranging from bacteria and protozoa to ions and have microporous to non-porous structures also[8].

Chlorination, membrane filtration, and chemical treatments are some of the modern water disinfection/treatment methods. On the other hand, boiling and chlorination have many other drawbacks[9]. Chlorination produces harmful by-products in water, so the amount of residual chlorine in water should be controlled prior to use. Boiling requires high temperatures, and less water is needed as the water evaporates. Membrane technology has evolved over time into a widely used approach for aquatic therapy.[10, 11] Evolution of membrane materials is necessary to improve the properties of existing membranes[12].

A membrane separation or treatment process mainly involves three basic principles: Adsorption, sieving, electrostatic phenomena. Membrane is a kind of material with selectivity Separation function that confines and permeates liquid substances and separates interfaces between liquid substances Two parts of a particular shape, solid or liquid. On the one hand there must be two interfaces and on the other hand the membrane must be present[13].

Microfiltration (MF) as well as ultrafiltration (UF) which are low pressure processes (0.1-2 bar for MF, 2-10 bar which effectively removes microorganisms, suspended solids (MF), and colloidal particles. High pressures (e.g., 8-20 bar) are required for nanofiltration (NF) and reverse osmosis (RO) (NF and 10e-0 bar for RO) [11] Nanofiltration is a newer membrane process. Water softening agent that removes magnesium and calcium ions. Simple organic compounds are removed, although the use of RO for desalination of brackish and sea water is very well recognised, this method can also be used to remove low water levels. Organic molecular weight compounds derived from water, either naturally and otherwise synthetically. [8]

Regardless, many advantages the membrane technology has its own disadvantages regarding the condition or the handling techniques which are as follow:

- (1) Membrane fouling avoidance and remediation methods
- (2) achievable improved separation between solutes
- (3) further processing of concentrates
- (4) chemical resistance towards water and limited lifetime
- (5) poor removal of contaminants in water treatment and
- (6) need for modeling and simulation tools[14].

1.4 Problem Statement

Water treatment is particularly important as the global demand for water is under constant pressure due to a growing world population and rising living standards around the world as compared previously. Such high demand covers both quantity and quality of water. Furthermore, in terms of poor sanitation and pollution. In addition, the industry is placing greater emphasis on environmentally friendly technology and integrated processes, and increasing its commitment to water reuse and waste reduction[15, 16].

Membrane technology aids in the recovery of clean water from polluted water. Recent advancements, including the development of more selective and permeable membranes, longer membrane lifetimes, and relatively short fouling and cleaning cycles[13], which are examples of recent advances in technology. The membrane would show higher flux and has antifouling character as advanced membrane.

1.5 Research Framework

The research has been expanded on four major phases.

1.5.1 Phase I

Phase I involves the successful synthesis of membranes with various additives. The polymer used is polyethersulfone (PES) with chitosan as reinforcing agents. To better understand the effect additive, membranes were synthesized using these additives separately or in combination.

1.5.2 Phase II

In the second phase, different characterization techniques have been performed to investigate the outcome of additives on various properties. The synthesized membranes were characterized by SEM, gravimetric analysis, ATR-FTIR, mechanical testing, contact angle measurements, permeability flux and salt rejection, Water retention and Mechanical Testing.

1.5.3 Phase III

the phase three is related with the process of dip-coating, that is actually the coating of the emulsion on the (pes) membrane that occurs stepwise or layer-by-layer with alternatively coated with PDAC(Poly-diallyldimethylammonium chloride). The coating occurs due to difference in changes or zeta potential.

1.5.4 Phase IV

In the stage, various characterization techniques were carried out to study the effect of different coated membranes on various properties. The synthesized membranes were characterized by SEM, ATR-FTIR, mechanical testing, anti-fouling,contact angle measurements, permeation flux and water retention/surface wettability and mechanical testing.

1.6Aims and Objectives

Following are main aims and objectives of research work

1. Fabrication of polyether sulphone membrane with fabrication of Chitosan composite membrane
2. Preparation of drug-based emulsion
3. Dip-coating
4. Aim of dip-coating of composite membrane is to increase
5. Permeability flux
6. Hydrophilicity/ Wettability
7. Anti-fouling

Chapter 2

Literature Review

2.1 Advances in Membrane Technology

Membrane technology has helped solve problems associated with treatment of water that is discarded or waste. Benefits of this technology is effect cost, reduced consumption of chemical and small footprint etc [17]. In essence, a membrane serves as a barrier to keep two phases apart by limiting the passage of certain components across it[18, 19]. The concept of membranes originated in the 18th century[20]. Since then, several developments have been made to boost the applicability of membranes for a wide range of applications[21, 22]

2.2 Benefit of Films in Water Treatment

Membrane techniques are used to provide the maximum quality water, regardless of the water source [23]. Membrane filtration, in contrast to other extra methods, removes various pollutants from the feed water, uses less chemicals, has a smaller environmental imprint, produces less precipitate, and is comparatively easier to maintain and run [24]. Membrane fouling, on the other hand, is a major flaw in membranes that restricts the improvement process[25, 26]. The sections below provide some data on membrane categorization and the different considerations that impact fouling[27].

2.3 Classification of Membranes

Based on pressure association to membrane, it is divided into two major categories. High pressure membrane and low-pressure membrane MF, UF and RO have different function of filtration as of separating material depends upon the pore size. From high pressure driven to low pressure driven the membrane technology is used to treat water[28, 29].

It is also possible to adjust the pore size of polymeric membranes during production[30]. The installation necessitates a high degree of flexibility and a little amount of area. Each time, we must select a polymer based on the task at hand. Polymeric membranes are often made from cellulose acetate (CA), polyacrylonitrile (PAN), polyimide, polycarbonate (PC), polyethylene (PE), polypropylene (PP), and polytetrafluoroethylene (PTFE). In general, polymers such as polyvinylidene fluoride (PVDF) ultra - filtration membranes are incorporated with nanomaterials such as metal/metal oxide or Chitosan to optimize the polymeric membrane's performance[31].

The contact angle, which is a measure of membranes hydrophilicity, represents the relationship between both the water and the membrane material. It has recently been established that polymeric membranes are naturally hydrophilic. [32]Polymeric membranes have a much stronger negatively charged and a neutral pH than ceramic membranes. When the dip- coating of drug loaded emulsion occurs with alternative positive and negatively charged chemicals are processed, electrostatic repulsion and attraction that generates, which aids in membrane fouling reduction. Smooth-surfaced membranes are also more prone to fouling than those of with rough surface membrane. The size of the pores in low-pressure driven barriers is significant because it dictates whether particulate will penetrate through the membrane[33].

In pressure-driven membrane technologies, a pressure applied to the solution at one side of the membrane acts as a driving force to separate it into a filtrate and a permeate flux (ro, nanofiltration, ultrafiltration and microfiltration). The distillate is a concentrated form that must be disposed of or otherwise handled, whereas the permeate is frequently clean water[21].

2.4 Membrane Morphology, Working Mechanism and Configuration

Membranes are classified as symmetrical or asymmetrical based on their structure. Membranes have symmetrical architecture, indicating that the penetrability of the membrane does not change as it passes out of the depth of the membrane[34]. Asymmetric membranes,

conversely, are made up of two layers: a fine functioning layer with low porosity and a very thin supporting layer (being-void space) that is extremely porous and aids in the production of hydraulic resistance. These structures can be used for high or low-pressure membranes. However, the configurations are different [35].

Flat sheet, hollow fiber, and tubular membranes are the most common designs in low-pressure membranes[36]. Variable module parameters and manufacture have the greatest impact on fouling propensity [37]. High-pressure membranes are utilized for the spiral structure of the wound in widespread use, with a high packing density for the creation of bulk volume of water [38].

Membrane modules are reliant on membrane running processes. There exist two flow configurations in their operational processes:

- Drift in a dead end
- Purification by crossflow

Membrane flow is usually determined by fouling and the flux of permeate across the membrane[29]. Membrane flow perpendicularly streams through a layer in dead end configuration, leaving several pollutant chemicals on the membrane surface [39]. The issue with this flow regime is that with reduced water output, the rate of fouling might increase[40].

2.5 Membranes UF, MF, NF, and RO

The membrane operates as a selective barrier in the separation of the membranes outlined thus far, allowing relatively unrestricted flow of one component while withholding another[41, 42]. The membrane in membrane contactors acts as an interface among two phases but does not govern the rate of permeant passage across the membranes[43, 44].

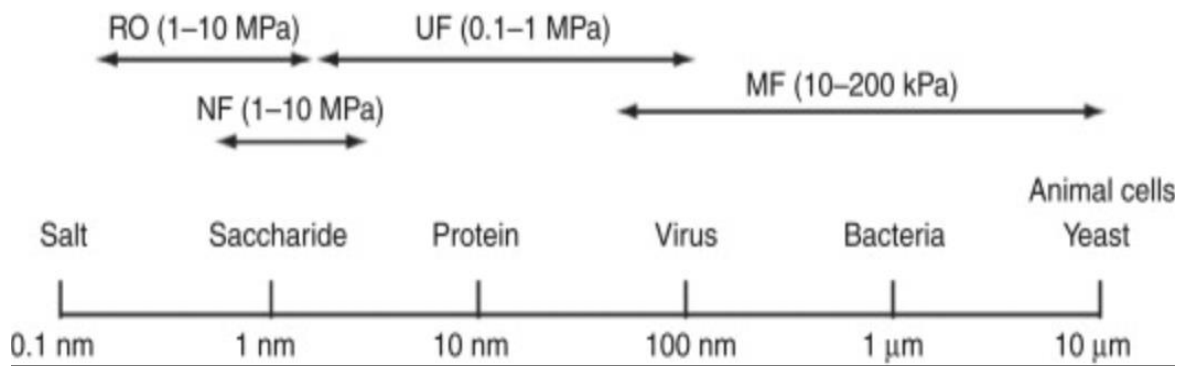


Figure 2. 1: Different size ranges for different filtration membranes. Pressure-driving membrane separation mode depending on the size of separation targets. RO, reverse osmosis; NF, nanofiltration; UF, ultrafiltration; MF, microfiltration

2.5.1 Microfiltration (MF)

This membrane have pore that range in size from 0. 1 to 10 m[45]. Membranes used for microfiltration (MF is the process of removing microscopic particles from gases and liquids, for example when separating proteins, purifying juice, or eliminating heavy metals[46].

2.5.2 Ultrafiltration (UF)

It has a pore size of around 0.01 m. The method that removes macromolecules and colloids from liquids (used, for example, to cleanse product streams in the food and beverage sector and for dyeing baths in the textile and transportation industries)[47, 48].

2.5.3 Reverse Osmosis

The second class of high-pressure membranes includes reverse osmosis and nanofiltration, where the separation process is solely dependent on the dissolution discrepancy between both the solvent and the solute included in the membranes[32]. Seawater desalination that used a pressure gradient is an aspect of reverse osmosis (RO), which removes all particles into water or other liquids[49, 50].

Classification of Membrane Filtration

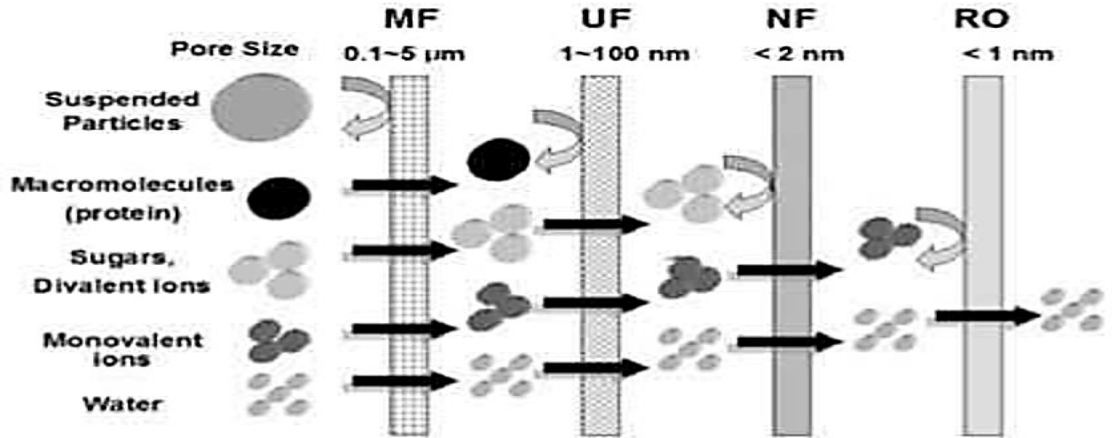


Figure 2. 2: Classification of membrane filtration based on size exclusion

2.6 Membrane Morphological Characteristics, Functionality, And Topology

The pore structure and solubility in water of UF/MF have been demonstrated to be important in membrane production methods. The penetration, hydrophilicity, and chemical stability to the filtration systems of a porous layer should be adequate. For high permeability, an asymmetrical membrane is an ideal choice. As a result, great effort is presently being expended to enhance the properties of membranes that is already existent in terms of anti-fouling qualities, higher mechanical strength, and chemical stability along with resistance[51].

2.7 Polyether Sulfone (Pes) Membranes

Polyether sulfone is a well-known polymeric substance that is frequently used in the production of membranes for a variety of purposes[52]. PES has an excellent tensile and hydrolytic stability, chemical and thermal resistance, and outstanding oxidative qualities due to its high temperature of glass transition (225 °C) and amorphous and transparent properties, which make it suitable for the preparedness of asymmetric membrane surface with different

surfaces and pore sizes depends upon the treatment of the membrane[53]. Asymmetrical PES membrane is typically made using a phase-separation method[54]. PES is recognized as a crucial polymer in the manufacturing of polymeric membranes used in water treatment. It's widely accessible on the commercial scale, and it's usually made by joining two functional groups (ether & sulfone group) to a backbone[55]. When used in membrane manufacturing, these polymers exhibit a variety of desired features, such as hydrolytic durability, high - dimensional stability, good thermal stability, and exceptional oxidative properties. the figure depicts the formula of PES followed by the powder form.

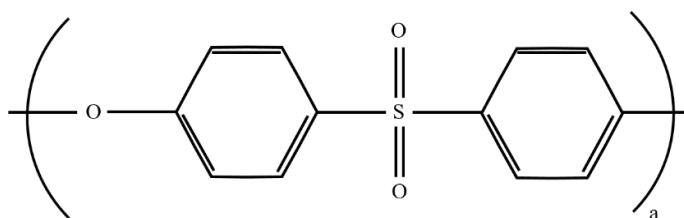


Figure 2. 3: Structural Formula Of Pes



Figure 2. 4: Powder form of PES

2.7.1 Chitosan

Chitosan is a linear polysaccharides chains with a 1, 4-glycosidic link generated by inadequate deacetylation of chitin, a key component of shells of crustaceans (e.g., crab, shrimp, and crawfish)[56]. Due to inadequate deacetylation, chitosan units are joined contains glucosamine and N-acetylglucosamine[57]. This molecule is particularly essential

due to its distinct biochemical properties [58, 59]. Because chitosan contains numerous amino (-NH₂) and -OH functional groups, it has a high degree of reactivity, as seen in Figure

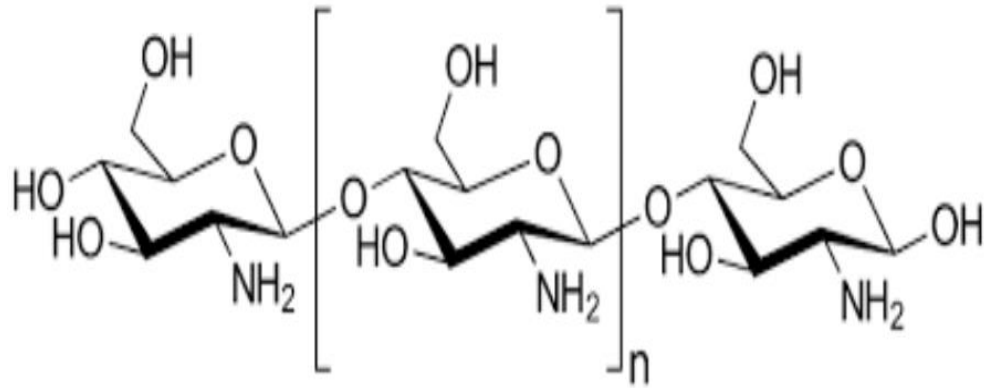


Figure 2. 5 Structural Formula of Chitosan

Chitosan is dissolvable acids but insoluble in inorganic liquids[60].When the pH falls below 7, the amino groups can be protonated, which results in the creation of chitosan which is water absorbing cationic polyelectrolyte. The amino groups in chitosan become deprotonated and hydrophobic when the pH approaches 7. The addition of numerous functional groups capable of forming covalent connections with chitosan might modify its characteristics (i.e., the degree of hydrophobicity can be altered). Chitosan, on the contrary hand, has the ability to be transformed into gel, films, pellets, and fibers[61].

2.7.2 Advances in hydrophilic modification and performance polyether sulfone (PES) membrane via additive (CHITOSAN) blending

The composition (additives, concentration, and solvent) of the doping solution, the non-solvent, or mixtures of non-solvents, and the coagulate bath or surroundings all influence the final membrane characteristics and performance[62]. The potential of fouling due to PES's high hydrophobicity restricts its extensive utilization, particularly for protein-contacting procedures and aqueous filtrations. Various studies have reported attempts to improve the hydrophilic nature of the PES surface of the membrane[63].

In general, the contact angle (WCA) established between the membrane-liquid boundary and the liquid-gas tangent is used to assess the membrane's hydrophilic qualities[64].

Hydrophobic in nature, commercial PES membranes have high mechanical, toxicological and temperature stability.[54]

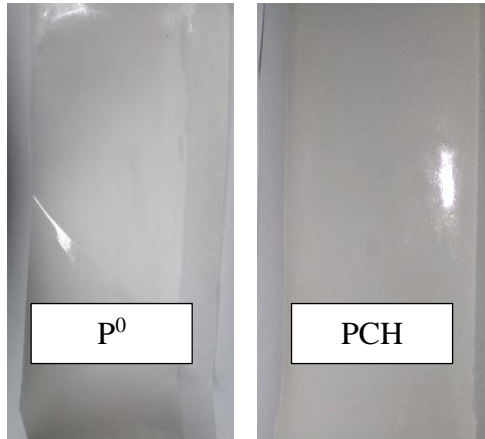


Figure 2. 6: Shows the PES and PCH membranes

3.7.3 Advantage Of Additive Pes Dip-Coating

Furthermore, polymers like polyvinylidene difluoride (PVDF) and PES which are frequently utilised in the creation of membrane materials that is polymeric in nature, have considerable hydrophobic characteristics.

Due to the promotion of hydrophobic interactions between organic or natural matter (BOM and NOM) in water, thus restricts their use in treating wastewater.

The end result is a procedure known as fouling when an accumulation of such undesirable elements forms on the membrane surface and pore inhibiting movement of fluid (water) which enhancing operational pressures requirements and decreases membrane lifetime. [17] To ensure sustainable water reuse, it is essential to address the issue of membrane fouling[65]. Here, we demonstrate how thin coatings formed of combinations of antibacterial hydrophilic polymer, PDAC, may give antifouling capabilities against bacteria or pathogens that may be present in water reuse application [66]

2.8 Drug Loaded Emulsion

APF, an antifouling polymeric composition were created but also assessed[67]. Cefotaxime's anti - fouling properties were nano—encapsulated using polycaprolactone as that of the shell material thru the process of nanoprecipitation. Dichloromethane (DCM) was employed to decompose the organic layer or the oil layer, that comprised polycaprolactone (PCL), whereas polyvinyl alcohol (PVA) present inside the liquid state (Sana Javaid, 2022) functioned as a binding agent[68, 69]. To enhance the empty formulation a gradual introduction of an organic phase into an aqueous phase were made. Cefotaxime were dissolved in the organic phase and then gradually introduced in with an aqueous medium just after process variables were adjusted so that it produce a stable composition.[31] An organic phase including cefotaxime and an aqueous phase were combined to create the antifouling polymeric nano formulation[32].

2.9 Components of Emulsion

Following are the components of the membrane.

2.9.1 PCL (polycaprolactone):

PCL is one of the first commercially available synthetic polymers, with a wide range of biodegradation and mechanical properties that can be finely tuned by adjusting the environmental driving forces (ie, microorganisms, enzymes, hydrolysis)[70]. A processing conditions to optimise the fabrication of biodegradable PCL devices, with a particular emphasis on drug delivery and tissue engineering. as well as green chemistry applications[71, 72].

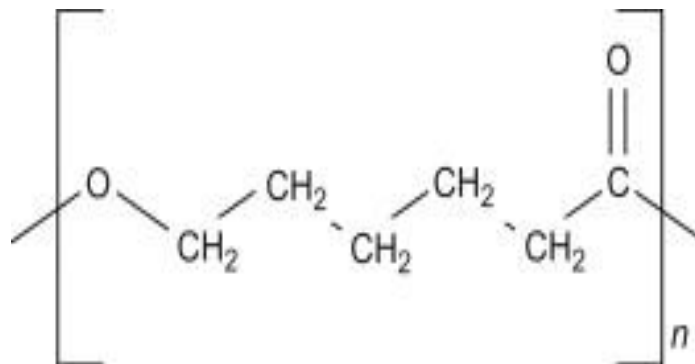


Figure 2. 7:Structure of polycaprolactone

2.9.2 PVA (polyvinyl alcohol)

oly(vinyl alcohol) (PVOH, PVA, or PVAI) is a synthetic polymer that is water soluble. Its idealised formula is $[CH_2CH(OH)]_n$ [73]. It's used in papermaking, as a thick former and emulsion stabiliser in PVAc adhesive formulations, a variety of coatings, and 3D printing[74, 75].

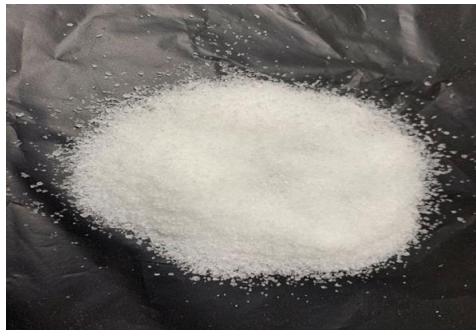


Figure 2. 8: Powder of polyvinyl alcohol

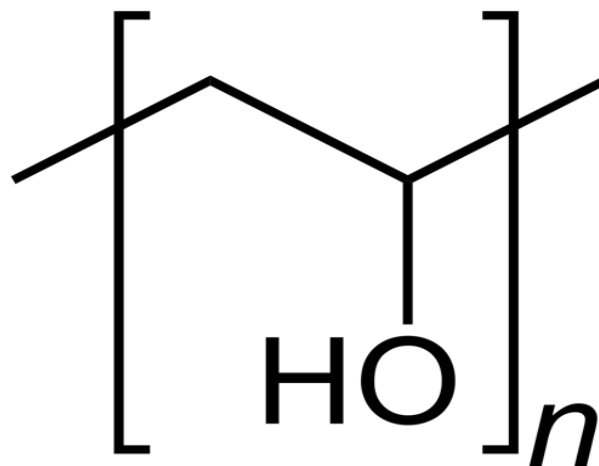


Figure 2. 9: Structural formula of polyvinyl alcohol

2.9.3 Drug(cefotaxime)

Cefotaxime is a cephalosporin antibiotic of the third generation[76]. That has wide range of spectra action against Gram - positive and gram and Gram-negative bacteria, as do other 3rd cephalosporins. For most situations, it is thought to be safe and effective in the same way[77].

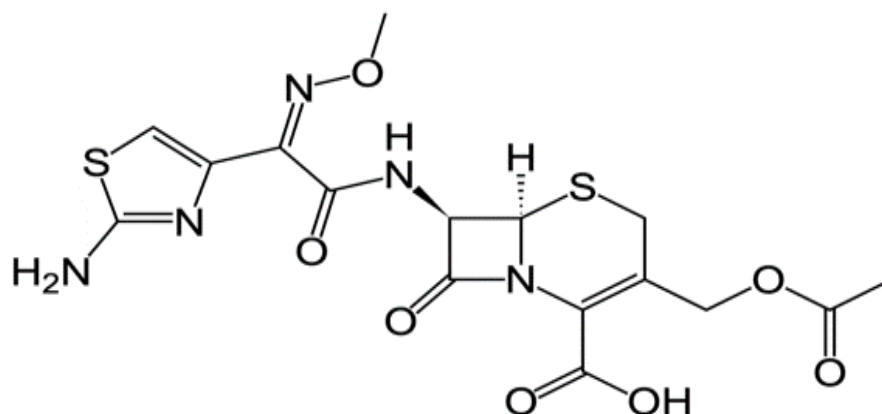


Figure 2. 10: Structure of cefotaxime

2.10 PDAC

PDAC was used as a positively charged liquid for dip coating (poly cationic solution). PolyDAC is a coagulant used in water purification. It coagulates and flocculates organic and inorganic particles like topsoil, clay, algae, microbes, and pathogens. The natural polymer could indeed remove organic matter such as fulvic and humic acids at high concentrations, resulting in reduced decontamination byproduct precursor chemicals and less colour.

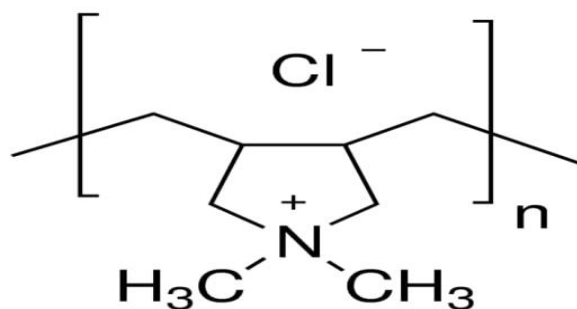


Figure 2. 11: PDAC

Chapter 3

Experimental Work

3.1 Materials

Analytical grade chemicals were used throughout the experiment. The membranes casting technique used /DISTILLED filtered water, whilst the chitosan/CNTs solutions used deionized water. Ultrason, Germany, supplied the polyethersulfone (58000 Mw). Sigma-Aldrich in Germany provided the N-Methyl-2-Pyrrolidone. Merck, Germany, supplied the polyvinylpyrrolidone (PVP, Mw 40,000 g/mol). The following materials were purchased from Sigma Aldrich, Germany: polycaprolactone (PCL) polyvinyl alcohol (PVA),(Mw-1400 g/mol), (Mw 3100 g/mol)-poly (diallyl dimethyl ammonium chloride)-(PDAC) (average Mw 200,000-350,000, 20 wt% solution) as well as dichloromethane (DCM) (Mw-84.93) of 99.9percentage clarity. Deionised water pure water with zero total solids (TDS0.00) was used for solution preparation and cleaning. As an antifouling functional moiety, cefotaxime (Mw 455.47 g/Mol in powdered form) was obtained from Nectar Life Sciences in India.

With an area density of 1.31 g/m³ mercerized bleached (100%) white pure cotton was made available by the National Textile University (NTU), Faisalabad Pakistan. Table salt (NaCl) of Sigma Aldrich (Germany) was employed as a buffer salt solution. The nutrient broth for (the bacterial culture was Mueller-Hinton II Agar Budapest, Hungary). A test for in vitro antimicrobial efficacy were conducted against gram positive and gram negative bacteria.

3.2 PES with chitosan and chitosan Mixed Matrix Membrane

The technique comprises the formation of membranes containing 17.5% wt. chitosan. As a support for the casting of membranes a polyester fabric sheet were employed.

3.3 Membrane Fabrication

The phase inversion approach has been reached out process for creating membranes. The same process was used to create four distinct membranes: PES with PVP, PES with additives, and PES with composites[78]. PES was mixed with NMP solvent in a media bottle to make a casting solution. The solution had heated to 60° C for 24h and agitated at 250 rpm[79]. The casting solutions were composed of numerous combination, as shown in the table. PES, PVP as a pore forming material, chitosan were all used.

3.4 Preparation Of A Nanocomposite Mixed Matrix Membrane:

17.5% w/w total polymer solution was made. All of the compounds were accurately weighed. For 24 hours, 3.5g of PES were dissolve regularly in 12ml of NMP and swirled at 250rpm. Continuous stirring for the following 24 hours after 2.5 w/w% PVP was introduced. The solution was agitated for 120 hours after the additions were added.



Figure 3. 1: Polymer membrane casting machine (Automatic Film Applicator, Elcometer4340 M43 6BU)

After sonicating for 30 minutes, the solution was heated and agitated for another 30 minutes. The solution was maintained for 2 hours to allow trapped air to degas. It was cast using a polymer membrane casting machine (Automatic Film Applicator, Elcometer4340 M43 6BU, Elcometer Limited, Manchester, UK) with water acting as a non-solvent at ambient temperature at a speed of 50–60 mm/s, added to a coagulation bath for 5 minutes, and then submerged in a water/isopropanol 70–30 solution for 19–20 hours. The membranes were then immersed in glycerol for 3-5 hours. The membranes were then rinsed with distilled water, air dried, and stored. Table 3.1 shows the membrane composition.

Table 3. 1: Percentage Composition of membranes

Polymer Membrane	PES %	Chitosan %
P	17.5	-
P/CH	17.5	0.75

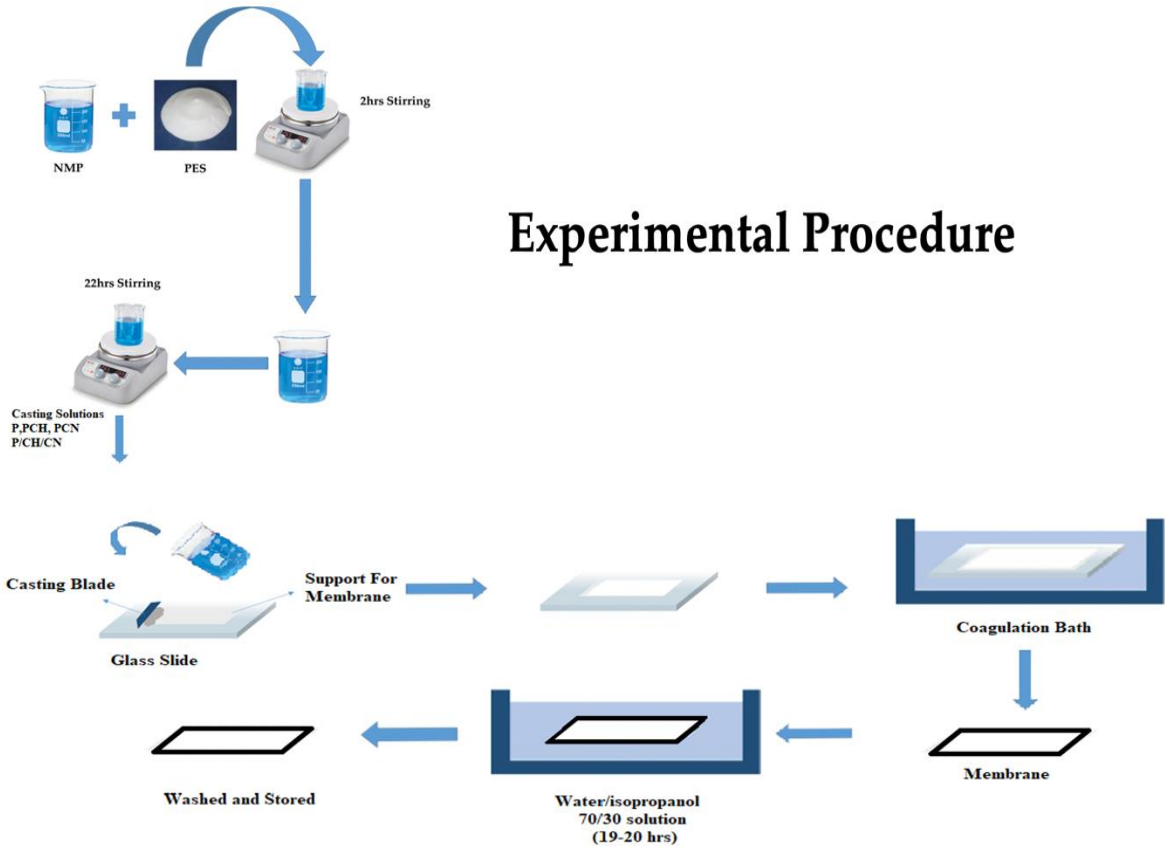


Figure 3. 2: Schematics for membrane synthesis

3.5 Antifouling Polymeric Formulation Synthesis Of Emulsion

By developing two phases separately through a nano-precipitation method that is used to optimise polymeric nano formulation process . for creating the blank phase actually through and organic phase differing concentration levels of PCL (25 mg, mg, milligrams (in mg, from 100 mg- 150 mg-200 mg) were dissolved in 2 mL of DCM at room temperature. PVA in different concentration (0.1%, 0.3%, 0.5%, 1%, and 2%) were stimulated for 10 mg / mililiters in liquid solution under 60 C temperature with constant mechanical stirring at for 1 hour until a clear solution was formed[80]. The proper selection of the cleaning agent or is the proportion that is of organic to aqueous medium, in addition to other unconventional variables, were key guideposts for nanoparticle stabilisation[81].

3.6 Dip-Coating Method

Dip-coating is the process involves submerging a substrate into the a tank filled with coating material, taking it away from the tank, and letting it dry. The covered component can next be driven to drain or baked to finish dry[82].

The dip-coating process occur due to difference in the zeta potential or the charge of membrane, emulsion and the PDAC. Alternatively dipping the membrane into the emulsion and the PDAC to attract charges for coating purpose. Following is the coating process according to difference in charges[83, 84].

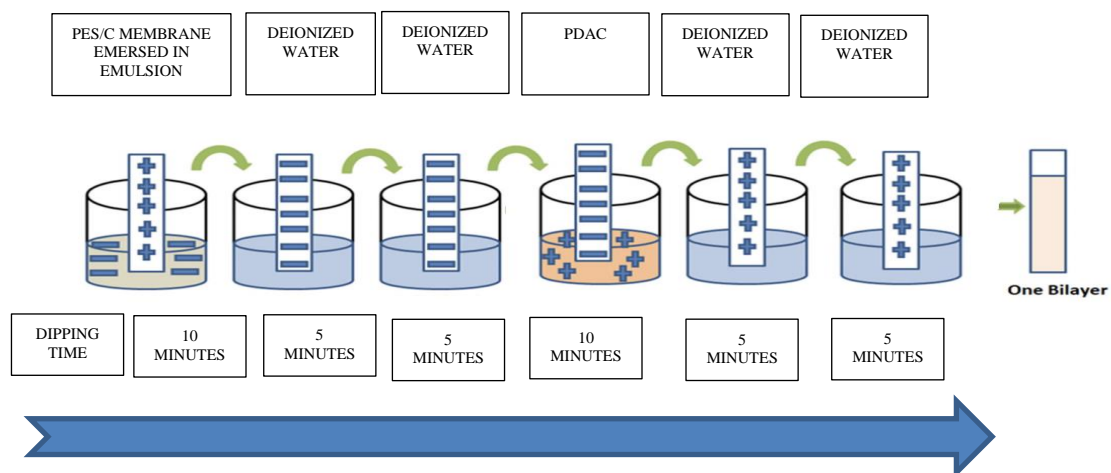


Figure 3. 3: Dip-coating process requires 40 mins for one bi-layer

The prepared membrane with chitosan was cut into 1 by 2 cm stripes, the membrane that is positively charged, first dipped for 10 minutes into APF emulsion (PCL) was dissolved in DCM whereas the PVA is used as surfactant that is negatively charged and after that the membrane is dipped into deionized water for 5 minutes each. Negatively charged stripes were then submerged in PDAC (neutral pH polycation solution) for the whole ten minutes following in positive charge followed by washing in DI water Two times for 5 minutes each in two separate beakers to attain the results. Then again the PES/chitosan membrane stripes were dipped in APF at neutral pH for 10 minutes before being washed twice with deionized water for 5 minutes in separate beakers (two) for the opposite charge of another single ion layer. As a result, a bilayer (1bL) of ions with opposite charges developed. The entire process of producing a single bilayer took time in minutes(40 mins). The identical process was utilized to cyclically create 1, 3, 5, 7 and 10 bilayers without drying the membrane in each stage. Fabricated fabrics with negatively charged APF top layers were investigated for slow-release antifouling activity and described for an in vitro antibacterial test. Figure depicts a schematic illustration of the layer-by-layer coating of PES/Chitosan membrane[85, 86].

In this way 5 membranes were created with coated emulsion of 1 bilayer,3 bilayer, 5 bilayer, 7 bilayer and 10 bilayers. The membranes were dried in air and labelled for further characterization techniques[84].



Figure 3. 4: Depicting the process of dip-coating formulated bi-layer coating

3.7 Samples Prepared

After dip-coating the membranes in to emulsion that is drugged based total six samples have been prepare for testing purposes. The samples that are further characterized are to be mentioned and coated according to series to get the properties. The samples are named according to the number of bi-layers coated over the surface of the membrane.

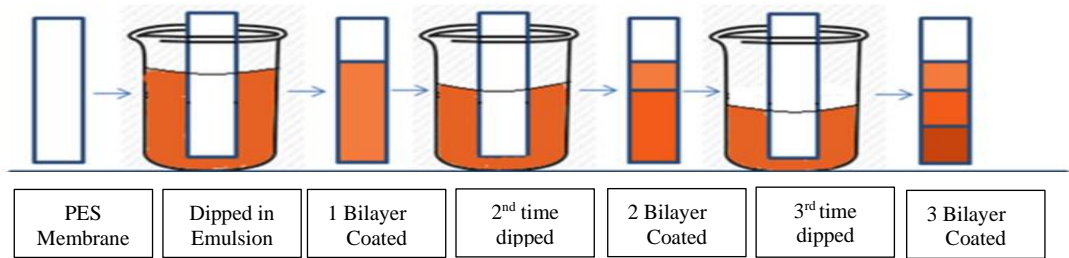


Figure 3. 5: Representation of fabrication of thin film gradients using layer by layer dip-coating technique.

After coating the bilayers with 1 coating, 3 coating, 5 coating, 7 coating and 10 coating, the samples are prepared with names , P^0 , P1, P2, P3, P4 and P5 respectively. The samples are shown in the latter Figure.

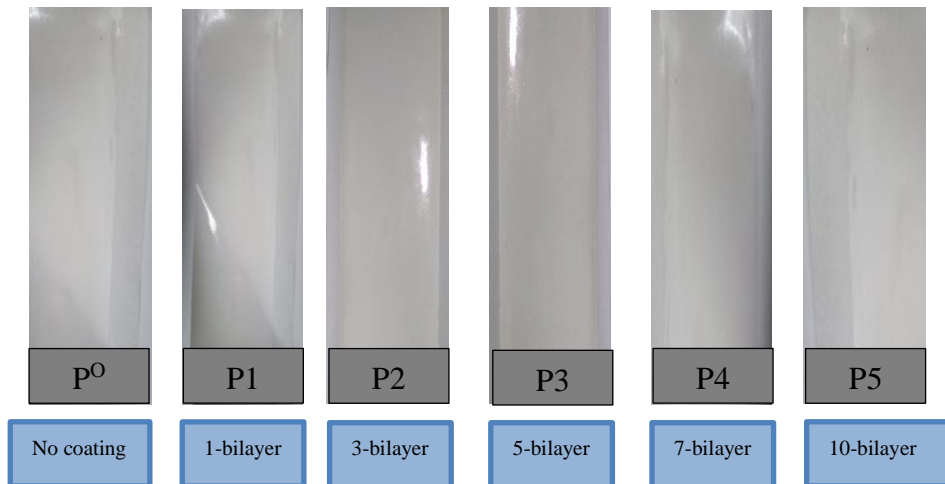


Figure 3. 6: Showing samples according to the coating

Chapter 4

Characterization Techniques:

4.1 Hydrophobicity and contact-angle measurement

The hydrophobicity attribute was investigated using the contact angle instrument (sessile drop method)[87]. A deionized water droplet had been injected into a 1 cm² dry membrane sample to produce a picture[88]. For the lowest error, the angle between both the membrane surface as well as the water drop got evaluated three times at random. KRUSS's DSA-25 drop shape analyzer was employed for this objective[89].

4.1.1 Surface Energy

Over the last 50 years, advances in physical chemistry have made it possible to quantify the adhesive bond[90, 91]. When the surface energy (or, more accurately, surface free energy) of the materials under consideration is known. Based on the Young-Dupre' equation, Van Oss, Chaudhury, and Good (1988) proposed the following relationship between the Gibbs free energy of adhesion (G_a), work of adhesion (W_a), contact angle of a probe L,S L,S liquid (L) in contact with a solid (S), and surface energy characteristics, of both the liquid and solid[92, 93].

Formula:

$$\Delta G_{L,S}^a = W_{L,S}^a = \gamma_L^{Tot} (1 + \cos\theta)$$

4.2 Surface Wet-Ability Testing

Membrane samples had been dried and thinly cut into strips (usually 2cm x 2 cm). Every single sample's weight was calculated by a digital balance. At 24°C, the 6 samples (po, p1,

p2, p3, p4, p5) were soaked in distilled water for 24, 48 and 72 hours[94]. The strips were removed, weighed to estimate the total weight gain by absorption of water[95]. The proportion of total extent of swelling (SW) was calculated using the formula [96]:

$$SW = \frac{W_s - W_o}{W_o}$$

Equation (1), where W_s is the swollen membrane weight and W_o is the dry membrane weight.

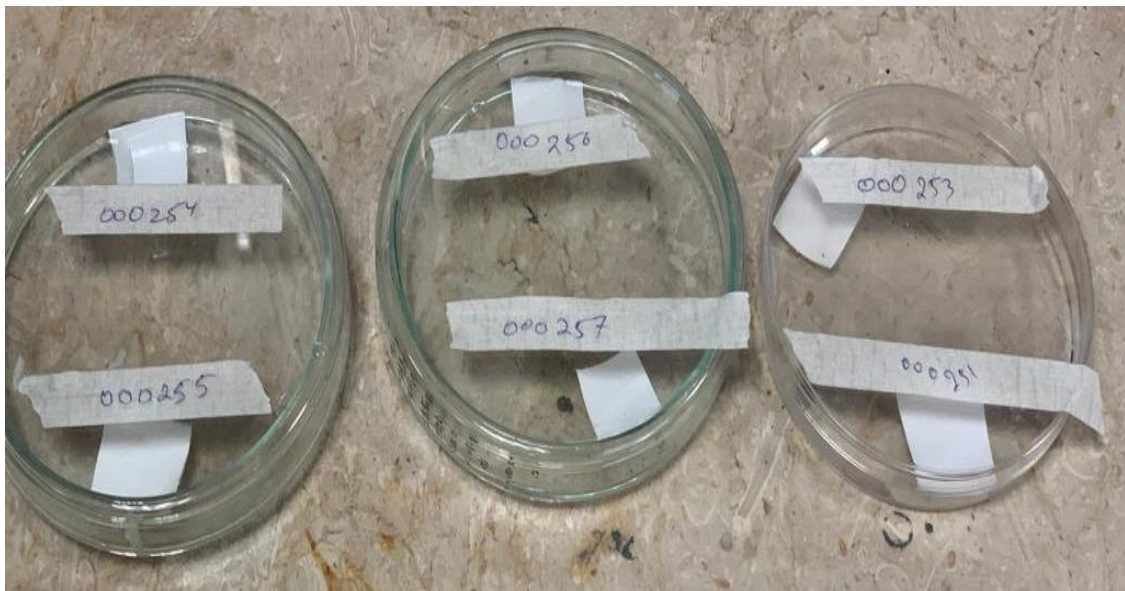


Figure 4. 1: Membranes dipped in water to absorb water and gain in weight for swelling ratio

4.3 FTIR

FTIR was used to investigate the membrane's functional groups. The dry membranes have been cut up into 0.5 cm² diameters for ATR-FTIR. The resolution were 1 to 2 cm⁻¹, and also the spectral range seems to be 400 to 3500 cm⁻¹. A BRUKER ALPHA II FTIR spectrophotometer was used for the experiment.

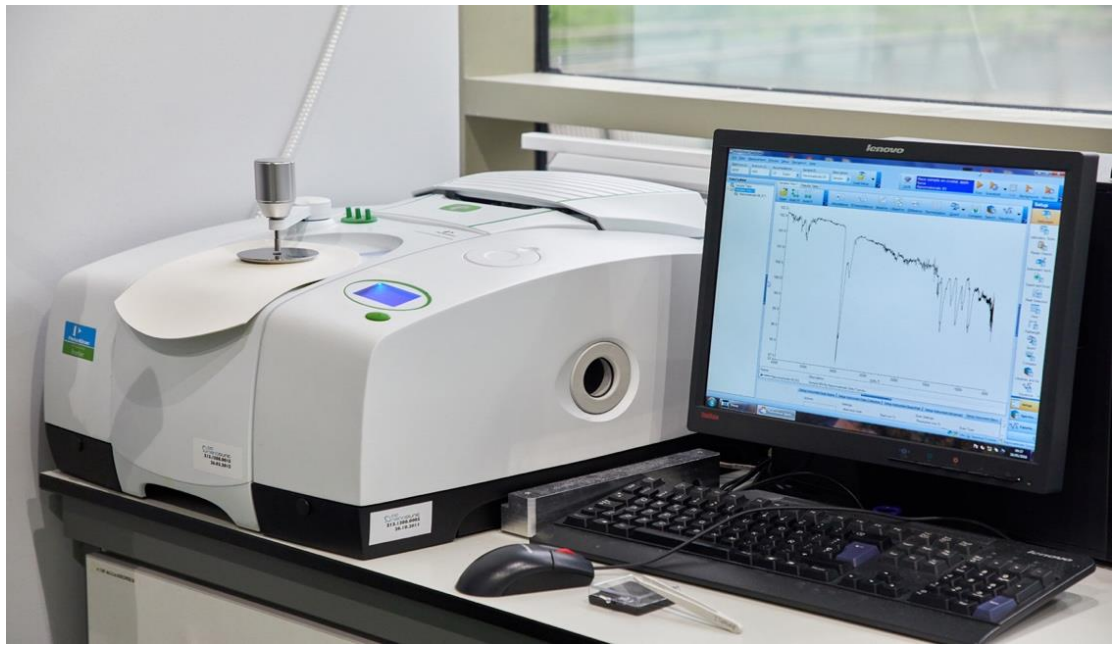


Figure 4. 2: ATR-FTIR (BRUKER ALPHA II FTIR)

4.4 Scanning Electron Microscopy

SEM was used to investigate the membrane shape and surface structure. SEM was carried out using a JEOL-JSM-6490LA with a working distance of about 10 mm, a functionally operating voltage of 10-20 kV, and a spot size of 35-60. The membranes were basically cut into 1 cm² pieces and frozen in liquid nitrogen to dry and break into minute fragments without disconcerting the cross section[97, 98].

4.5 Mechanical Examination

ASTM D882 was used to cut membrane samples into dog-bone shapes. At a regulated temperature of 21°C, the mechanical properties of membrane surface were investigated using a tensile tester, the Universal Tensile testing Machine (UTS) (Shamizdu AG-X Plus)[99]. Prior to testing, total of five sample strips from every membrane were checked, each taking measurements 25 mm by 3 mm and having a thickness of 0.3 as measured with a micrometre[100]. The samples were examined at a strain rate of 0.5 mm/min and a gauge length of 12.5 mm, as shown. Each sample's maximum stress was determined and the slope

of a linear portion of the stress-strain curve was utilized to calculate Young's modulus. Elongation but also tension have been determined at the break[101].

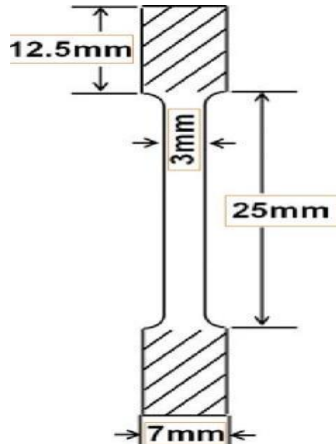


Figure 4. 3: Dog-Bone style

4.6 Optical profilometry

In optical profilometers can be used to evaluate the roughness of surfaces which mechanical profilometers could indeed reach[102]. Because the measuring principle is partially enclosed, optical measurements can be performed through with a transparent layer.

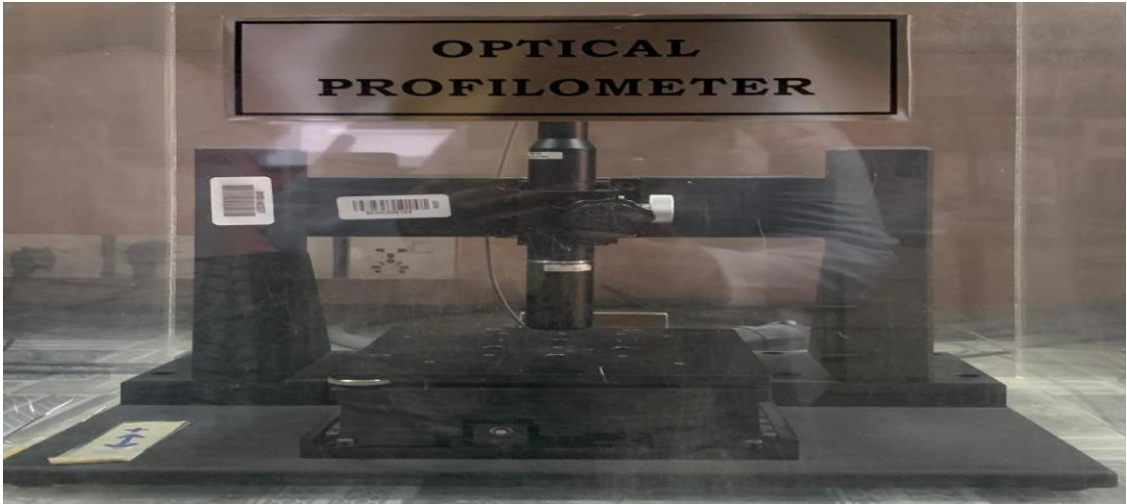


Figure 4. 4 : Shows Optical Profilometry

4.7 Water flux and BSA

The flux rate was used to calculate the permeation flux of the membranes, which is defined as the amount of fluid passing through a membrane as a function of time, area, volume, and so on. The membrane sample was put on the inside of a vacuum-connected filtration arrangement that was held at pressure conditions. The distilled water flow through the membrane was timed and measured. As a result, the data gathered was entered into Equation (3)

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

Equation (3)

The flux of the bovine serum albumin (BSA) has been determined to evaluate the anti-fouling characteristics of the membrane surface. One gramme of BSA has been dissolved for one liter of water to create a ppm solution[103, 104]. The pH of this alkaline solution was 8.22. The determined solution concentration was 0.1. At a pressure of 0.1 MPa, this solution was projected thru the synthesized membranes.

4.8 Anti-fouling tests

A qualitative agar well diffusion experiment was employed to test antimicrobial activities against two strains of bacteria, E. coli and Staphylococcus aureus. Bacterial cells were streaked into newly produced nutrient broth and cultured overnight at 37 C. Bacterial colonies were isolated from cultured medium using an infected wire loop and placed in a autoclaved that was set up before 10-mL saline solution[105]. The bacterial inoculum was vortexed to ensure evenly distribution and optical densities corrected using 0.5 McFarland standards. A total of 25 mL of MHA solution were poured onto 9-mm Petri plates in the existence of an ethanol lamp in a streamlined flow hood[102, 105].

The solid agar with 37 degrees C in incubator overnight. Using a paper puncture of 2mm, 5 samples was put into the middle of each Petri dish for both positive and negative bacterial strain. In addition to one control that is positive and other one is negative which were created

on agar plate[106]Petri plates were covered with lids, piled upright, and then put in a 37 C incubator. The repelled action against bacteria causes it to create a zone on inhibition, and the results was shown by the mean standard deviation by study the trend of zone of inhibition the antibacterial trend is studied [107]

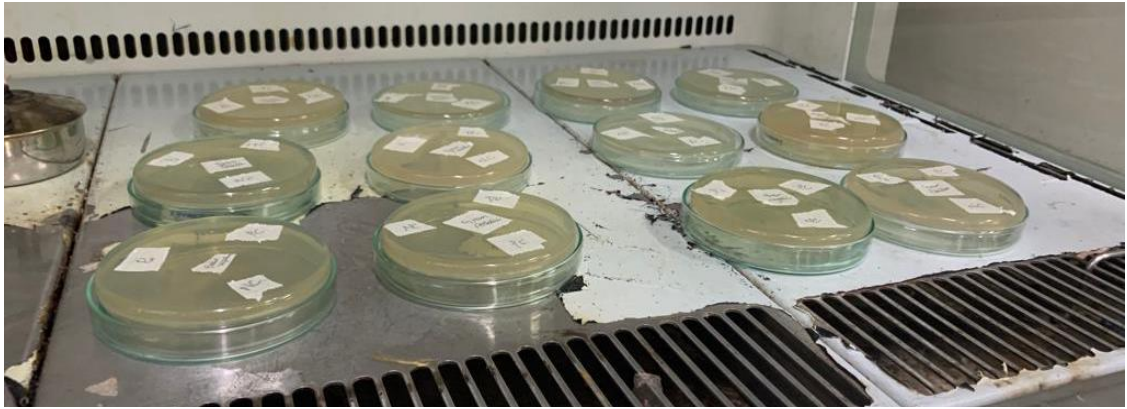


Figure 4. 5 shows theTest driven for membrane anti-fouling by placing bacterial strains both positive and negative in agar formulated in petri dishes

4.9 Analysis of Antimicrobial halo

The inhibition zone or antimicrobial "halo" is formed as a result of the antimicrobial material disk's inhibition of microbial growth[108]. In comparison to the rest of the plate, there is a transparent ring zone close to the sample where the microorganisms have grown properly (opaque zone)[109]. [83, 84]By using formula calculate the normalised width of the each "halo" (nwhalo).

Formula:

$$nw_{halo} = \frac{d_{iz} - d}{2d}$$

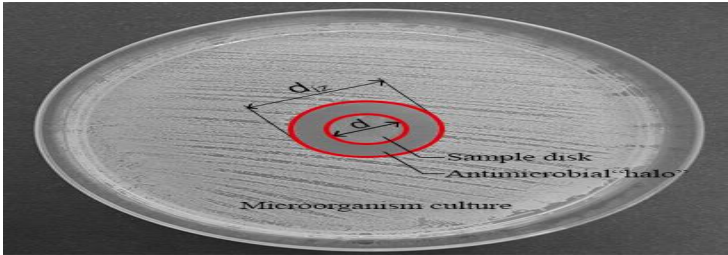


Figure 4. 6: Determining the halo by the measurement of zone of inhibition

Chapter 5

Result And Discussion

5.1 FTIR

Graph represents FTIR analyses of PCL, cefotaxime, and anti - fouling nanomaterials on the membrane in the 600 to 4000 cm^{-1} range. PCL's characteristic peaks are 3314 cm^{-1} , which showed good O-H bonding and stretching vibrations, and 1239.076 cm^{-1} , which shows strong bonding and C-O stretching and includes an alkyl ether group. Other peaks in the antifouling emulsion spectra at 1151.89, 1071.35, and 718.20 cm^{-1} coincided to C-O stretching and C-H bending vibrations. In the nano-precipitation spectra, FTIR studies clearly illustrated the compatibility of PCL and drugs thus, these findings confirm stability.

The ATR Ft - ir spectra in Figure 4.1 depict the majority of the distinct peaks of the PES polymer. Peaks at 1577.32 cm^{-1} depicts strong C=C bending intensity has shown ring structure of benzene and 1485 cm^{-1} with C-C bond stretching are present in all membranes and thus are coherent with the Polyethersulfone structure.

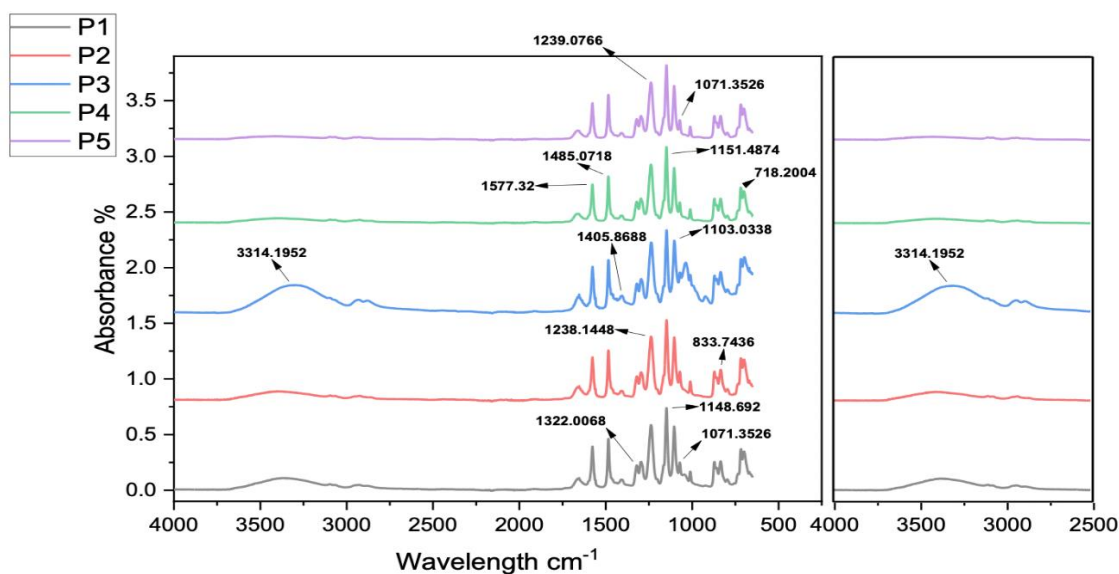


Figure 5. 1: ATR-FTIR Spectra for membranes

The composite membrane may also exhibit these peaks in P/CH and bilayered structures with 1, 3, 5, 7, 10 bilayer coatings. Bands that can be seen at cm^{-1} are evidence that the ether and carboxylate structures have undergone C-O stretching. The existence of an aromatic ether group inside the polyether sulfone configuration is identified by literature as C-O-C stretching at 1238.14 cm^{-1} . The sulfonyl (O=S=O) group produces the signal at 1148.6 cm^{-1} . As according 834.74 cm^{-1} CO, CH vibrations, CNTs may be present. The chitosan is present because the -C-O-C- bonds match the absorbance peak at 1103.03 cm^{-1} . The methyl groups generate two weak bands at 1322 as well as 1405.86 cm^{-1} that are only found in the spectrum of polyether sulfone concentrations much higher than 0.75 and 0.1 wt.% of the additives, respectively. There is no discernible transition in the spectra upon adding chitosan, CNTs, or a Chitosan/CNTs composite to any of the membranes.

5.2 Scanning Electron Microscopy

Utilizing SEM, it was possible to examine the composite membrane's top surface shape and cross-section structure. The asymmetrical morphology of the generated membranes, as illustrated in Figure 5.2, is composed of a dense upper layer and macro-void structure at the bottom. While P/CH/CN along with 1 and 5 layer coating showed have a dense top layer demonstrating flawless polymer solution mixing, the and coated one with 10 layers exhibit an agglomeration at the top.

The microscopy in Figure (c), (f) and (i) show the cross - section of the membranes. As has been shown, these membranes are assembled in an asymmetrical manner with a gradient-like structure. The upper layer of the Polymeric membranes is all dense. Also apparent is a porous sublayer made up of channels, which resemble finger like structures. Whenever there are channel connections and channel formation merged.

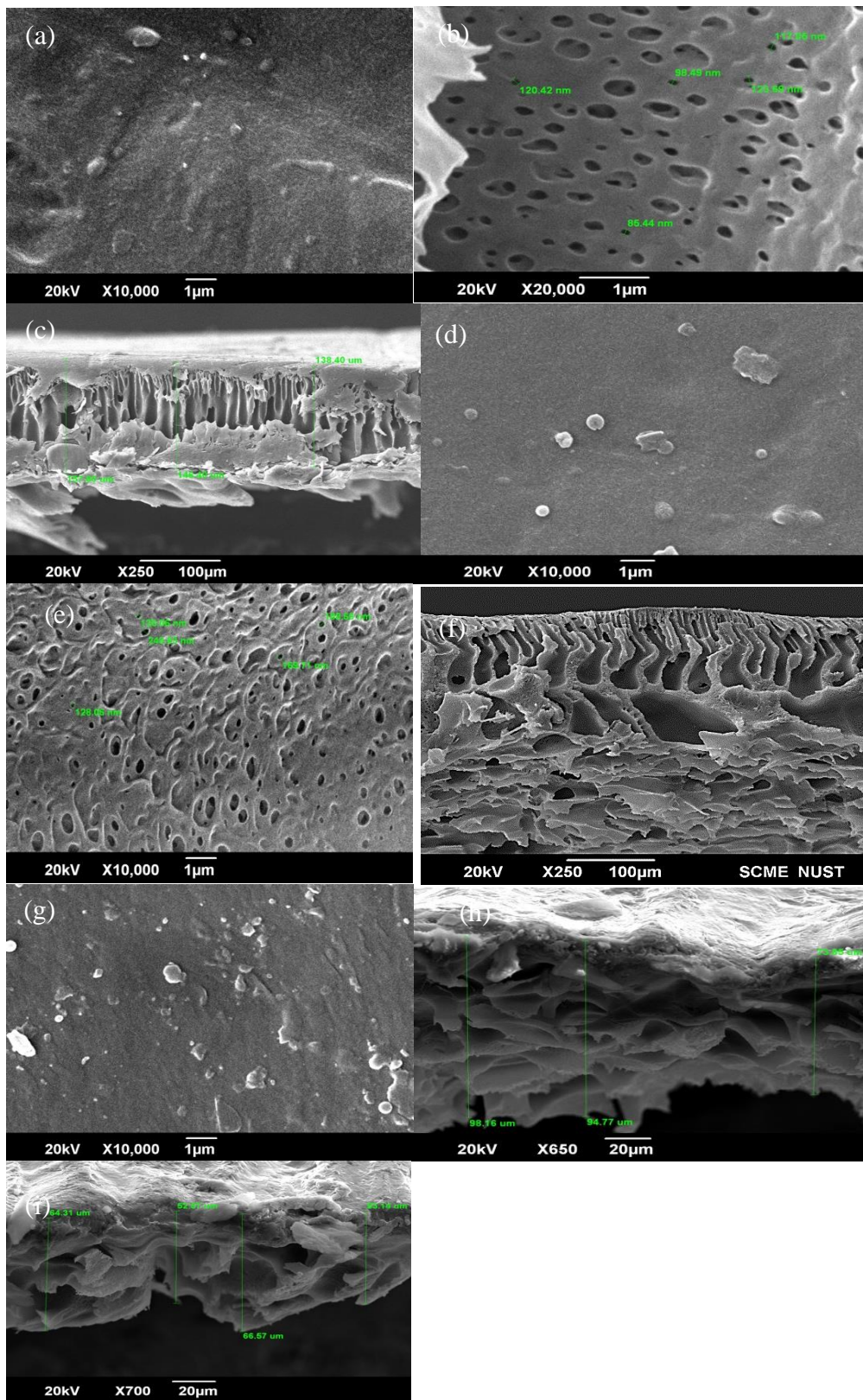


Figure 5. 2: In this figure (a), (b), (d), (e), (g) and (h) directs the topographic SEM image and (c), (f) and (i) shows the Cross-sectional SEM image

5.3 Hydrophobicity And Contact-Angle Measurement

The dip coating of the membrane causes it to become more hydrophilic due to emulsion[110]. The chitosan incorporating makes PES is on margin of being from hydrophobic to hydrophilic but after emerging the membrane and treatment with the Polycaprolactone as it is marginally hydrophilic because it contains polar groups but has only moderate hydrogen bonding and is not hydroxylic[111–113]. The chemical structure of polycaprolactone is polar because of the ester group so hence it is hydrophilic in nature[111]. The contact angle is measured of the PES/chitosan membrane that are coated. The results are shown that contact angle dropped from 81.435° to 66.038° given in the following Figure 5.2

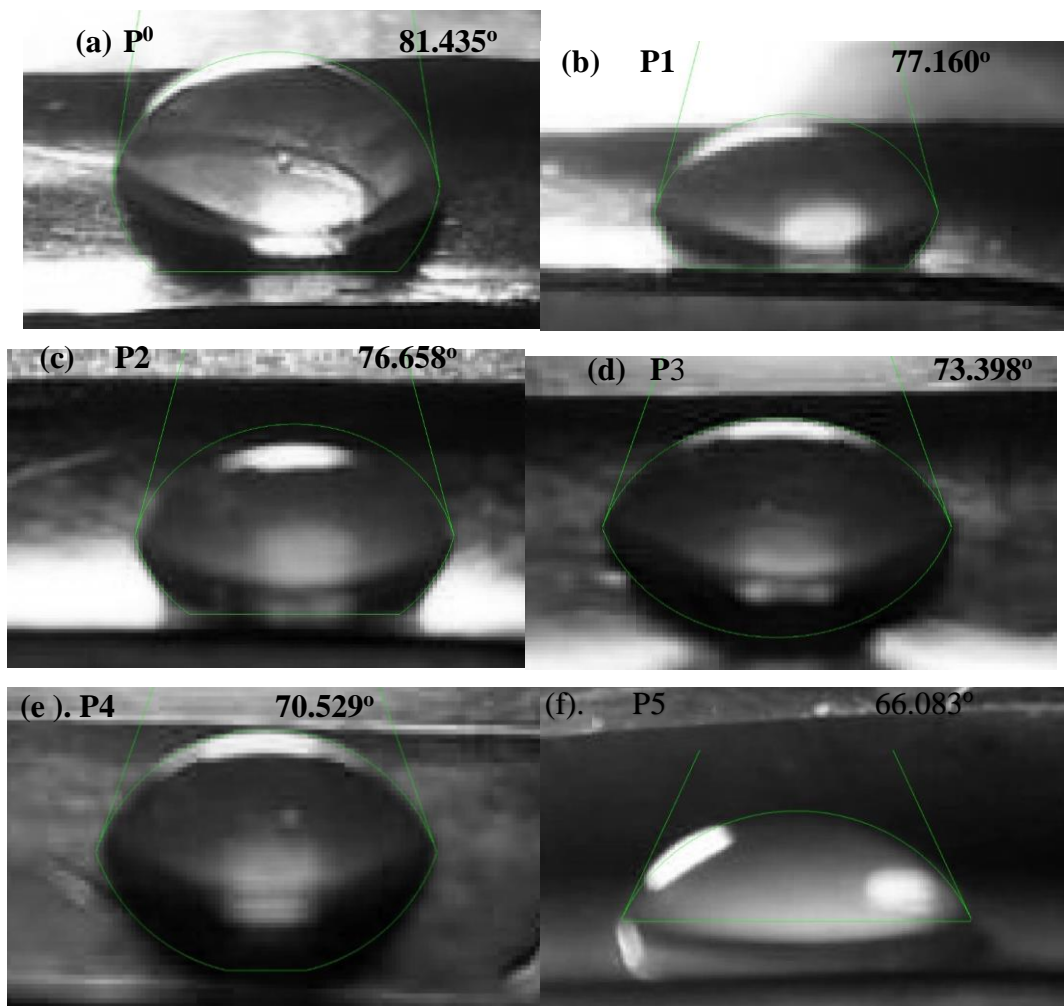


Figure 5. 3: This image depicts the evaluation on contact angle through goniometer and calculated according to angle for either increase in hydrophobicity or hydrophilicity

Table 5. 1: The table given the values of contact angles against the membrane with ascending coating

Membranes with emulsion coating	Average Contact angle $\theta(\pm)$
P0	81.43
P1	77.16
P2	76.658
P3	73.398
P4	70.529
P5	66.083

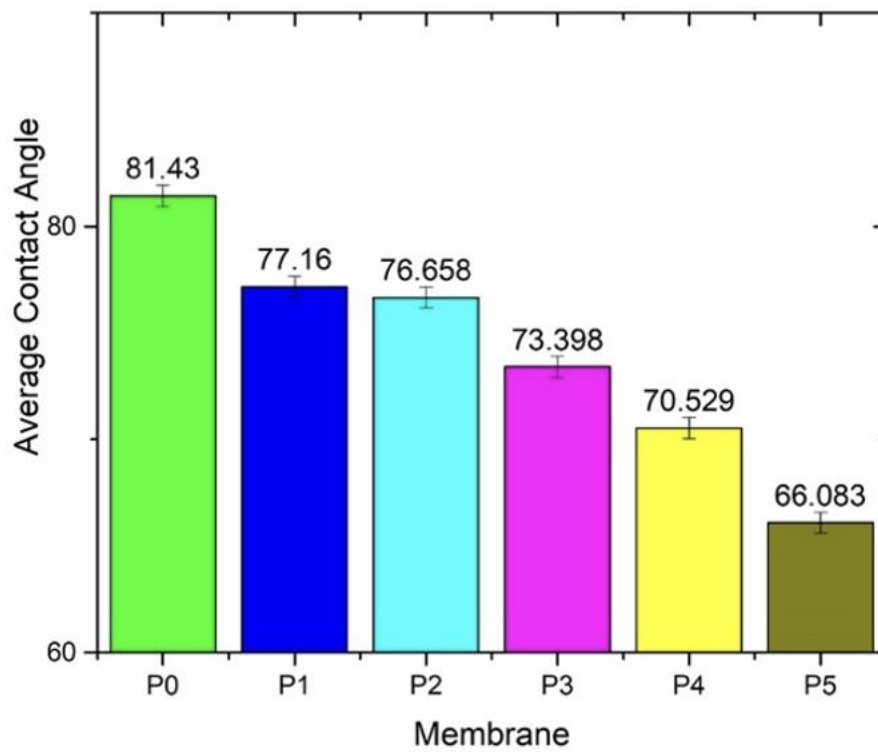


Figure 5. 4: It shows the percentage of contact angles of membranes on average with regarding the no. of attempt as well the no. of membranes i-e moving from hydrophobicity to hydrophilicity

7.3.1 Surface Energy

It is obvious that the contact angle value decreases with the number of increases in the bilayer from P1 To P5 that is because of the increase in average roughness of membranes and hence the surface energy is also increased[114, 115]. The surface energy determines the hydrophilic character as well as the friction forces with water in contact[116].

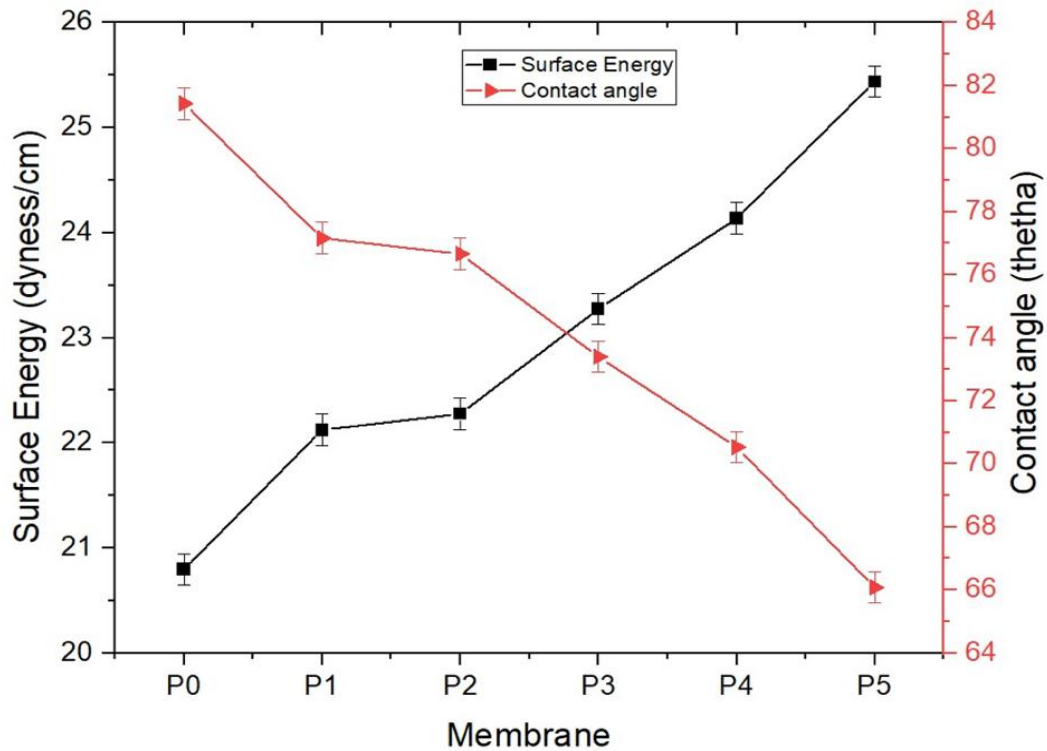


Figure 5. 5: The contact angle value and the correlated surface energy value

5.4 Surface Wet-Ability Testing

The hydrophobic nature of PES so, the percentage for water retention was lowest in Pes but when with additive it enhances it hydrophilic nature and becomes on margin to water retention to water acceptance[117]. The dip-coating process with with Polycaprolactone (PCL) was dissolved in dichloromethane (DCM) and it is polar in nature and has ether bond in it so, the surface becomes hydrophilic[112, 113]. As the coating of bi-layer increases from

PO to P5, with no coating to 1, 3, 5, 7, 10 bilayers respectively. The water uptake percentage also increases as shown in Figure the surface wettability test.

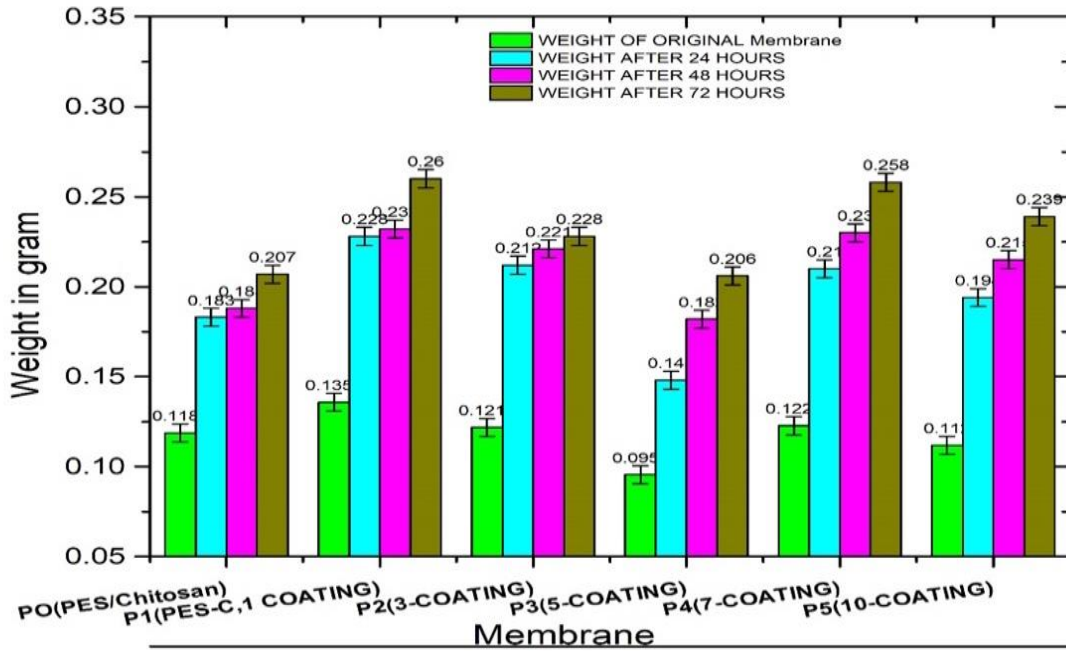


Figure 5. 6: It shows the water uptake ratio against membranes

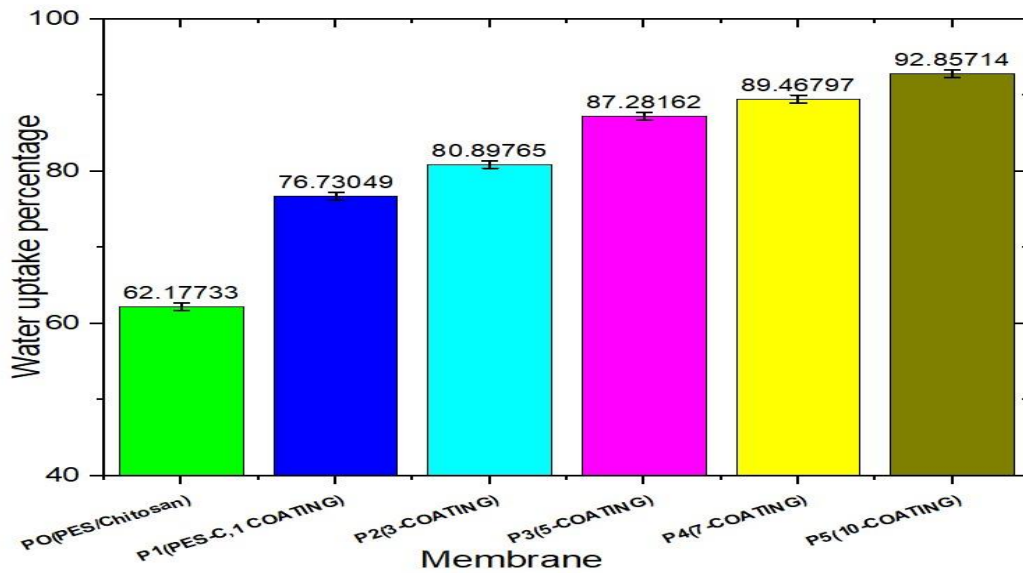


Figure 5. 7: The figure shows the water uptake percentage of averaged out values of membranes' surface wettability

5.5 Mechanical Examination

Membranes serve a variety of functions. Membranes with a high mechanical strength have been considered necessary in the synthesising of multifunctional membranes (Singh K, 2014). Membranes with a high polymer concentration have fewer void space and flaws in their structure, resulting in fewer cracking sites[118] .The mechanical tensile strength graph are shown in Figure

Because chitosan is soluble in water, P membranes demonstrated greater strength. By enhancing macro void creation during immersion and weakening the mechanical characteristics of the membranes, water-soluble fillers have the potential to reduce mechanical characteristics.[119] Materials with a higher water solubility dissolve in water. As a result, voids appear where the material previously existed. The crack subsequently spreads to these new regions, resulting in membrane tear[118]

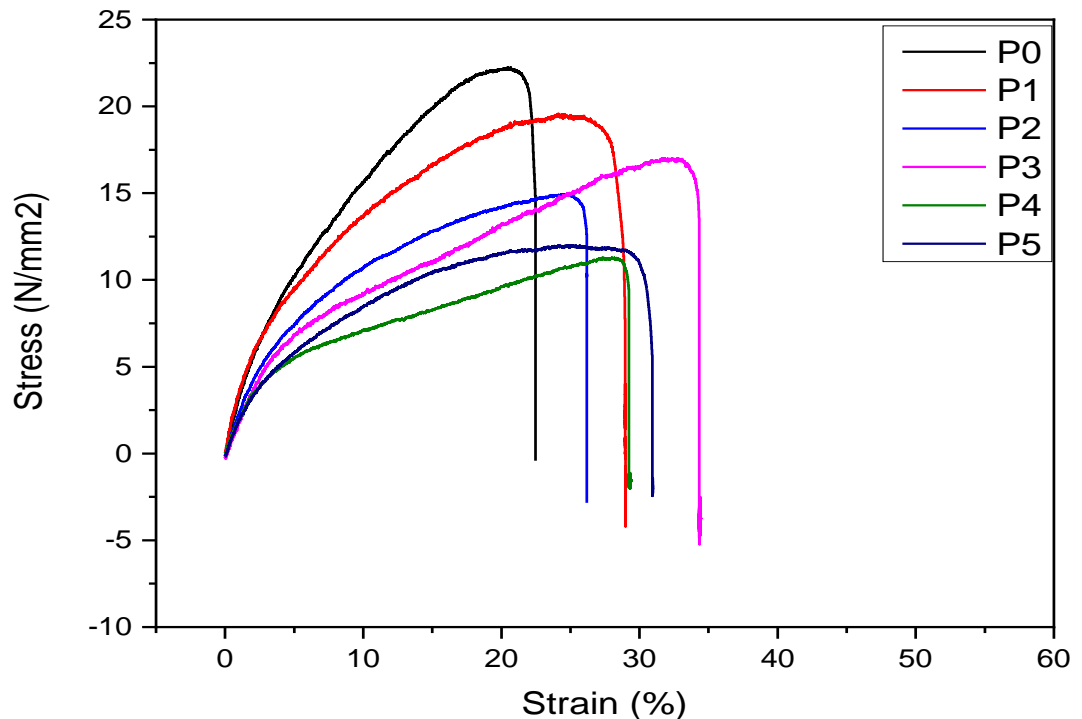


Figure 5. 8: depicts the tensile strength of membranes

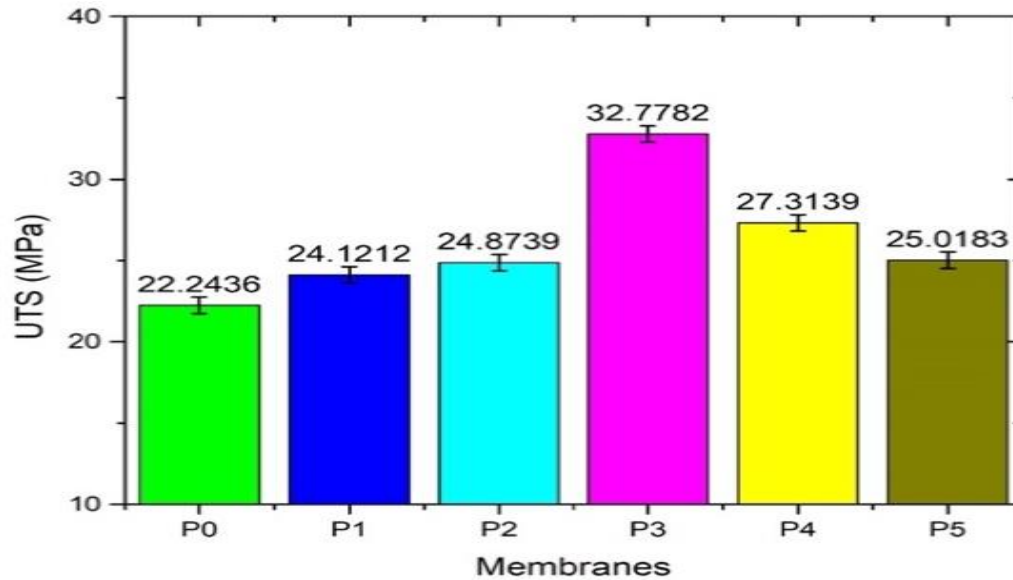


Figure 5. 9: Shows the ultimate tensile strength against the(Mpa) against membranes

5.6 Optical Profilometry

Table summarizes surface roughness is among the manufactured layers' many properties. The surface roughness for manufactured membrane samples has been examined utilizing optical profilometry as well as the findings are shown in Table. Membrane surface roughness is a highly effective characteristic in terms of fouling variables. Because of the presence has less surface roughness, which improves the surface coverage of the PES membrane.[120] The integration of activated emulsion by coating into in the PES/chitosan membrane leads to a rise in surface roughness in following membranes[121, 122]. These findings could be attributed to the meso and micro - structural coated and base material, which contribute to enhanced membrane porosity. As a result, the roughness of the PES membrane zone As the % of layer by layer PCL emulsion increases, the roughness of a PES membrane region increases. A "nodular" topology as well as interrelated cavity channels were discovered for integrated PES membrane.

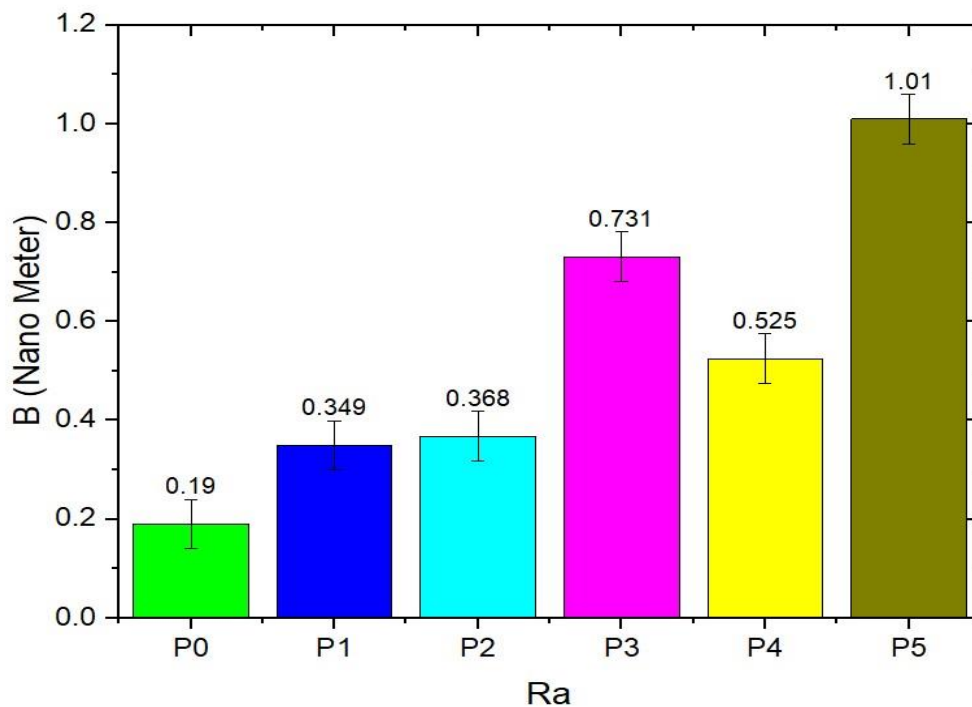


Figure 5. 10: Shows the optical profile of membranes (average roughness)

5.7 Antibacterial Assay

Two sample strains, *Escherichia coli* and *S. aureus*, were employed inside an agar culture diffusion experiment to assess the antibacterial activity of optimised membrane and drug-loaded membranes with varied bi-layer coatings [41]. Using cefotaxime a pharmaceutical drug used as an antibiotic, serving as just a control sample and a polymer based drug serving as a negative control. The pronounced zone of inhibition was seen against both bacterial strains. For the polymeric blank membrane used as a negative control against *E. coli* and *S. aureus*, there was no zone of inhibition in either plate [123].

Drug sustained release from the hydrophobic polymeric membrane was linked to antibacterial activity [34]. The high beta-lactams durability of cefotaxime that prevents bacterial growth was found to become the mechanism of antibacterial action. Compared to other strains P5 showed larger zone of inhibition against [124]

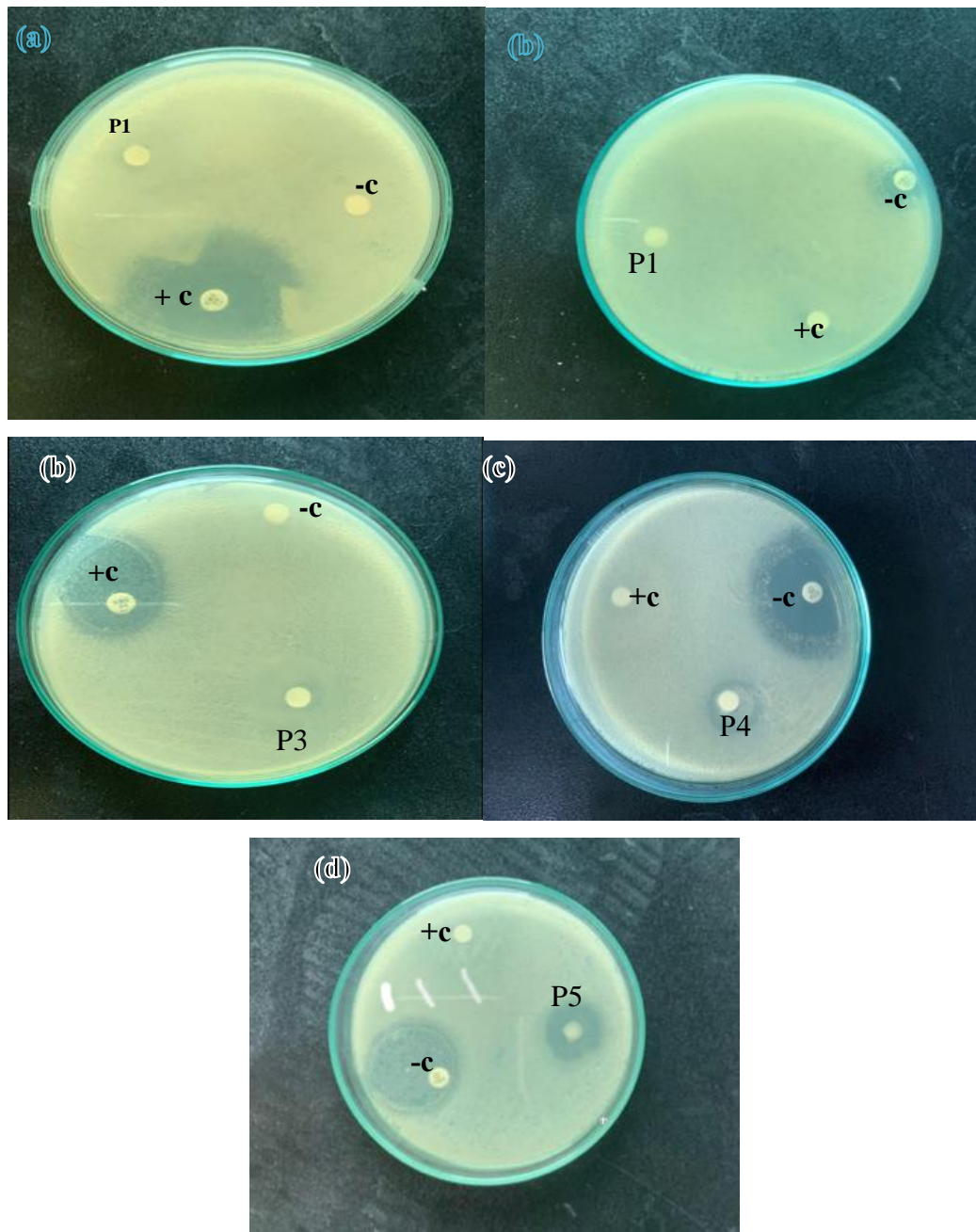


Figure 5. 11: The image depicts the antibacterial activity (resistiveness) of pes/Chitosan dip-coated in emulsion membranes (a)po (b) p1 (c) p2 (d) p3 (e) p4 (f) p5 having null coating, 1-bilayer, 3- bilayer, 5-bilayer, 7-bilayer & 10- bilayer respectively towards the Gram negative bacteria E.coli

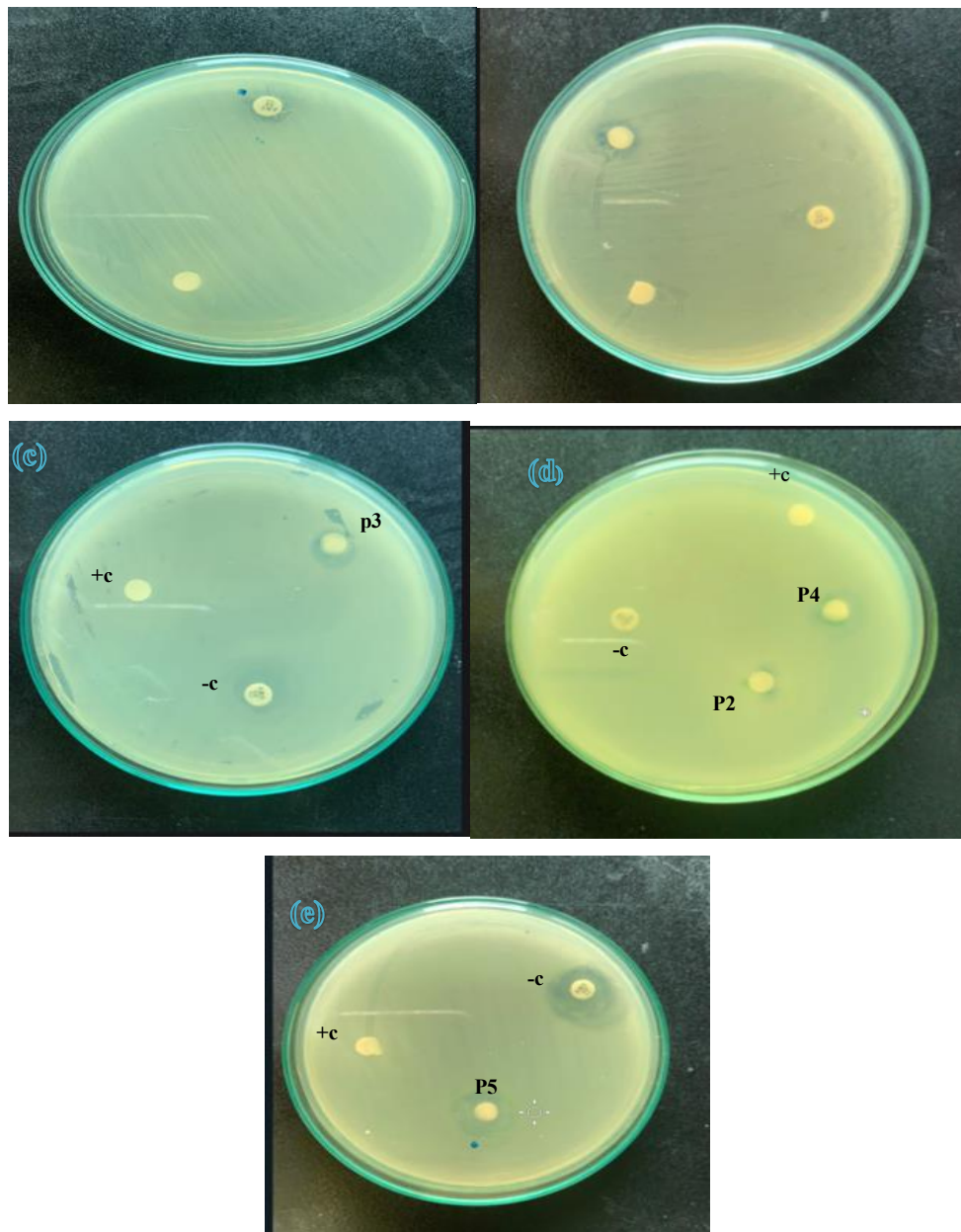


Figure 5. 12: The image depicts the antibacterial activity (resistiveness) of pes/Chitosan dip-coated in emulsion membranes (a)po (b) p1 (c) p2 (d) p3 (e) p4 (f) p5 having null coating, 1-bilayer, 3- bilayer, 5-bilayer, 7-bilayer & 10- bilayer respectively towards the Gram-positive bacteria *S. aureus*

Figures show the results of the examination of the manufactured membranes for bacterial resistance to *S. aureus* and *E. coil*. Figure 14 shows the antimicrobial "halo" that was created by measuring the normalized width, the diameter of the disc, as well as the diameter of a inhibitory zone. Figure depicts the results of incubation for 24 hours at 37 °C. Because of the

existence of drug-based emulsion in the prepared samples, the fabricated membranes exhibit bacterial receptivity. Higher concentrations of emulsion coating as layer-by-layer on the membrane were found to have a more pronounced antibacterial effect. As moving towards 1 bilayer coating to 10 bilayer coating. The results showed that the Polycaprolactone (PCL) was dissolved in dichloromethane (DCM) incorporated PES membranes had a better zone of inhibition, making them well-suited for water treatment filtration[125].The membranes fabricated in the research for water for anti-fouling, which causes pores to clog and renders the membranes not good for filtration purposes. Prepared PES membranes with Polycaprolactone (PCL) can be utilized as significantly work as antifouling. Anti - microbial effectiveness of the primed PES uf membrane can therefore be used for antifouling and enhanced flux.[106]

The outcomes of the agar disc diffusion test clearly show that pristine membrane has no antibacterial activity. The membranes, Membrane PES-Chitosan Coated with drug-based emulsion on the other hand, showed increasing antibacterial activity against *S. aureus* and *E. coli*.

5.8 Zone Of Inhibition

Pure drug antibacterial activity was higher than any of the empty or coated membrane that have maximum zone of inhibition for gram positive and gram negative bacteria strains[126]

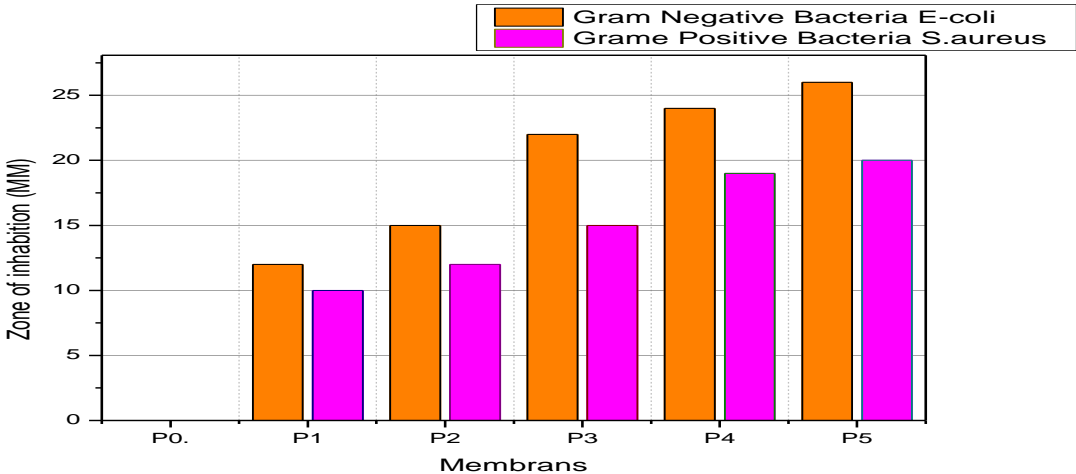


Figure 5. 13: depicts the zone of inhibition of membranes used in both gram positive and gram negative bacteria

7.8.1 Analysis of Antimicrobial Results

The antibacterial halo was calculated with respect to the zone of inhibition and demonstrated in the following figure

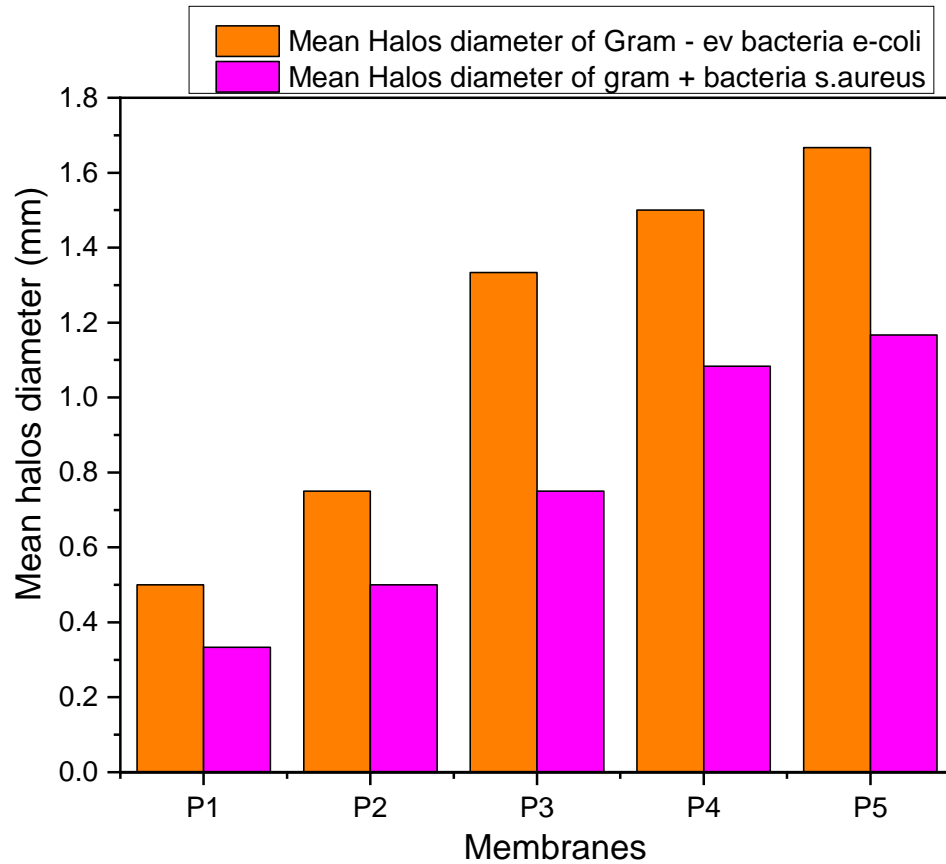


Figure 5. 14: Depicts measurement of halo inhibition

7.8.2 Water flux and BSA flux

The water flux of the Pes chitosan is high as compared with that of PES membrane without any additive incorporated. When this PCH is coated with the PCL incorporated with the PVA and cefotaxime as a antifouling agent, the water flux becomes relatively high due to the strong linkage between the PCL and PVA through covalent bond[103, 127]. PVA has water soluble characteristic. So, as the pressure increases the flux also increases over time. This can be explained by the membranes' increased hydrophilicity due to the presence of chitosan. During the phase inversion process, chitosan also served as a pore forming agent. The higher flux was caused by the increased chitosan content in the PCH blend membrane. This decline in

flux is due to the Polymeric membrane matrix mechanical deformation. Pure water fluxes would be severely reduced during membrane compaction for membranes with hydrophilic additives, which could be due not only to the immiscibility of the additive and membrane material, but also to the presence of a large number of macro voids in the sublayer. It confirms that the introduced hydrophilic chitosan played a significant role in improving the antifouling property of the polysulfone membrane. A more hydrophilic surface resulted from increased hydrogen bonding between water molecules and the membrane surface. As a result, the binding interaction of BSA protein molecules with the membrane surface was reduced.

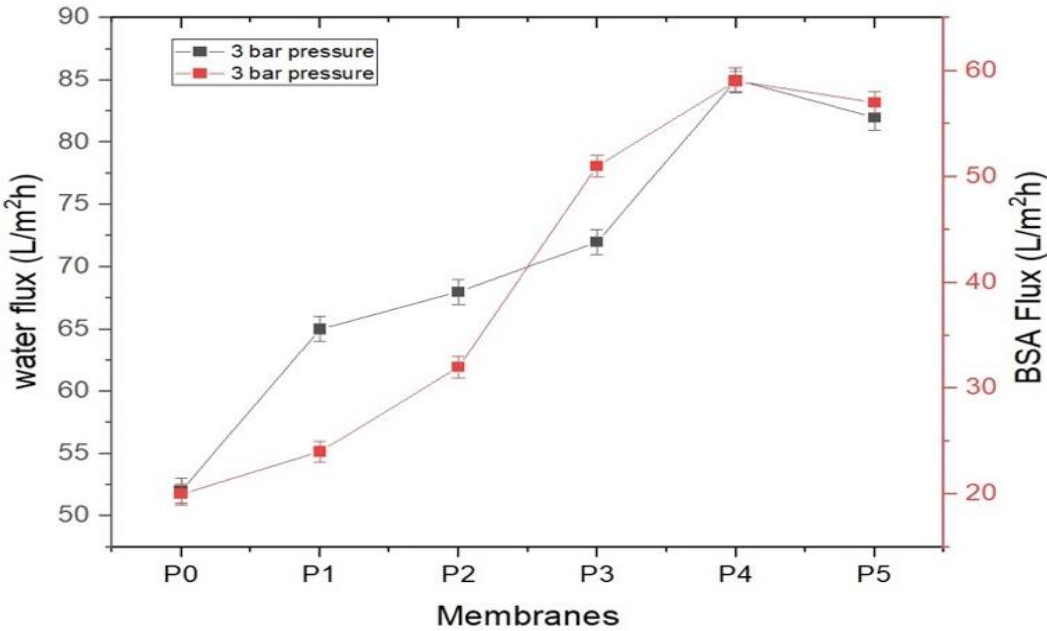


Figure 5. 15: shows the water and BSA flux of membranes

All of the BSA analyses show an increase in permeability recovery caused by the magnetic field on the process after physical and chemical cleaning procedures, especially when the solution was subjected to magnetic induction prior to permeation. These findings are very promising because the improvements in flux recovery would allow for the use of less cleaning solution and a reduction in manufacturing time.

Table 5. 2: Summary of properties for fabricated membranes

Properties	P^o	P1	P2	P3	P4	P5
Water retention (%)	62.18	76.73	80.90	87.28	89.47	92.86
Contact Angle (θ)	81.43	87.16	76.65	73.39	70.52	66.08
Surface Roughness (nm)	0.19	0.349	0.368	0.731	0.525	1.01
Ultimate Tensile Strength (MPa)	22.2436	24.1212	24.8739	32.7782	27.3139	25.0183

Conclusion

The method of phase inversion used to create polymer CNT/chitosan nanocomposite membranes. On the PES, the additives were Chitosan. PES functional groups are confirmed by ATR-FTIR results. The contact angle result also shows that the CNT/chitosan composite membrane has higher hydrophilic properties, as the contact angle and water uptake abilities improved dramatically after the addition of the drug-based emulsion dip-coating. The mechanical strength of a membrane containing chitosan, PCL Polycaprolactone, and cefotaxime, which is water soluble, decreases, causing the formation of micro spaces and a decrease in mechanical strength. The anti-fouling property improves as the layer by layer coating increases from 1-3-5-7-10, respectively, but membranes exhibit higher antifouling with gram-negative bacteria such as E.coli than with gram-positive bacteria such as S.aureus. These results show that CNT/chitosan composites dip-coated with PCL have a significant remarkable potential for water desalination and should be investigated further.

Recommendations

Based on the research provided, it is recommended to use this innovative composite coated with emulsion containing drug to create a membrane for antifouling and dye removal from water. Further modification through surface modification in the membrane construction recommended to achieve distillation for additional salts. The membrane's anti-fouling property is good, but to make it stand out in the long term, a variety of broad-spectrum drugs should be used to increase its applicability. The water flux is slow due to the thickness of the membrane and the layer-by-layer coating. Through SEM and various characterization techniques, the membrane demonstrates perfect layer by layer coating.

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