



# Engineering of Polymer Membranes Incorporated with High Performance Antifouling Functional groups

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## Certificate

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## *Dedication*

“We cannot help everyone but everyone can help someone”

*By Ronald Reagan*

In all we dedicate our efforts in this work to humanity.

## *Acknowledgements*

We owe our gratitude to all those people who have made this project work possible and because of whom our graduate experience has been one that we will cherish forever.

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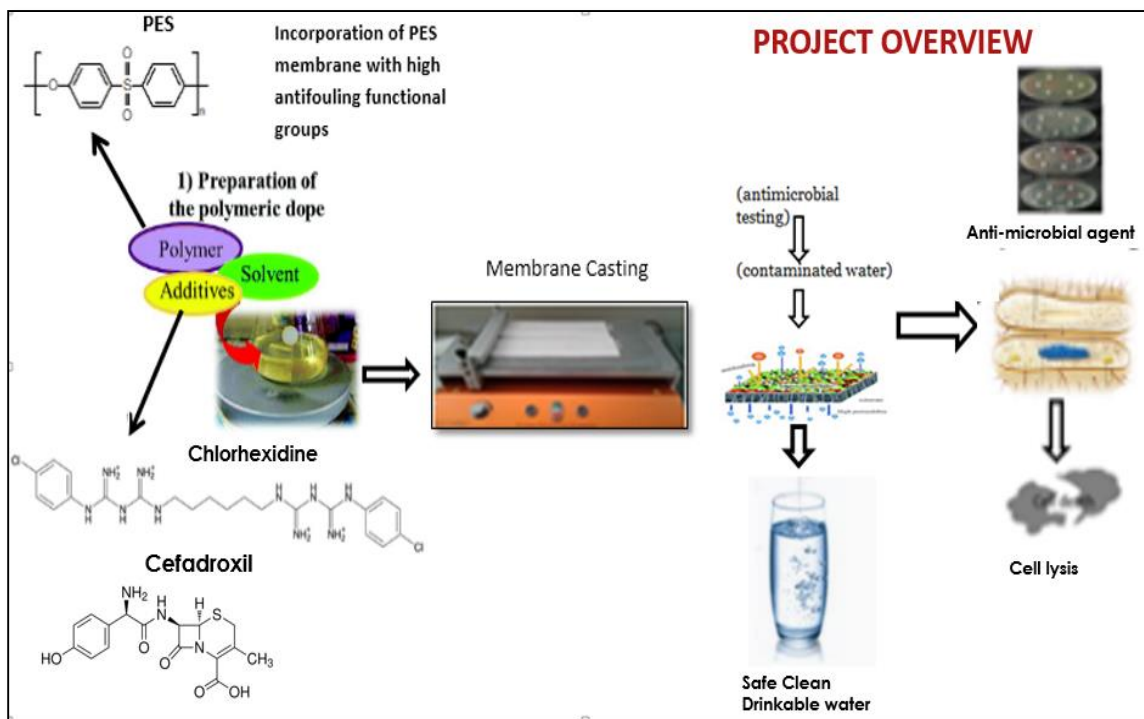
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# LIST OF ABBREVIATION

<i>E.coli</i>	<b>Escherichia coli</b>
<i>B.cereus</i>	Bacillus cereus
<i>S.typhi</i>	Salmonella typhi
<i>S.aureus</i>	Staphylococcus aureus
<i>A.fumigatus</i>	Aspergillus fumigatus
PES	Polyethersufone
WHO	World health organization
SEM	Scanning electron microscopy
EDS	Energy dispersive x ray spectroscopy
XRD	X ray diffraction
FTIR	Fourier transform infrared
Nm	Nanometer
C <sup>0</sup>	Celsius
ml	Milli litre
CHX	Chlorhexidine
CF	Cefadroxil

# Abstract:

A versatile approach towards enhanced energy efficient and long term utilization of Poly Ether Sulphone (PES) membranes has been developed. Bactericidal functional groups were incorporated to fabricate antifouling polymer membranes via phase inversion method. The effect of added antifouling groups on the morphology and performance of the newly fabricated membranes was investigated in terms of flux and fouling parameters. The resulting membranes were characterized by FTIR, Scanning Electron Microscopy (SEM), AFM, and Sessile drop method before further subjected to water permeation and antifouling tests. The water contact angle measurement confirmed the increased hydrophilicity of the modified membranes and pore density increases with an increase in antiseptic loading. The pore size however decreased as observed by SEM. In addition, it has been observed that the antifouling property has been increased up to seventy five percent.





# Chapter 1

## INTRODUCTION

Since late eighteenth century, polymer filtration membranes have been a center of focus of research and became a prosperous industry in twentieth century. In commercial applications today, usage of membrane technology spans over water purification to gas separation, with a market that is growing remarkably due its promising advantages such as low operating costs, high permeability and ambient temperature operation.[1] In todays' world however, two of the greatest challenges for associated industry, involves providing sustainable supplies of clean water and energy efficient systems at affordable cost. Membranes are employed in this process for making the overall system energy efficient. One of the major drawbacks of membrane is the fouling problem that leads to flux decline as well as induces unfavorable effect to its efficiency and economic feasibility leading towards reduction in membrane life time. Nevertheless there is a need of improved membranes, with higher feed flux and most important of all, such membranes are required which are less prone to various types of fouling and are more resistant to bacterial growth. It has been well reported that fouling of membrane is majorly caused by deposition and adsorption of biomolecules (bacteria) to the membrane surface and internal pores.[2]

Polyethersulphone (PES), a thermoplastic polymer has been in extensive use for manufacturing asymmetric membranes due to its reliable mechanical and thermal resistances.[3] Nonetheless membranes made of such polymer fouls, because of its considerably low hydrophilic character. Over the past few years various researchers have investigated different modification methods such as coating, incorporation of nanoparticles or modification by small organic antimicrobial agents in order to enhance its hydrophilicity. Among the available methods, blending of nanoparticles has attracted a great deal of attention, however the leach out of these particles during filtration process is the issue to be resolved. Considering such issues, in this process the antifouling

functional groups of adequate size are blended with Polyethersulphone in order to enhance the antifouling properties of membrane which will result in its comparatively long term utilization.

This report aims to describe the novel processes of addition of antifouling functional groups to make polymeric membrane less susceptible to bacterial growth (making them effective in terms of antifouling), considering the work already being done for this purpose. This report describes the materials and morphologies commonly found in today's commercial polymeric membrane. Based on retentate size, membranes, such as micro filtration and ultrafiltration, are introduced. Water retention test, antibacterial tests, antifungal tests, mechanical tests are introduced for membrane performance comparisons. In this report membrane fouling is discussed as chief obstacle to the more energy efficient utilization of membranes in water treatment. Mechanism of membrane fouling is described along with approaches commonly used to limit fouling including incorporation of antimicrobial nanoparticles, salts as biocide and modification by small organic antimicrobial agents.

In the present work the influence of antibacterial additives on performance and antifouling properties of membranes have been investigated. The membrane structure and properties were characterized using AFM, SEM, FTIR and water contact angle measurements. Fouling resistance of the newly synthesized membranes was also studied.

# Chapter 2

## LITERATURE REVIEW

**This short review of literature aims to elaborate membrane technology and the challenges associated with this, this review of literature assisted us to better identify the problem and to look for actual challenges that needs to be resolved.**

### 2.1 MEMBRANE FILTRATION

#### *2.1.1 MEMBRANE:*

A semi permeable thin sheet, capable of sorting out substances as a result of driving force applied across it. It offers a physical barrier which effectively removes unwanted substance i.e. bacteria and salts etc.

Membrane filtration is widely recognized technology for water treatment. Growing environmental concerns and increasing global plea for clean water make membrane filtration a choice for various industries. Membranes are used to remove suspended and dissolves constituents from water. The cost of membrane based system is significantly reduced by modern advancement in membrane technology i.e. production and design. These systems do not require large space as conventional system therefore the installation cost is lower. Operating costs are less because Current membranes are highly efficient produces more water using reduced energy.[4]

#### *2.1.2 TYPES OF MEMBRANE PROCESS*

There are four widely recognized membrane processes

1. Micro-filtration
2. Ultra-filtration
3. Nano-filtration
4. Reverse osmosis

***MICROFILTRATION:***

Microfiltration defined as the membrane filtration processes that use membrane having pore size ranging from 0.1 to 1 micron. Operating pressure of feed water is low approximately 15-16 psi.

Materials separated by microfiltration include algae, sand, cysts and certain bacterial species. It does not effectively block organic matter and viruses.

***ULTRAFILTRATION:***

Ultrafiltration membranes have pore size ranging from 0.001- 0.1 microns. Operating pressure is 30-100 psi. These membranes separate all bacterial species separated by microfiltration and some viruses.

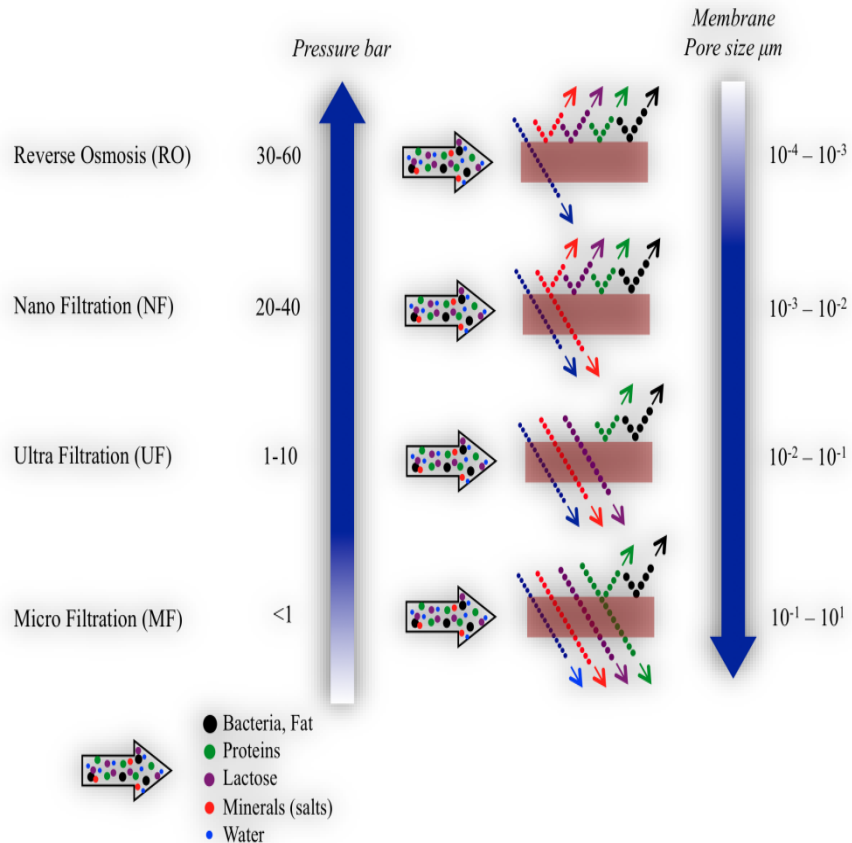
***NANO FILTRATION:***

These membranes have pore size of 0.0001-0.001 microns and operating pressure is 90-150 psi. Nano filtration membranes remove all viruses, bacteria, cysts and sand etc. these membrane demand more energy when compared with micro and ultra-filtration membranes. Nano filtration membranes remove hardness from feed water therefore called softening membranes.

***REVERSE OSMOSIS MEMBRANE:***

RO membranes effectively separate all inorganic impurities from water. Other materials effectively removed by such membrane includes bacteria, organic substances, viruses, cysts etc. capital and operating expenditures are high and high level pretreatment is needed for some cases.[5]





**Figure 2.1 Membrane Process Characteristics**

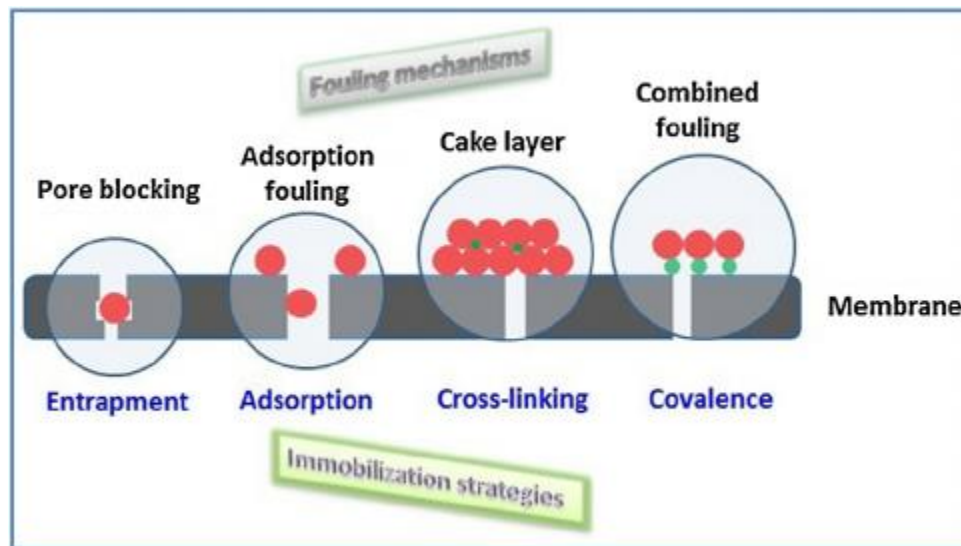
## 2.2 FOULING: A MAJOR CHALLENGE IN MEMBRANE FILTRATION

A major problem to the extensive employment of membranes technology for water cleansing is fouling. It is defined as accumulation of colloidal or particulate substance in the pores of a membrane or on its surface that alter the membrane transport characteristics. When water containing substances i.e. microbes, particulates, macromolecules and colloids is passed through membrane these substances deposit in membrane's pores and on top of its surface result in the creation of cake layer that significantly reduces water flux and leads to variation in membrane rejection characteristic. Fouling leads to continuous flux decline Therefore significantly increase membrane operating cost due to required intermittent cleaning and membrane

replacement after certain time interval. The cost also increases due to increased energy demand for attaining higher flux.[6]

### **2.2.1 FORMS OF FOULING:**

Fouling can take various forms that include adsorption, deposition cake/gel layer formation and pore blockage.



**Figure2.2 Forms of Fouling**

### **ADSORPTION:**

It takes place when particular interaction between membrane and particles occur. It happens due to surface energy and phenomena of thermodynamic equilibrium. There are mainly three types of interactions chemical bonding, weak bonding due to Vander walls forces and electrostatic attraction. The type of functional group present determines the type of interaction. Monolayer of particles and other substances can form and offer additional hydraulic resistance to water flow through membrane. This layer can form even in absence of flux. This is most common problem and is generally irreversible. Hydrophobicity of some materials presents in feed water increase their affinity toward the surface of membrane and allows them to precipitate during surface interaction. Membranes fouled by this mechanism cannot be refurbished without chemical cleaning

due to the fact that desorption is thermodynamically unfavorable. The adsorbed substances on surface of membrane modify its surface properties i.e. hydrophobicity, charge. Thermodynamic aspect of adsorption differentiates it from other kinds of deposition that occur due to body forces exerted on particle and thermodynamic equilibrium does not take place. Monolayer adsorbed material is more strongly bonded to surface of membrane than multilayer deposit. Concentration polarization aggravates the degree of adsorption if amount of adsorption is reliant on concentration.

***PORE BLOCKAGE:***

It results from entrainment of particles into pores of membrane. Entrained particles are difficult to remove and cause pore closure that leads to flux decline. Pore blockage occurs very speedily in the early phase of filtration when the membrane surface is nude and direct interaction between the particle and pore of membrane is possible. Pore blockage leads to enhanced local flux through open pores.

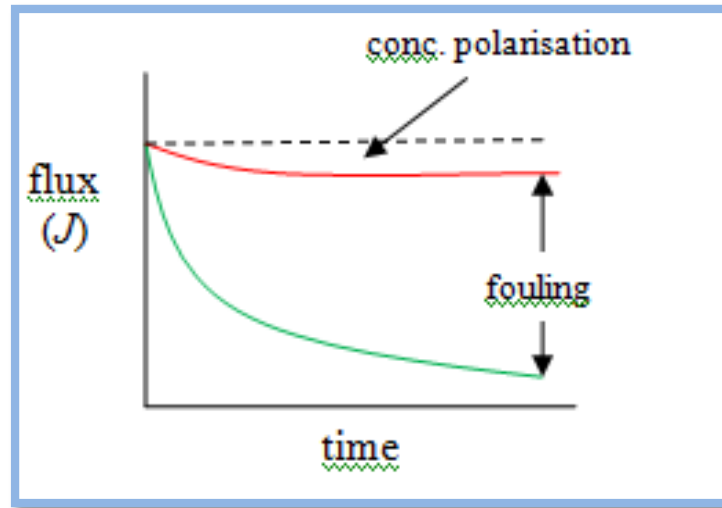
***DEPOSITION/CAKE FORMATION:***

The process in which particle collect layer by layer on surface of membrane and provide added hydraulic resistance to water flow through membrane is called cake formation and additional resistance offered is called cake resistance. Various kinds of solute i.e. active or inert colloids are present in the cake layer. Single cake layer buildups on membrane surface inhibit direct interaction between further fouling substance and membrane surface despite of the fact that the further foulants are active one. The primary cake layer act as pre filter and remove the substances having high fouling potential. If active foulant first reach membrane surface and form cake layer and inter particle deposit on the layer subsequently. This form more adhesive layer and leads to irreversible fouling. The morphology of cake layer decrees flux decline and contact among the membrane surface and deposited layer decide reversibility of fouling.

***GEL FORMATION:***

The process by which consolidation of extremely concentrated molecules occur near the membrane surface as a result of concentration polarization is called gel formation.

When the attractive force dominates the electrostatic repulsive forces the transition from concentration polarization to fouling occurs.



**Figure 2.3 Effect of Fouling and Concentration Polarization on Flux**

In actual practice feed water contains various materials during filtration; therefore, fouling comprises more than one form working at the same time. Membrane characteristics, operating parameters, and feed stream properties dictate the relative importance of various fouling mechanisms. [7]

### **2.2.2 TYPES OF FOULING:**

Depending on the attachment strength of deposited material, fouling is classified into reversible and irreversible fouling.

#### **2.2.2.1 REVERSIBLE FOULING:**

Fouling that can be removed through a robust force is called reversible fouling. It can be further divided into back washable and non-back washable fouling.

#### **BACK WASHABLE FOULING:**

It can be handled by reversing the direction of water flow through the pores of the membrane in between filtration cycles.

***NON-BACK WASHABLE FOULING:***

It cannot be controlled through hydraulic backwashing at cessation of every filtration cycle. It can be detached by chemical cleaning.

***IREVERSIBLE FOULING:***

Materials deposited on the surface of membrane that cannot be removed by back pulsing, chemical cleaning, back flushing, crossflow leads to irremediable fouling and result in permanent flux reduction.[8]

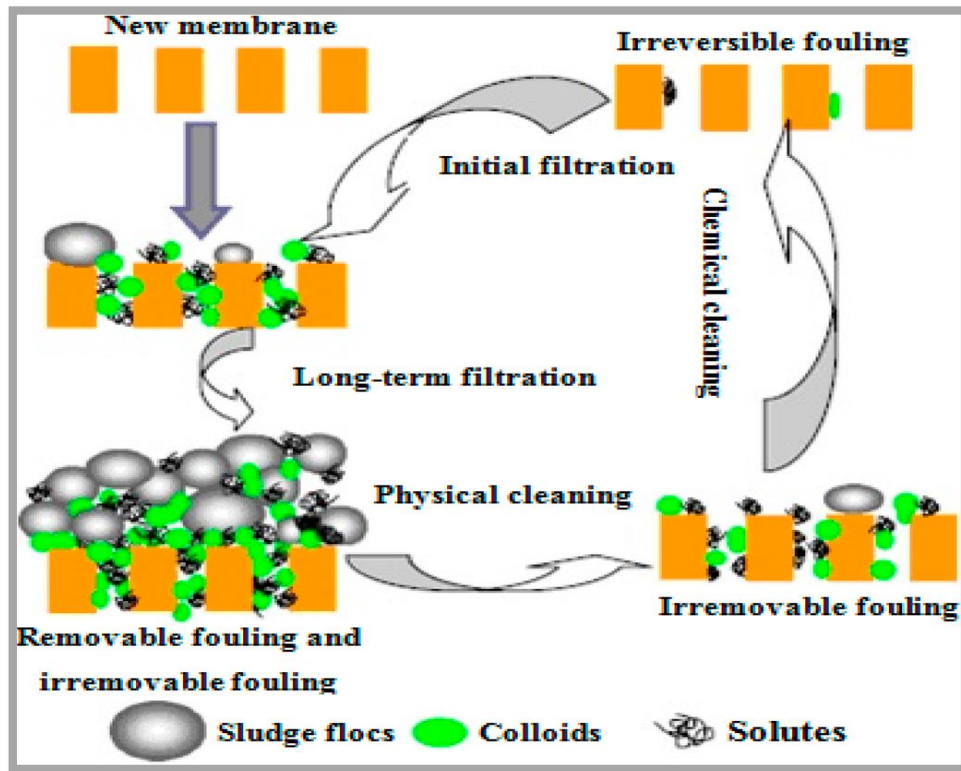
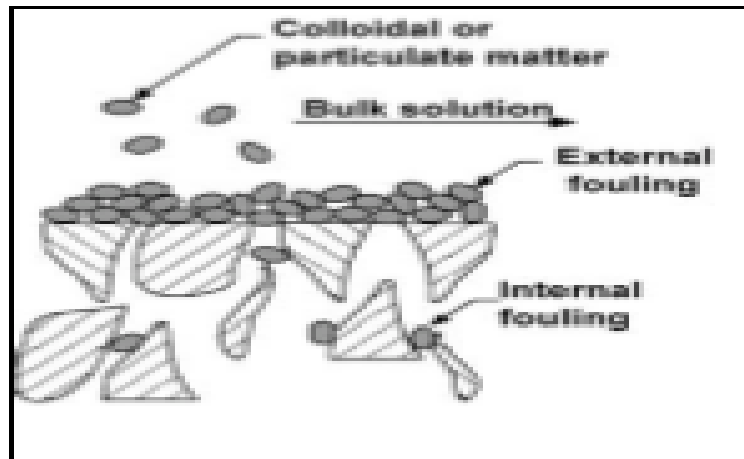


Figure2.4 Types of Fouling

***2.2.3 FOULING IN POROUS MEMBRANES:***

Pore flow membranes undergo two type of fouling:



**Figure 2.5 Fouling In Porous Membrane**

***Surface fouling:***

Adsorption of molecule onto membrane surface leads to surface fouling. Reverse osmosis nonporous membranes experience only surface fouling.

***Internal fouling:***

Internal fouling is caused by molecule entrapment in the pores of membrane. Entrapped particles are very difficult to remove therefore internal fouling is irreversible.[6]

***2.2.4 FACTORS AFFECTING FOULING:***

Fouling is an intricate phenomenon that occurs because of interaction between solute and membrane. Fouling is swayed by three aspects

***MEMBRANE CHARACTERISTICS:***

Fouling is affected by the membrane properties that include charge, hydrophilicity and surface topography. It is also dependent on pore structure of membrane. It is usually seen that membranes that have hydrophilic surfaces are not as much prone towards fouling than membranes having hydrophobic surfaces. Charge on membrane surface is important for processing charged species. Generally microorganism, particles and macro molecule are charged therefore to reduce fouling we have to minimize electrostatic attraction. Relative size of pore and solute is very crucial. Researchers found that membranes having larger pore have high initial flux than membranes with relatively small pore but

eventually flux decline with time.it is very essential to discern that pore blocking has more pronounced effect than pore narrowing on flux reduction.

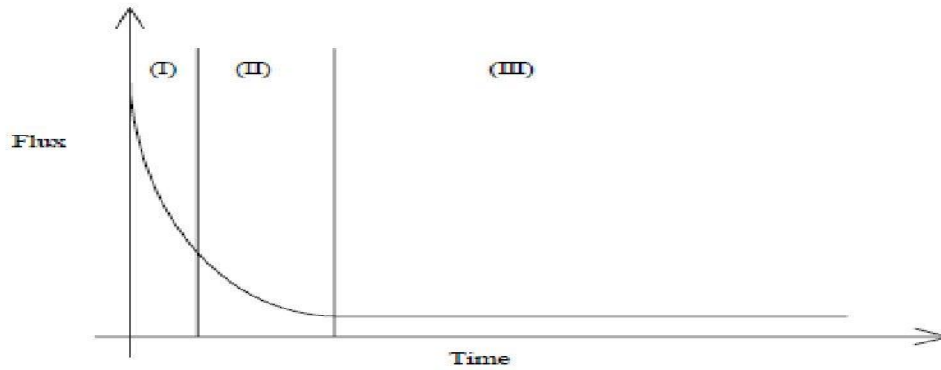
***FEED WATER PROPERTIES:***

The properties of substances present in water affecting fouling comprise of hydrophobicity, functional group content, charge on substances present in water and physical structure. As a result of above mentioned solute properties, some solution properties including PH, cation and salt content affect the degree and behavior of fouling .salts deposit on membrane surface due to reduced solubility or adsorb on it through charge interaction. Variation of PH affects the solubility of solute.

***OPERATING CONDITIONS:***

Operating conditions strongly influence the membrane fouling along with membrane and solute properties. Operating parameters including temperature, pressure and flow rate affect the fouling. Temperature variation enhances or suppresses fouling; this is due to the fact that temperature affects the solute solubility, viscosity and diffusivity. During ultrafiltration rise in temperature leads to low fouling.at high flow rate the deposited substances /particles tend to detach from membrane surface thud fouling is minimized.in ultrafiltration flux increases as a result of increase in transmembrane pressure but when concentration polarization reaches maximum point and gel layer has formed there is no more increase in flux.[9]

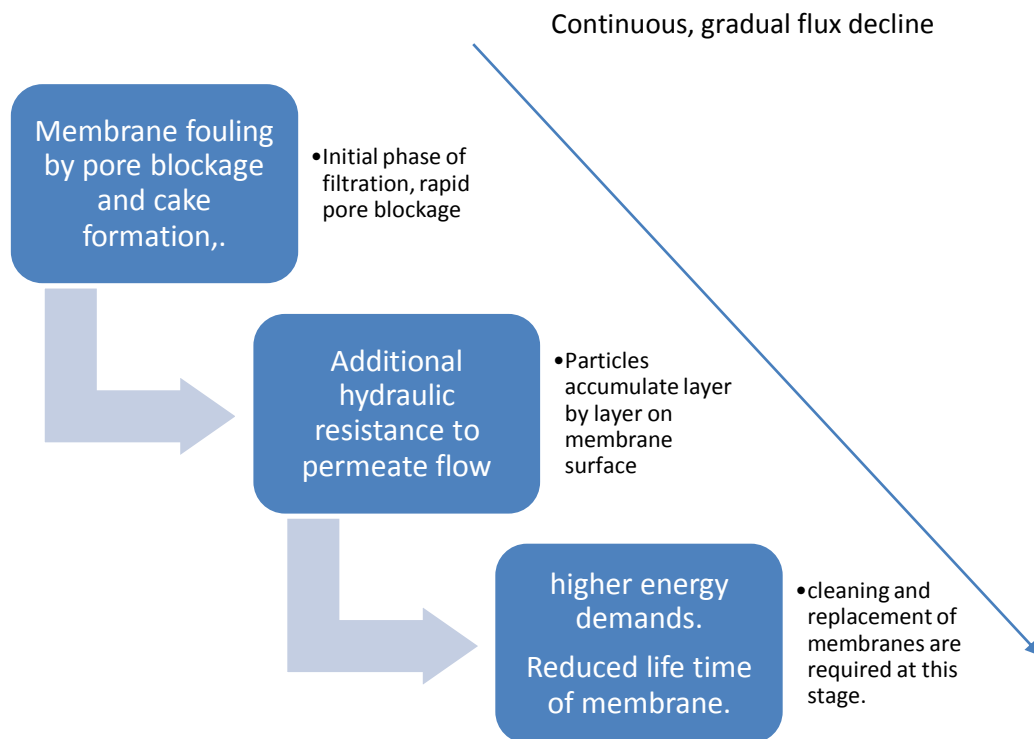
***2.2.4 MECHANISM OF FOULING:***



**Figure 2.6 A Schematic Presentation of the Three Stages in Flux Decline**

This is characteristic flux –time graph for ultrafiltration. The flux variation with time is divided into three distinctive stages:

1. Rapid initial drop of flux
2. Extended period of gradual flux decline
3. Steady state flux



**Figure 2.7 Effect of Fouling**



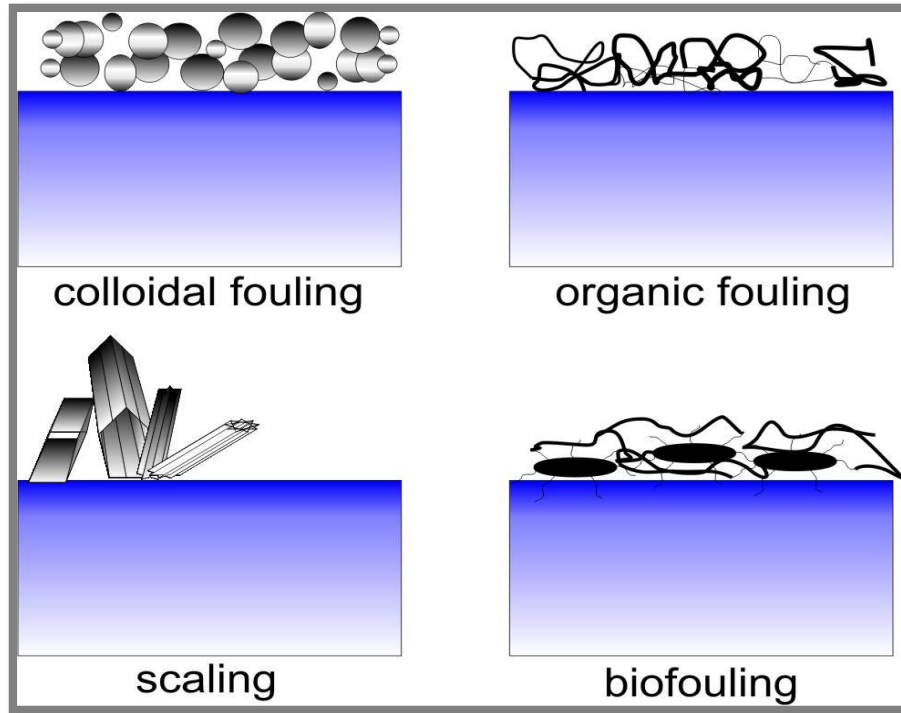
Membrane fouling by pore blockage and cake layer formation provides added hydraulic impedance to permeate flow that cause continuous flux decline. Membrane opposition is increased by pore blockage while an extra layer of resistance is provided by cake layer formation. These two processes i.e. pore blockage and cake layer creation is considered important fouling mechanism.

The first stage of flux decline is related to pore blockage. . Pore blockage occurs very rapidly in the early phase of filtration when the membrane surface is nude and direct interaction between the particle and pore of membrane is possible. At the start of filtration process membrane pores are clean and open hence leads to maximum flux in the beginning. As filtration proceed particles and colloids in the feed water interact with membrane pores and if relative size of particle is comparable to pore size it is retained in the pore and lead to pore blockage and reduced flux. When the colloid and pore have same size and shape than complete pore blockage occur otherwise it is mostly partial blockage. Pore blockage proceeds more rapidly than cake layer formation due to the fact that few particles and colloids are sufficient to cause complete pore blocking.

Second stage of flux reduction can be attributed to cake formation. Particles accumulate layer by layer on membrane surface and provide added hydraulic resistance to water flow through membrane. Cake layer formation proceeds slowly therefore the flux gradually decreases with time. Another reason of flux decline is that resistance of cake increases with time due to growth and formation of additional layers by further deposition of foulants.[8]

#### ***2.2.5 TYPES OF FOULING BASED ON FOULANTS:***

Fouling can be divided into four categories depending upon fouling materials: inorganic fouling /scaling, Bio-fouling, particle/ colloidal fouling and organic fouling. [10]Division is based on the fact that each type of foulant significantly affects membrane performance and has different cleaning procedures and ways to encounter.



**Figure2.8 Types of Fouling Based on Foulant**

***PARTICLE/ COLLOIDAL FOULING:***

Colloidal particles are abundant in natural water. These particles have size ranging from few nanometers to micrometers. Aquatic colloids include manganese oxide, clay minerals, suspended matter, organic colloids, iron, calcium carbonate precipitates and silica. Most colloids have negative charge at normal PH of water. The surface charges on colloids determine their surface properties and reflect chemical composition of water. When colloids accumulate on to the surface or in the pores of membrane it leads to flux decline and poor separation characteristics of membrane. Hence adversely affects the quality and quantity of filtered water.

In case of pressure driven membranes we need to consider two situations. For Nano-filtration, reverse osmosis and few ultrafiltration membranes colloidal fouling results from particles/colloids deposition on the surface of membrane and cake layer formation. This layer offers added hydraulic resistance to water flowing through membrane and leads to reduced flux. In microfiltration and ultrafiltration membranes pore clogging by

the colloids is added fouling mechanism along with colloid deposition on membrane surface. The size of colloids relative to pore size of membrane determines the extent of pore clogging and cake layer formation.

### ***INORGANIC FOULING /SCALING:***

The accumulation of hydroxide, salts and oxide from feed water on membrane surface is called Inorganic fouling /Scaling. Precipitation of salt crystal occurs when the concentration of salts may surpass the saturation due to temperature changes or water exclusion. Calcium bicarbonate is abundantly present in natural water. Following equilibrium exist between Calcium bicarbonate that is readily soluble in water and calcium carbonate which is poorly soluble.



Calcium carbonate formed in this reaction is insoluble in water and thus precipitates out. Driving force for precipitation are salt concentration and salt solubility which depend on temperature. Calcium, bicarbonate, barium, magnesium and sulphate are the major depositing ion.

### ***ORGANIC FOULING:***

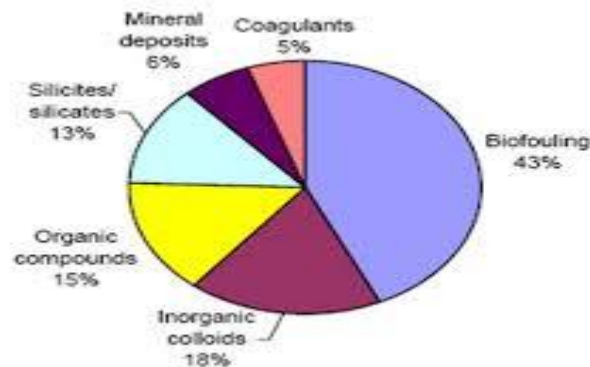
Materials which are insoluble in water and stick to membrane surface lead to organic fouling. These materials include macromolecules, anti-foaming agents, oil and proteins. These foulants contribute to formation of organic gel layer on surface or pores of membrane. The early stages of layer formation are caused by adsorption. In colloidal fouling suspended particle accumulates while in organic fouling dissolved substances deposit. Same sort of gel layer form in both cases in most cases a mixed layer is formed.

### ***BIO-FOULING:***

It is special type of organic fouling. Bio-fouling involves accretion of microorganism i.e. bacteria, algae and viruses on membrane surface. This type of fouling occurs as result of interaction among microorganism, membrane material and water flow parameters. [11]

Growth of microorganism attached to the surface leads to formation of biofilm. Besides stabilizing the colonies this film also protect the organism from sterilizer and from being detached by moving water.[12]

One of the most frequently encountered fouling forms in large and small scale system installed for treating surface and waste water is Bio-fouling. Bio-fouling can be a major and tenacious operational challenge with considerable economic consequences, if not handled properly and left uncontrolled. Only Pretreatment cannot avoid bio-fouling.[13]



**Figure2.9 Foulant Contribution towards Fouling**

***BIOFOULING:***

Characklis defined bio-fouling as deposition and growth of macro and microorganism including bacteria, fungi, algae and protozoa. Pre filters can be used to remove larger microorganism e.g. algae, protozoa and fungus cell from feed water. Bacteria and some fungi needs to be considered further.[14]

**2.3 BIO-FOULING: THE ACHILLES HEEL OF DEVELOPMENT**

In systems that incorporate membrane bio-fouling signifies the Achilles heel of development due to the fact that through pretreatment all other types of fouling i.e. organic, inorganic and colloidal can be encountered. Micro-organism however are capable of multiplication and if we remove 99.99% of organism the remaining cell are enough to grow at the cost of biodegradable substances in input stream. Bio-fouling can be a major and tenacious operational challenge with considerable economic

consequences, if not handled properly and left uncontrolled. Only Pretreatment cannot avoid bio-fouling.[15]

Microorganisms remain pervasive in every practical system except it is maintained sterile by giant and constant work. The possibility of bio-fouling is characterized by the microbes and the feed quantities. Bio-fouling induce extensive technical complications and fiscal loss [1]. Bio-fouling will be a growing problem as membrane technology is gaining importance for encountering rising demand of treated water.

### ***2.3.1 ADVERSE EFFECTS OF BIO-FOULING:***

#### ***FLUX REDUCTION:***

Membrane surface is covered with low permeability film which causes flux decline through membrane.

#### ***MEMBRANE DEGRADATION:***

Acidic by-products are produced by micro-organism which accumulate on membrane surface and cause membrane deterioration.

#### ***INCREASE IN SALTS:***

The permeate quality is affected due to increased amount of salts passing through membrane. The dissolved ions accumulate on membrane surface due to bio-film formation and lead to increase concentration polarization.

#### ***INCREASE IN TRANSMEMBRANE PRESSURE:***

To maintain constant flux rate feed pressure increases due to bio-film resistance having low permeability.

#### ***INCREASED ENERGY CONSUMPTION:***

To encounter bio-film resistance and flux reduction high energy is required.[16, 17]

### ***2.3.2 MEMBRANE FOULING CONTROL:***

Fouling remains the principal bottleneck which reduce the membrane efficacy and widespread application. If it is controlled properly by using appropriate techniques will leads to reduced operational cost and extensive membrane life. Fouling control measures consist of physical and chemical processes. Physical procedures comprise of

backwashing in between filtration cycle, application of critical Transmembrane Pressure, high velocity and hydrodynamic shear force lead to transient flux increase but demand high energy intake. Application of chemical disinfectant i.e. NaOCl, HCl, HNO<sub>3</sub> and NaOH recovered initial membrane permeability. But these methods are costly, may cause chemical contamination ,significant membrane damage and can produce lethal byproducts.[18]

### ***PROPOSED SOLUTIONS:***

1. Novel fouling impervious membrane chemistry
2. Modify the feed spacer configuration by changing the spacer thickness
3. Practicing non-oxidative biocide[13]

Our focus was on novel fouling impervious membrane chemistry. We modified membrane chemistry through incorporation of antimicrobial agent to handle the fouling problem.

### ***2.3.3 BIOFOULING CONTROL METHODS:***

The traditional approach for biofouling control involves selecting those materials for membrane manufacturing which have little affinity for bacteria or can be scrubbed simply. A different method is to prepare membrane with bacteriostatic properties via modification of membrane surface. So that membrane can efficiently prevent the growth of microbes. [19]

The methods of modifying membrane include polymer coating, blending, grafting and adding antimicrobial agent during membrane manufacturing.

#### ***Polymer Blending Method:***

This approach leads to alteration of surface properties only bulk characteristic and morphology of membrane is affected to a little extent.[20]

#### ***Grafting approach:***

The grafting practice employs polymers which are hydrophilic in nature or plasma treatment to create surfaces that have anti-fouling properties.[21] Through this approach

any polymeric material can be modified but recently polyamide, polyethersulfone and polypropylene membranes were modified through grafting approach.[22]

***Inorganic additives:***

the antifouling characteristic of membrane are modified through incorporation of inorganic additives i.e. silver[23], titania[24], alumina[25], zirconia[26] ,silica[27] Nano particles.

***Surface coating:***

The modification of membrane surface by coating it with additives is a simple approach that can be implemented to existing membrane forming processes with greater ease. This coating result in modification of membrane surface characteristic i.e. charge, roughness and hydrophilicity and leads to increase in bio-fouling resistance.

***Antimicrobial additives:***

Additives have been employed for making membrane surfaces having antifouling properties. These additives include chitosan [28], quaternary ammonium salt and phosphonium salts [29], polyethylene oxide [30], heavy metals such as copper[31] .

Our approach was to physically blend anti-microbial agent into polymer to modify it antimicrobial and anti-fouling characteristics.

## **OUR CONTRIBUTION**

### **2.4 PROBLEM STATEMENT:**

Bio-Fouling of polymer membranes leading to flux decline, inducing unfavorable effect to its efficiency and economic feasibility, in water purification system.

### **2.5 SELECTION OF MATERIALS FOR MEMBRANE SYNTHESIS**

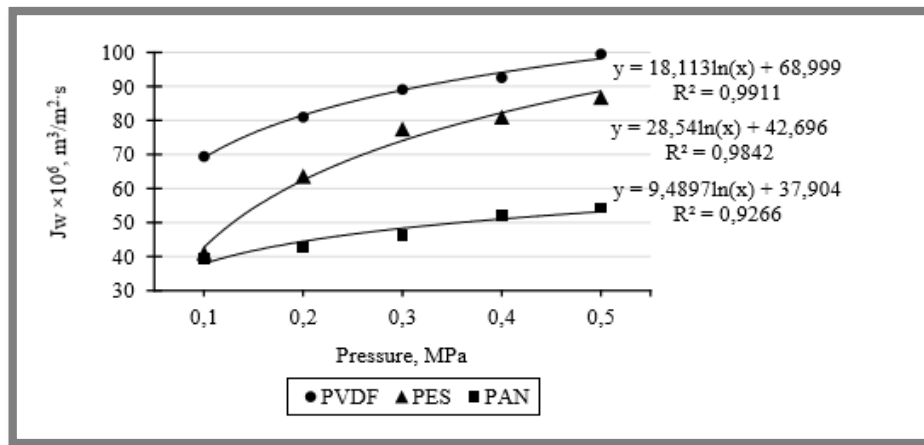
#### ***2.5.1 SELECTION OF POLYMER MATERIAL:***

It is well known that membranes are accompanied by the intrinsic fouling phenomena which lead to the decline of the membrane performance as a result of the increased system resistance, specifically in porous polymer membranes, that include microfiltration

and ultrafiltration membranes. Studies reported in literature show that fouling of membrane is related with the properties of membrane forming polymer and substances dissolved in feed water. Therefore fouling can be minimized through selection of suitable membrane material. The membrane properties that have significant influence on fouling phenomena include roughness, charge and wettability and pore size distribution. All these characteristics are governed by membrane forming material.

Membrane are prepared from various polymer i.e. polyethersulfone (PES), polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN) ,poly propylene(PE) Cellulose acetate(CA). However, polyethersulfone (PES), polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN) are widely used polymer for synthesizing commercially available water purification membranes. In a previous study the vulnerability of these membranes to the fouling prodigy was determined. Transport properties of synthesized membrane from these materials were determined through flux measurement at various transmembrane pressures.

If the flux values are higher over the pressure range it means low input energy is required for that membrane and that material is energy efficient.



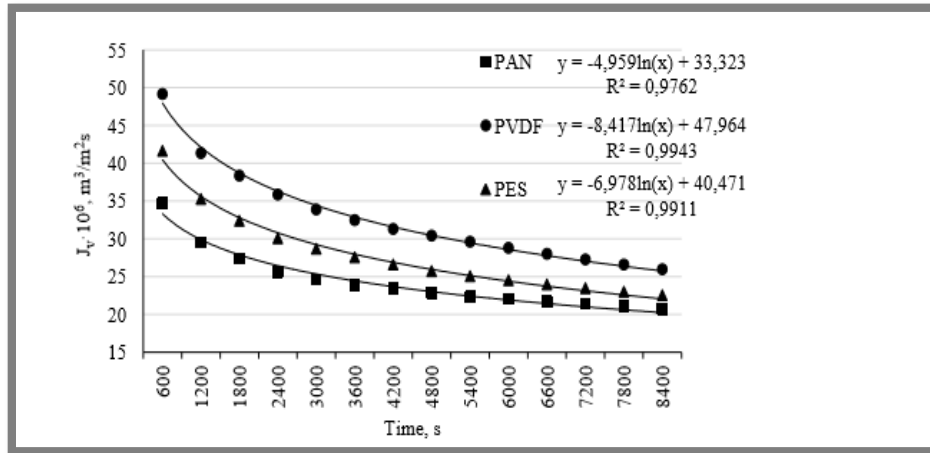
**Figure2.10 Flux Variations of Different Membrane Forming Materials with Pressure**

During filtration process it was observed that permeate volume continuously declined with time for each membrane. The flux reduction over time was related with progressive



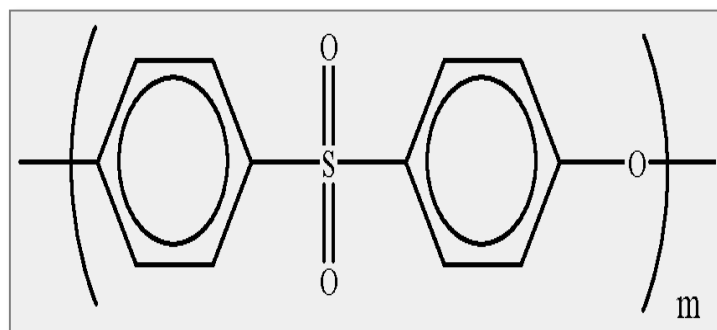
fouling of membrane. It was concluded that PVDF membrane are more susceptible to fouling than other two polymer membranes.

PAN membrane has greatest fouling resistant due high hydrophilic nature of membrane material. PES membrane had intermediate fouling resistance.



**Figure2.11 Reduction in Flux due to Fouling of Different Membranes Forming Materials.**

As our focus is to make antifouling membrane therefore polyethersulfone is suitable material to manufacture membrane for its intermediate flux and fouling performance. Along with these properties PES has high temperature tolerances. It has good mechanical stability and chemical resistance. Hence we selected this polymer to fabricate membrane.



**Figure2.12 Polyethersulfone**

### 2.5.2 SELECTION OF ANTI-MICROBIAL AGENT:

It was found in the literature that several anti-microbial agents had been incorporated into PES to manufacture membrane used for water purification. These agents include nano particles and salts. Through this approach the antifouling properties of membrane were improved. But these techniques have some drawbacks. The salts have very limited range of anti-microbial activity. Secondly, the salts are inorganic in nature therefore when blended into organic polymer leads to inhomogeneous dispersion that result in non-uniform anti-microbial and antifouling properties of membrane. These materials also leach out from membrane which results in reduced membrane life. The leached out particle are present in permeate and hence dangerous for human-beings. It is not economical to prepare nanoparticles and salts on large scale.

Our objective is to make organic membrane by blending antimicrobial agent into PES.

Hence we decided to add antiseptic agent into PES which are organic in nature therefore homogeneously disperse in membrane and leads to uniform antifouling properties. The points to be considered are that these antiseptic agents should have wide range of anti-microbial activity, be least toxic to humans and contain various functional group into their structure so that can easily interact with PES. Based on these requirements we selected chlorhexidiene and 22efadroxil.

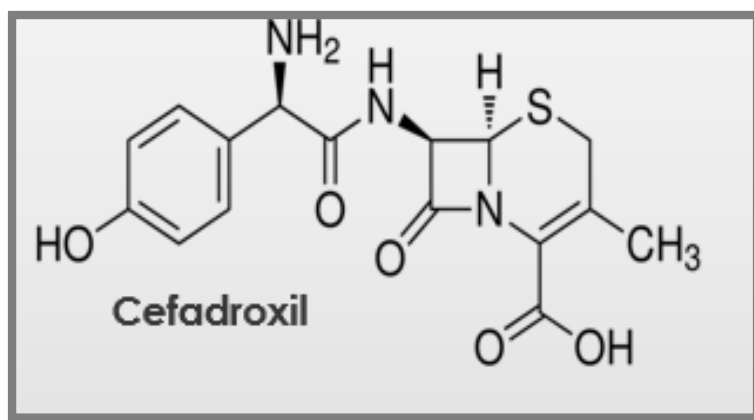
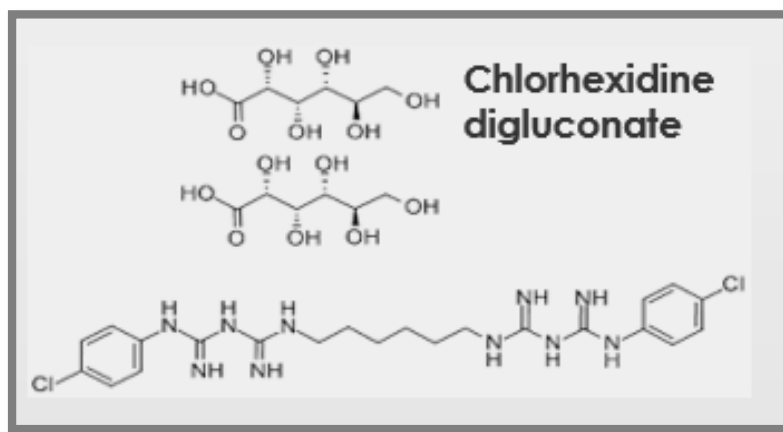


Figure2.13 Structure of Cefadroxil

Chlorhexidine has broad range of anti-microbial activity. It is effective against fungi, gram positive and gram negative bacteria and some viruses. It has high kill rate. It kills 100% microorganism in 20 seconds, it is widely used in disinfectants for hands and mouth, as mouthwash, in cosmetics (creams, toothpaste) and in pharmaceutical products (eye drop). It is available in form of the dihydrochloride, diacetate, and digluconate. Its salts dissociate at physiologic PH and produce cation. The cation interacts with negatively charge group present in cell wall or cell membrane of microbes and leads to cell lysis. Depending upon concentration Chlorhexidine act as bactericidal or bacteriostatic.



**Figure 2.14 Structure of Chlorhexidine**

**Table 1.1 Virucidal Activity of Chlorhexidine Gluconate**

TABLE 15.6. <i>Virucidal activity of chlorhexidine gluconate</i>			
Virus	Viral family	Activity	Concentration (%)
Respiratory syncytial virus	Paramyxovirus	+	0.25
Herpes hominis/simplex	Herpesvirus	+	0.02
Polio virus type 2	Enterovirus	-	0.02
Adenovirus type 2	Adenovirus	-	0.02
Equine infectious anaemia virus	Retrovirus	+	2.0
Variola virus (smallpox)	Poxvirus	+	2.0
Herpes simplex type 1/type 2	Herpesvirus	+	0.02
Equine influenza virus	Orthomyxovirus	+	0.001
Hog cholera virus	Togavirus	+	0.001
Bovine viral diarrhoea	Togavirus	+	0.001
Parainfluenza virus	Paramyxovirus	+	0.001
Transmissible gastroenteritis virus	Coronavirus	+	0.001
Rabies virus	Rhabdovirus	+	0.001
Canine distemper virus	Paramyxovirus	+	0.01
Infectious bronchitis virus	Coronavirus	+	0.01
Newcastle virus	Paramyxovirus	+	0.01
Pseudo rabies virus	Herpesvirus	+	0.01
Cytomegalovirus	Herpesvirus	+	0.1
Coxsackie virus	Picomavirus	-	0.4
Echo virus	Picomavirus	-	0.4
Human Rota virus	Reovirus	-	1.5
Human Immunodeficiency Virus Type I	Retrovirus	+	0.2

Table 2.2 Bacteriostatic Activity of Chlorhexidine Gluconate

Test organism	MIC (mg/L)		
	No. of strains	Mean	Range
<b>Gram-positive cocci</b>			
<i>Micrococcus flavus</i>	1	0.5	
<i>Micrococcus luteus</i>	1	0.5	
<i>Staphylococcus aureus</i>	16	1.6	1-4
<i>Staphylococcus epidermidis</i>	41	1.6	0.25-8
<i>Streptococcus faecalis</i>	5	36	32-64
<i>Streptococcus mutans</i>	2	2.5	
<i>Streptococcus pneumoniae</i>	5	11	8-16
<i>Streptococcus pyogenes</i>	9	3	1-8
<i>Streptococcus sanguis</i>	3	9	4-16
<i>Streptococcus viridans</i>	5	25	2-32
<b>Gram-positive bacilli</b>			
<i>Bacillus cereus</i>	1	8	
<i>Bacillus subtilis</i>	2	1	
<i>Clostridium difficile</i>	7	16	8-32
<i>Clostridium welchii</i>	5	14	4-32
<i>Corynebacterium spp</i>	8	1.6	0.5-8
<i>Lactobacillus casei</i>	1	128	
<i>Listeria monocytogenes</i>	1	4	
<i>Propionibacterium acne</i>	2	8	
<b>Gram-negative bacilli</b>			
<i>Acinetobacter anitratus</i>	3	32	16-64
<i>Acinetobacter lwoffi</i>	2	0.5	
<i>Alkaligenes faecalis</i>	1	64	
<i>Bacteroides distastosis</i>	4	16	
<i>Bacteroides fragilis</i>	11	34	8-64
<i>Campylobacter pyloridis</i>	5	17	8-32
<i>Citrobacter freundii</i>	10	18	4-32
<i>Enterobacter cloacae</i>	12	45	16-64
<i>Escherichia coli</i>	14	4	2-32
<i>Gardnerella vaginalis</i>	1	8	
<i>Haemophilus influenza</i>	10	5	2-8
<i>Klebsiella aerogenes</i>	5	25	16-64
<i>Klebsiella oxytoca</i>	2	32	
<i>Klebsiella pneumoniae</i>	5	64	82-128
<i>Proteus mirabilis</i>	5	115	64->128
<i>Proteus morganii</i>	5	73	16-128
<i>Proteus vulgaris</i>	5	57	32-128
<i>Providencia stuartii</i>	5	102	64-128
<i>Pseudomonas aeruginosa</i>	15	20	16-32
<i>Pseudomonas cepacia</i>	1	16	
<i>Pseudomonas fluorescens</i>	1	4	
<i>Salmonella bredeney</i>	1	16	
<i>Salmonella dublin</i>	1	4	
<i>Salmonella gallinarum</i>	1	8	
<i>Salmonella montivideo</i>	1	8	
<i>Salmonella typhimurium</i>	4	13	8-16
<i>Salmonella virchow</i>	1	8	
<i>Serratia marcescens</i>	10	30	16-64

**Table 3 FUNGISTATIC ACTIVITY of CHLORHEXIDINE**

<b>TABLE 14.2</b>		
<b>Fungistatic Activity of Chlorhexidine</b>		
<b>Organism</b>	<b>No. of Strains</b>	<b>Mean MIC (mg/L)</b>
<b>Mold fungi</b>		
<i>Aspergillus flavus</i>	1	64
<i>Aspergillus fumigatus</i>	1	32
<i>Aspergillus niger</i>	1	16
<i>Penicillium notatum</i>	1	16
<i>Rhizopus</i> sp	1	8
<i>Scopulariopsis</i> spp	1	8
<b>Yeasts</b>		
<i>Candida albicans</i>	2	9
<i>Candida guilliermondii</i>	1	4
<i>Candida parapsilosis</i>	2	4
<i>Candida pseudotropicalis</i>	1	3
<i>Cryptococcus neoformans</i>	1	1
<i>Prototheca zopfii</i>	1	6
<i>Saccharomyces cerevisiae</i>	1	1
<i>Torulopsis glabrata</i>	1	6
<b>Dermatophytes</b>		
<i>Epidermophyton floccosum</i>	1	4
<i>Microsporum canis</i>	2	4
<i>Microsporum fulvum</i>	1	6
<i>Microsporum gypsum</i>	1	6
<i>Trichophyton equinum</i>	1	4
<i>Trichophyton interdigitale</i>	2	3
<i>Trichophyton mentagrophytes</i>	1	3
<i>Trichophyton quinquearum</i>	1	3
<i>Trichophyton rubrum</i>	2	3
<i>Trichophyton tonsurans</i>	1	3

# CHAPTER 3

## MEMBRANE SYNTHESIS AND CHARACTERIZATION

### 3.1 FABRICATION OF PES-CHLORHEXIDINE AND PES- CEFADROXIL MEMBRANES:

- Fabrication of membranes was carried out by first preparing 20%w/w solution of PES in NMP and addition of Chlorhexidine and Cefadroxil in various percentages. These percentages were chosen on the basis of MBC (Minimum Bactericidal Concentration) of these anti-microbial agents available in literature [32-34].
- The solutions were kept for magnetic stirring for 24 hours in order get homogeneous solution.
- Polyester support was fixed on the metallic plate and wetted with NMP so that polymeric solution does not penetrate the support.
- An appropriate amount of solution was poured in casting knife and thin films were casted by the use of thin film applicator.
- The metallic plate was removed and placed in coagulation bath containing distilled water. As the water is non-solvent for PES, phase inversion occurred by solvent –non solvent exchange in coagulation bath.

### 3.2 CHARACTERIZATION OF MEMBRANES

Several following techniques were employed to account for the efficacy of membrane newly fabricated polymer membranes:

### ***3.2.1 Fourier Transform Infrared Spectroscopy (FTIR):***

FTIR was carried out in order to identify the presence of functional groups of PES, chlorhexidine and Cefadroxil. This was also essential as the anti-microbial agents could leach out during phase inversion due to their low molecular weight.

### ***3.2.1 Scanning Electron Microscopy (SEM):***

SEM Joel 6490A was used to carry out scanning electron microscopy analysis in order to evaluate morphology, pore sizes and topography of membranes. Samples of approximately 0.25cm<sup>2</sup> sizes were taken as a representative of the specific membranes, mounted onto the brass block and coated with gold through sputtering in order to deposit a thin conductive layer to carry out SEM.

### ***3.2.2 Energy Dispersive Spectroscopy (EDS):***

EDS was carried out in order to have an elemental analysis for identifying the presence of anti-microbial agents in the membranes.

### ***3.2.3 CONTACT ANGLE MEASUREMENTS:***

In order to investigate the effect of anti-microbial agents on surface wettability of membranes, sessile drop method was used. Sample of membrane was placed on the stage. A drop of 5-10µl ultrapure water was placed on to the surface of membranes through the tip of needle. High-pixel camera was used to capture the image of water droplet. In order to minimize the experimental error contact angle was measured at 5 different location for each membrane type and 5-6 readings were averaged at each point.

### ***3.2.4 ATOMIC FORCE MICROSCOPY (AFM):***

For evaluation of roughness and estimating the pore size of membranes tapping mode of Atomic Force microscopy was used.

### ***3.2.5 MECHANICAL TESTING:***

As permeation through water filtration membranes requires high pressure due to the small size of pores and the modification of membranes results in change in the pore-size and morphology of membranes, therefore mechanical test was carried out in order to evaluate the effect of anti-microbial agents on the mechanical properties of membranes. **ASTM**



**D882-10** standard (Dimensions: 60 x 20 mm, Gauge length: 30mm, Strain rate: 5mm/min) was used for mechanical testing of membranes. Tensile testing of membranes along with support was carried out till failure of membrane along the gauge length and fracture strength was observed for each sample.

### **3.2.6 WATER RETENTION:**

In order to measure the bulk hydrophilicity of membranes, water retention test was conducted. In this test, membranes specimens weighting approximately 0.1 grams were taken and dipped for 24 hours in ultrapure. Samples were then weighted on weight balance and the wet weights were noted. These samples were then oven-dried at 60<sup>0</sup>C for 5 hours and their dry-weights were recorded. Percentage of water uptake was calculated by the following formula:

$$\text{Percentage of water uptake} = \left[ \frac{\text{Wet weight} - \text{Dry weight}}{\text{Wet weight}} \right] \times 100$$

### **3.2.7 WATER PERMEABILITY FLUX:**

**ASTM D5886** was used to for the water permeability test of membranes. Following formula was used to evaluate the flux measured at different pressures.

$$J = V/At$$

J= flux, L/h m<sup>2</sup>

V= Volume of water, liters.

A= effective area of membrane, m<sup>2</sup>

t= time to flow, hours.

The graph of flux change with pressure was recorded and the relative flux at each pressure was compared.

### **3.2.8 EVALUATION OF NON-LEACHABILITY OF ANTI-MICROBIAL AGENTS:**

Zone of inhibition test was conducted in order to evaluate leachability of anti-microbial agent from the PES membrane. Auto-claved nutrient agar were poured in petri plates, incubated for 24 hours, and then checked for contamination. Fresh cultures of bacteria were spread onto plates with swab and membrane's samples were placed in their marked

position with activated side upwards. The plates were then placed for incubation for 24 hours to allow bacterial growth, after bacterial growth the presence or absence of zone around the membrane and positive control was evaluated.

### ***3.2.9 ANTI-BACTERIAL AND ANTI-FUNGAL ACTIVITY OF ANTI-MICROBIAL AGENTS:***

In order to evaluate our selected antimicrobial agents against various bacterias and fungus first wells were made inside agar plates and then antiseptics dissolved in water were filled inside these wells. Bacterias and fungus are spread over the whole plate uniformly before the filling of wells. These plates were incubated for 24 hours to allow bacterial growth.

### ***3.2.10 ANTI-BACTERIAL TESTING OF MEMBRANES:***

For anti-bacterial testing of our modified PES membranes “Parallel Streak Test” (AATCC 147 (modified)- Parallel Streak Test) was carried out.[35] Fresh culture of bacterias were spread over the prepared nutrient agar plates and membranes, with their active side towards bacteria, were placed at their marked position, positive control was placed in the center and PES membrane was used as a negative control. According to this test, if positive control inhibit bacterial growth around it and negative control do not inhibit bacterial growth then the standard condition has been established inside the petri plates. Further the inhibition of bacterial growth at the place where bacterias were in direct contact with membrane can be evaluated to check the effective killing of bacterias.

### ***3.2.11 ANTI-FUNGAL TESTING OF MEMBRANES:***

For evaluation of anti-fungal activity of our membranes “parallel streak method” was used (AATCC 30 –Antifungal Test).[36] Fungal spores were spread over the prepared agar plates and membranes, with their active side towards fungus, were placed at their marked position, positive control was placed in the center and PES membrane was used as a negative control. According to this test, if positive control inhibit Fungus growth around it and negative control do not inhibit fungus growth then the standard condition has been established inside the petri plates. Further the inhibition of fungus growth at the place where fungus was in direct contact with membrane can be evaluated to check the effective inhibition of fungus growth.

### **3.2.12 ANTI-FOULING EVALUATION OF SELECTED MEMBRANE:**

For evaluation of anti-fouling capability of modified membranes, a membrane with highest concentration of Chlorhexidine and PES membrane was selected. LB broths containing various bacteria's were allowed to filter through membranes in order to cause artificial fouling of membranes in less time. Flux at same pressure before and after the passage of LB broth of bacteria was evaluated to see effect of fouling. Following model was used to evaluate fouling:

$$J = \text{TMP} / \mu R_m$$

$$J = \text{TMP} / \mu R_t$$

**J = flux, m/sec**

**R<sub>m</sub> = intrinsic resistance of membrane, m<sup>-1</sup>**

**R<sub>t</sub> = Total resistance to filtration, m<sup>-1</sup>**

**TMP = Trans-membrane pressure, Pa.**

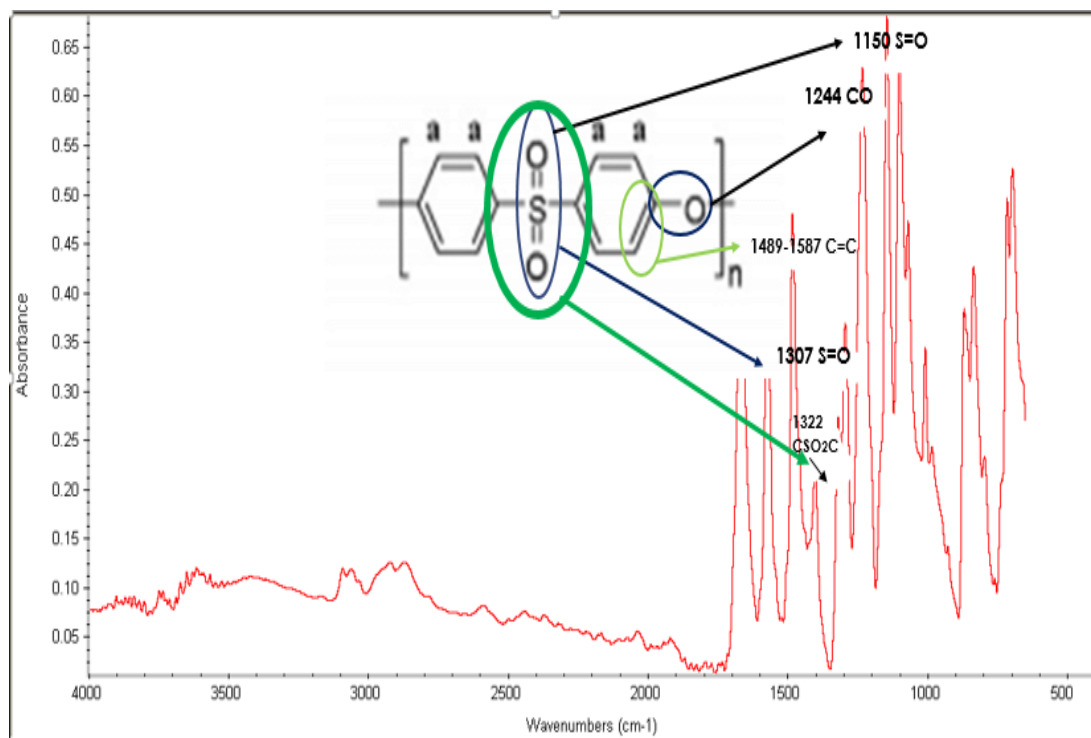
**μ = Absolute viscosity of water, kg/m**

# CHAPTER 4

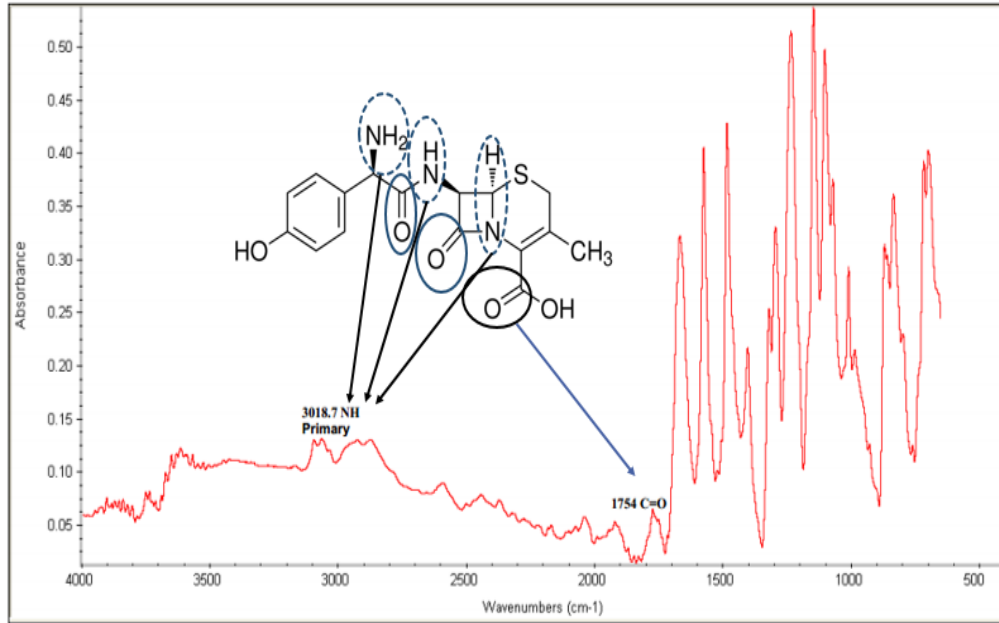
## RESULTS AND DISCUSSION

### 4.1 Fourier Transform Infrared Spectroscopy:

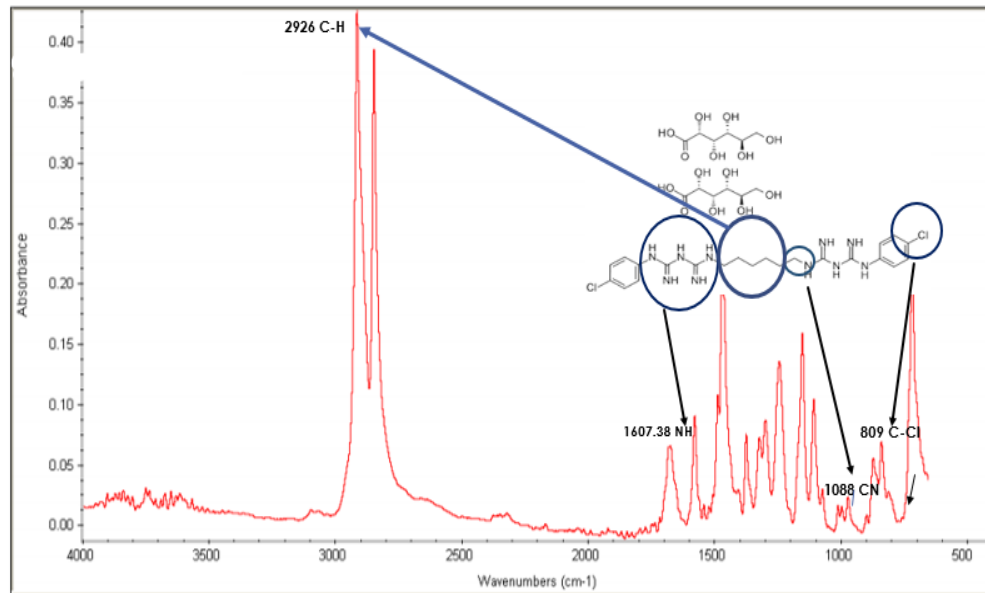
Figure 4.1, 4.2 and 4.3 shows FTIR spectroscopy of PES membrane, membrane blended with Cefadroxil and Chlorhexidine respectively. FTIR proves the presence of antimicrobial agents [37-40] in the membrane, as all functional groups have been identified in FTIR analysis.



**Figure 4.1 FTIR spectroscopy of simple PES membrane.**



**Figure 4.2 FTIR spectroscopy of PES membrane containing Cefadroxil.**



**Figure 4.3 FTIR spectroscopy of PES membrane containing Chlorhexidine.**

## 4.2 CONTACT ANGLE MEASUREMENTS:

Sessile Drop Method was used for the analysis of wettability of membranes. Figure 4.4 shows that water contact angle decreases consistently as Chlorhexidine concentration is increased, indicating the presence of hydrophilic functional groups. Figure 4.5 shows that water contact angle decreases by addition of Cefadroxil but with increasing the concentration of Cefadroxil there is no consistent decrease in contact angle, indicating that functional groups in Cefadroxil are not highly hydrophilic. The enhanced hydrophilicity results in the increase in water flux through the membranes. As PES membrane are relatively hydrophobic[41], the modification of membranes through antimicrobial agent results in increased hydrophilicity.

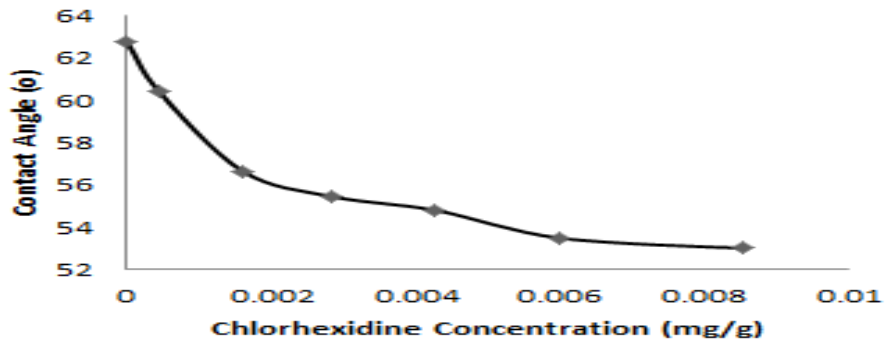


Figure 4.4 Contact Angle of Chlorhexidine modified membrane

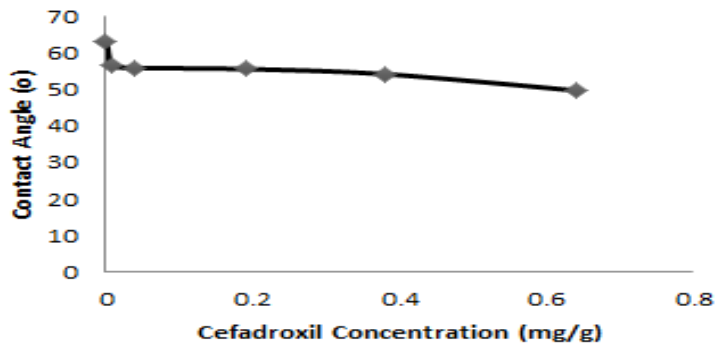


Figure 4.5 Contact Angle of Cefadroxil modified membrane.

### 4.3MECHANICAL TESTING:

Figure 4.6 and 4.7 shows that modification of PES membrane with Chlorhexidine and Cefadroxil respectively, results in increase in the fracture strength of membranes. As water filtration membranes have to tolerate high pressures during operation and modification of membranes with antimicrobial agents results in improved mechanical strength therefore it can be concluded that pores of membranes have not been increased to such an extent that could lead to degradation of mechanical strength of membranes.

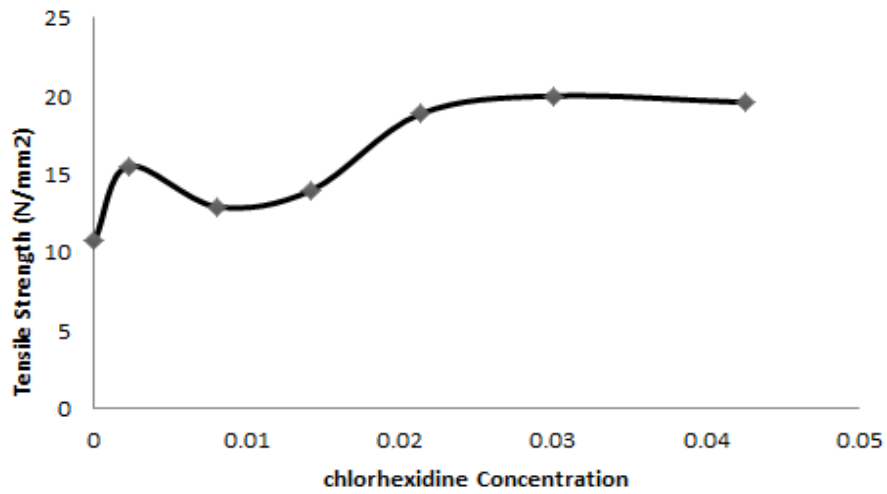


Figure 4.6 Tensile test results of membranes modified with chlorhexidine.

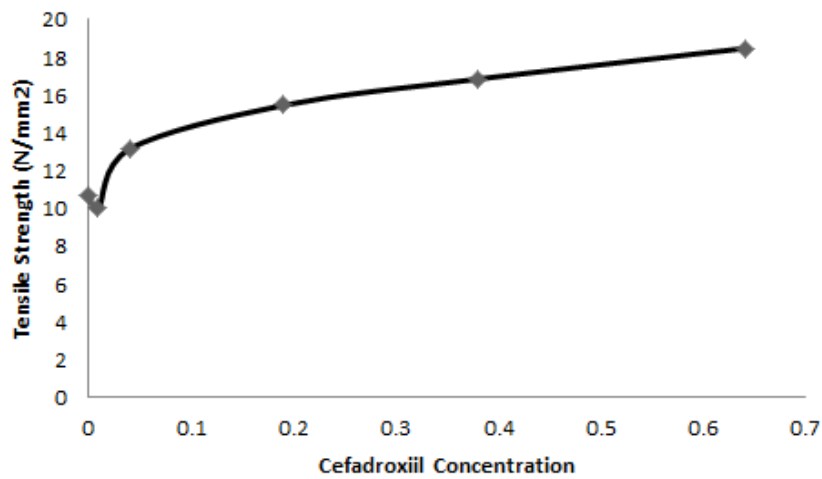


Figure 4.7 Tensile Test results for Membrane modified with 35efadroxil

#### 4.4 WATER RETENTION TEST:

Figure 4.8 and 4.9 shows the results of water retention test conducted for evaluating bulk hydrophilicity of membranes. In case of PES membranes modified with cefadroxil, water uptake first increases with increase in concentration and then becomes constant, indicating that further increase in concentration of cefadroxil does not increase bulk hydrophilicity of membranes. In case of PES membranes modified with chlorhexidine, water uptake of membranes increases with concentration of chlorhexidine and approaches a higher value of water uptake as compared to membranes containing cefadroxil. These results of bulk hydrophilicity are consistent with the results of contact angle measurement, used to evaluate surface hydrophilicity.

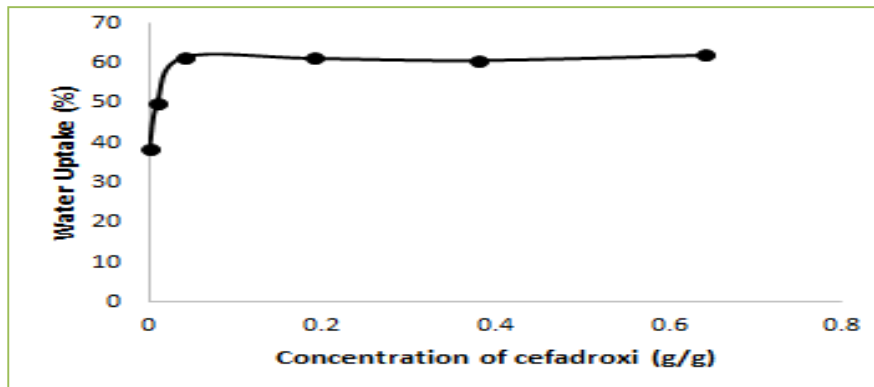


Figure 4.8 Water retention test for PES membranes incorporated with cefadroxil.

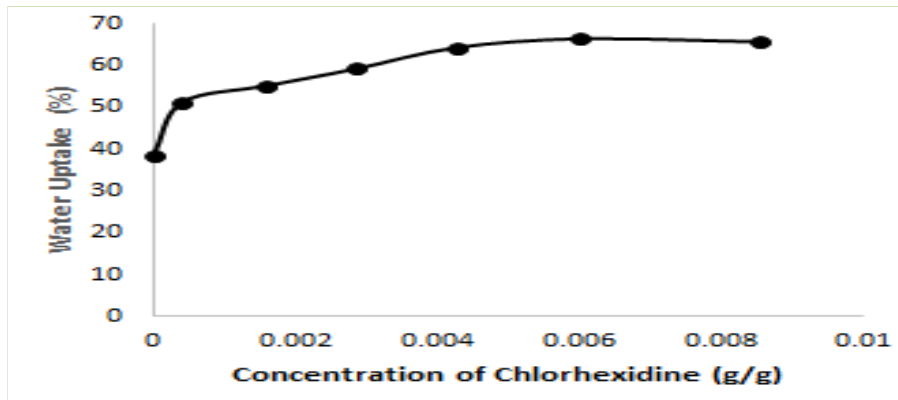
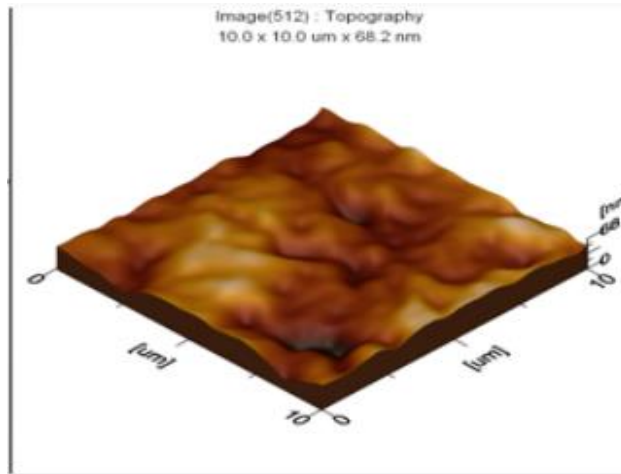


Figure 4.9 Water retention test for PES membranes incorporated with chlorhexidine.

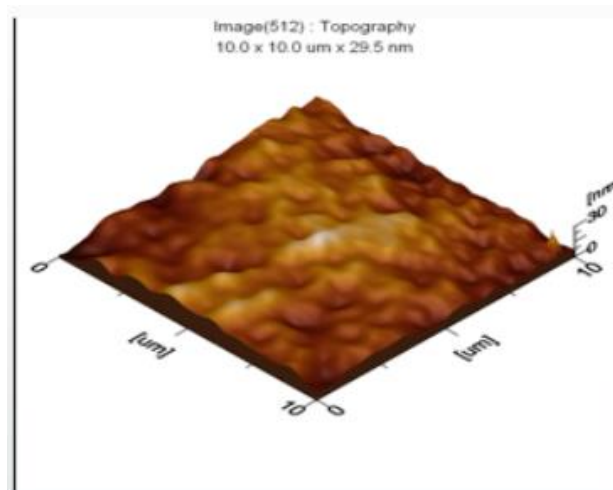


#### 4.5 ATOMIC FORCE MICROSCOPY:

Figure 4.10 and 4.11 shows the surface topographical image scanned by AFM. The measure of roughness shows that roughness decreases with the addition of Chlorhexidine, the decrease in roughness means that there will be less spaces for the foulants to get attach to the membranes and hence reduction in fouling.



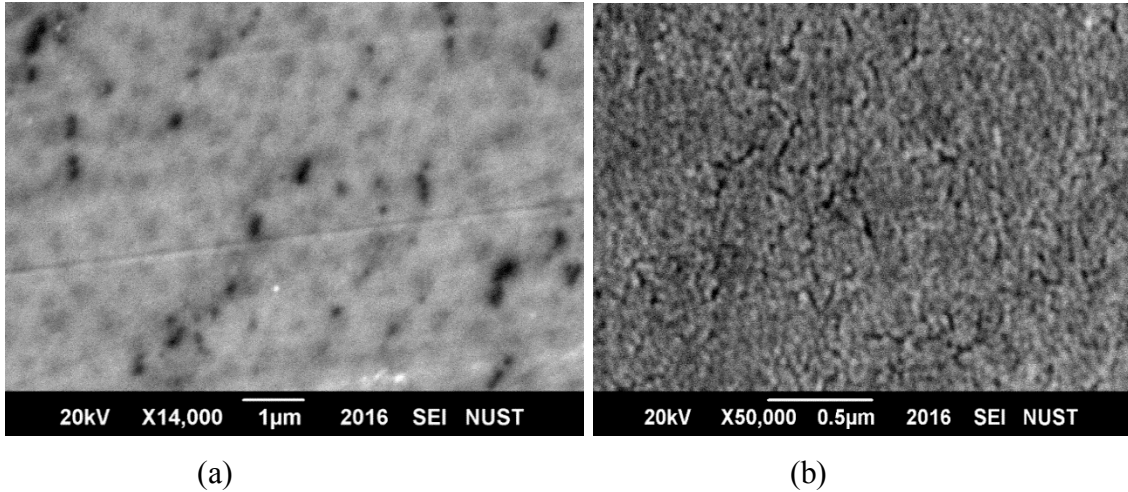
**Figure 4.10 shows the Surface Topography of PES membrane**



**Figure 4.11 shows the surface topography of PES membrane containing 0.00852mg Chlorhexidine**

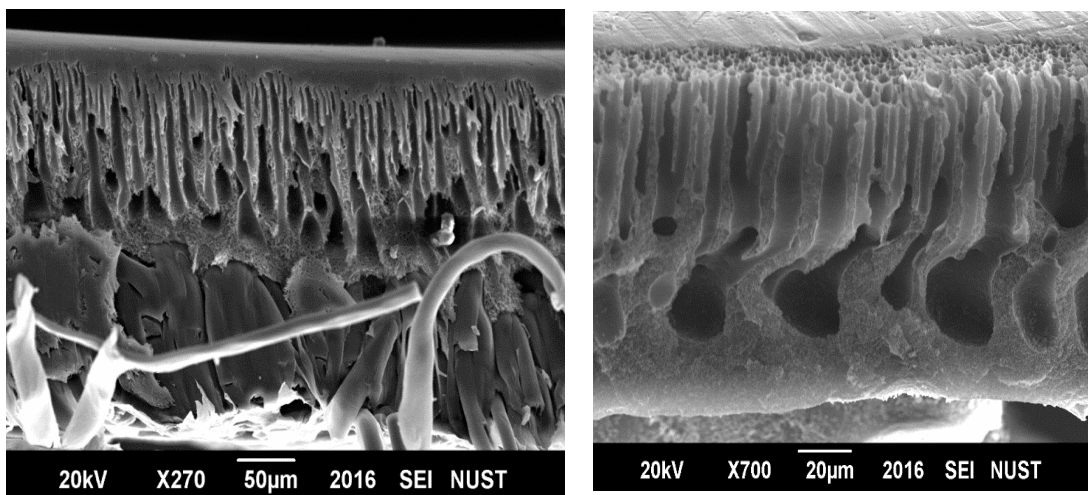
#### 4.6 SCANNING ELECTRON MICROSCOPY:

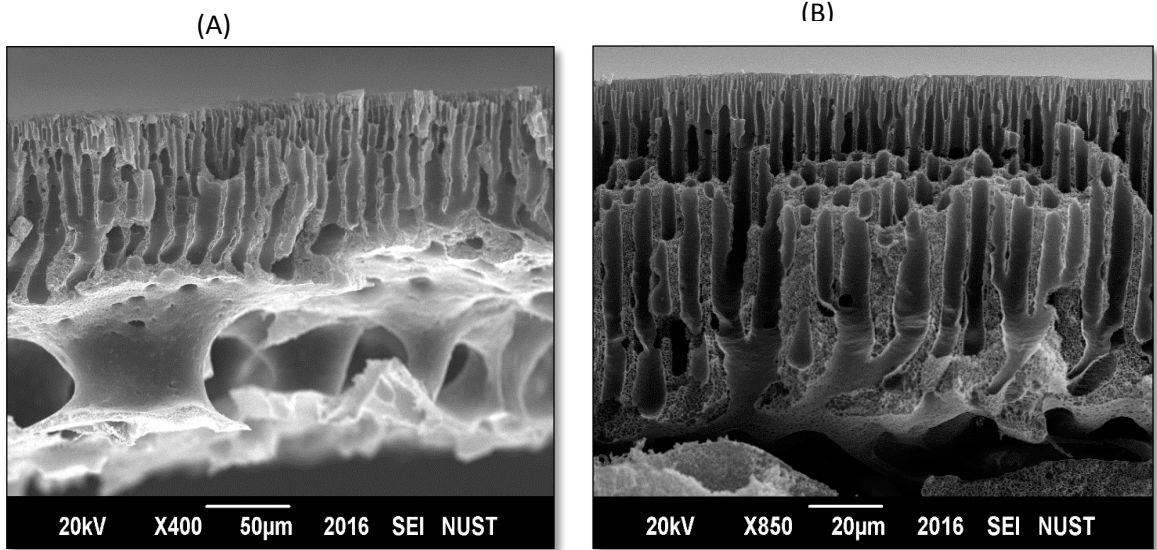
Figure 4.12 shows the surface pore size and pore density for PES and membrane containing 0.00852 CHX, pore size decreases with the addition of chlorhexidine in the membranes as well as pore density increases indicating that membranes incorporated with chlorhexidine is capable of higher flux and better permeate quality.



**Figure 4.12 (a) shows surface pores of PES and (b) shows surface pores of PES membrane incorporated with 0.00852mg of chlorhexidine.**

Figure 4.13 shows the cross-sectional view of membranes, it is proved from these SEM images that membranes are asymmetric in their structure. Asymmetry in membranes results in both better permeate quality due to smaller surface pore size and higher flux as the pores at bottom are larger in size providing least resistance for the permeate to flow.





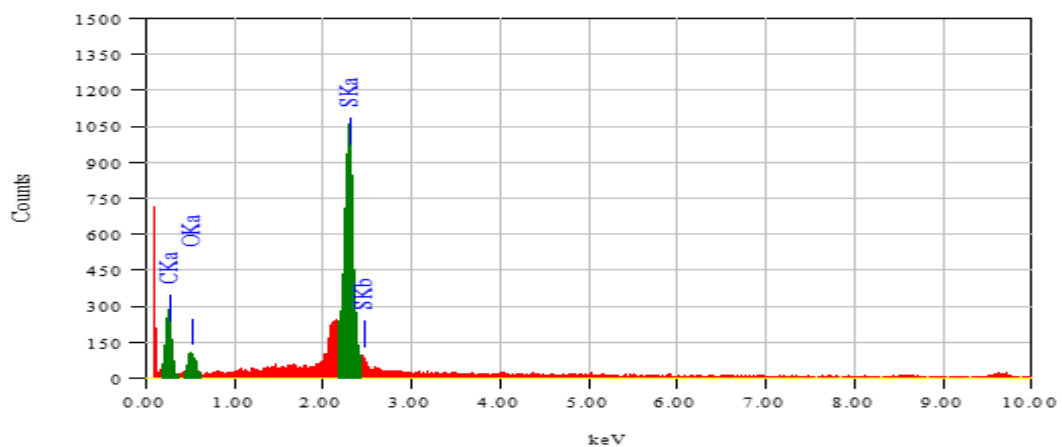
(C)

(D)

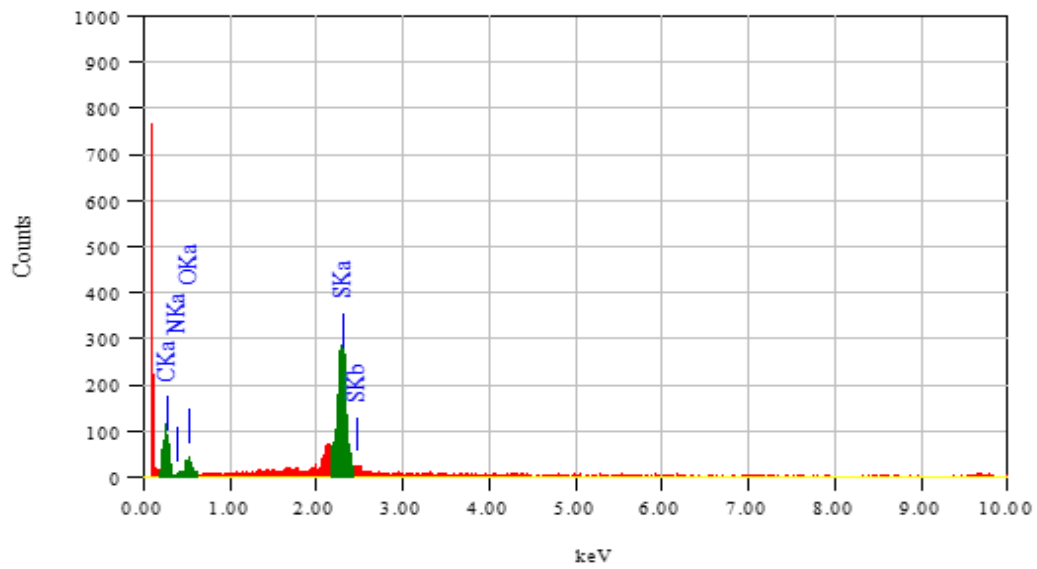
Figure 4.13 showing cross-sectional view of membranes (a) PES (b) 0.00426CHX (c) 0.19CF (d) 0.009CF

#### 4.7 EDS (Energy Dispersive Spectroscopy)

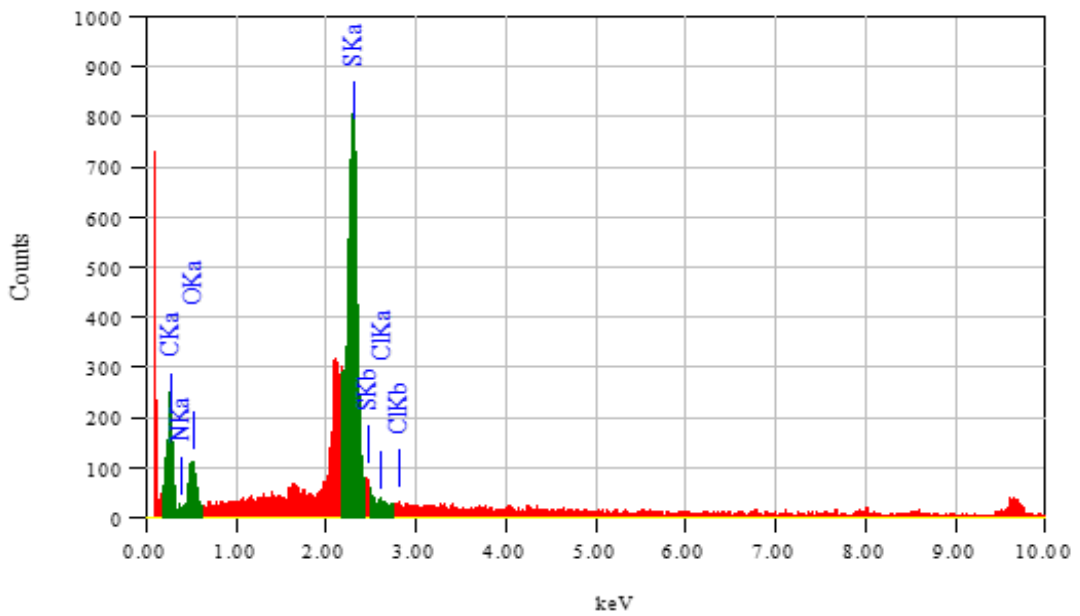
EDS shows the presence of additional elements present in Cefadroxil and chlorhexidine i.e nitrogen and Chlorine + Nitrogen respectively. This proves the presence of Anti-microbial agent are present inside membranes.



(a)



(b)



(c)

Figure 4.14 showing EDS analysis for (a) PES (b) Cefadroxil (c) Chlorhexidine incorporated membranes

#### 4.8 WATER PERMEABILITY FLUX:

Figure 4.15 shows that with increase in pressure the flux increases linearly. The comparison of flux at constant pressure shows that with increase in concentration of Chlorhexidine or Cefadroxil in PES membrane flux increases. The effect is more prominent in Chlorhexidine incorporated PES membrane. The increase in flux is due to increased hydrophilicity of the membranes due to addition of anti-microbial agents.

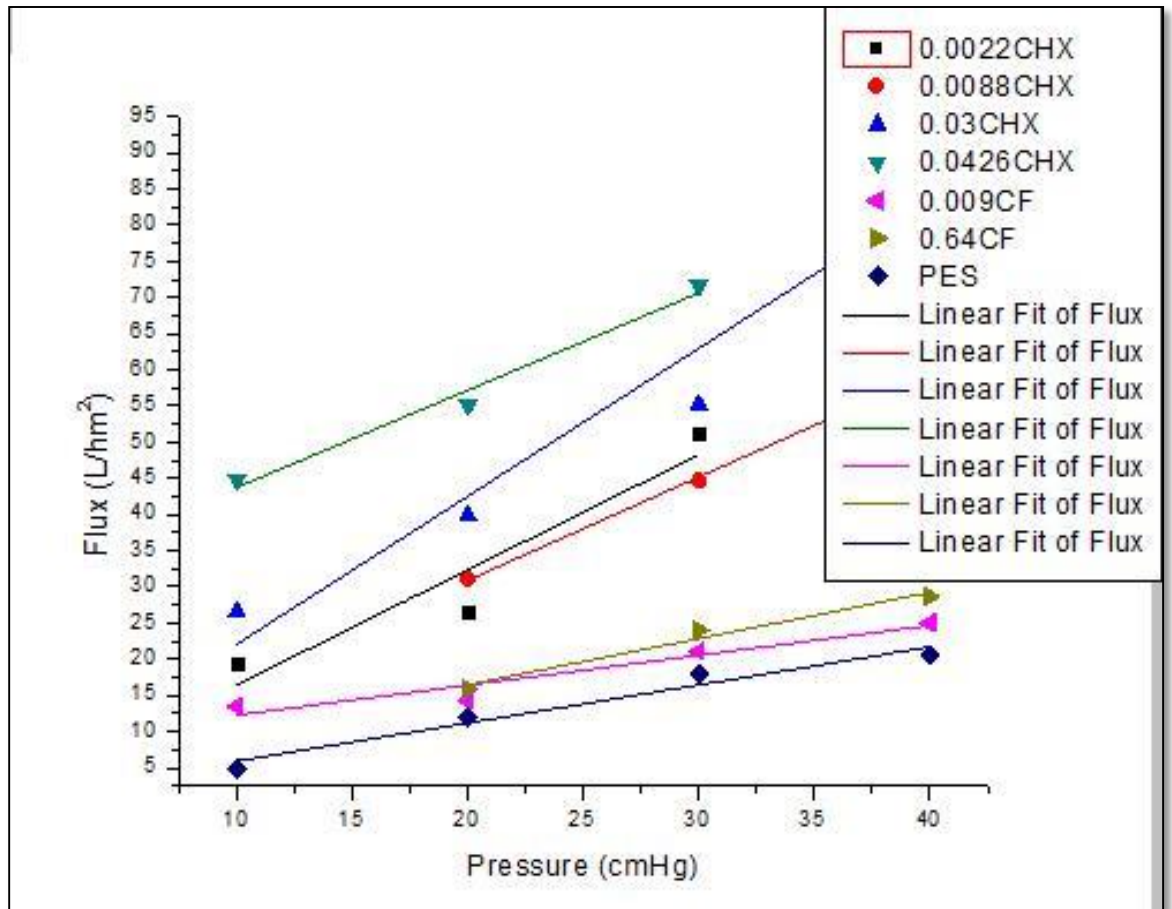
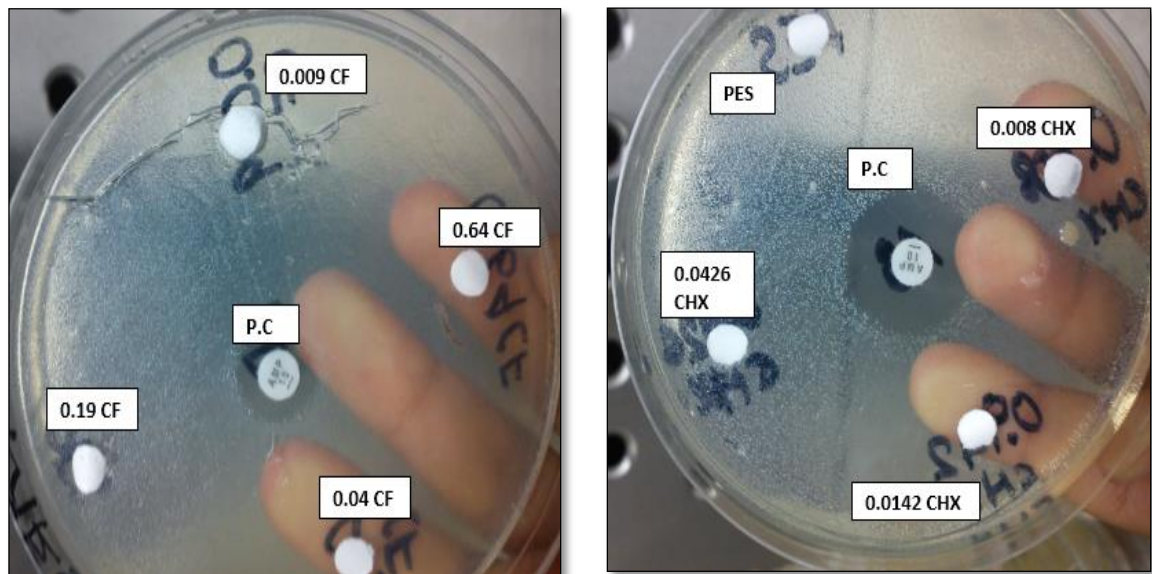


Figure 4.15 shows variation of flux at different pressure for different membranes.

#### 4.9 EVALUATION OF NON-LEACHABILITY OF ANTI-MICROBIAL AGENTS:

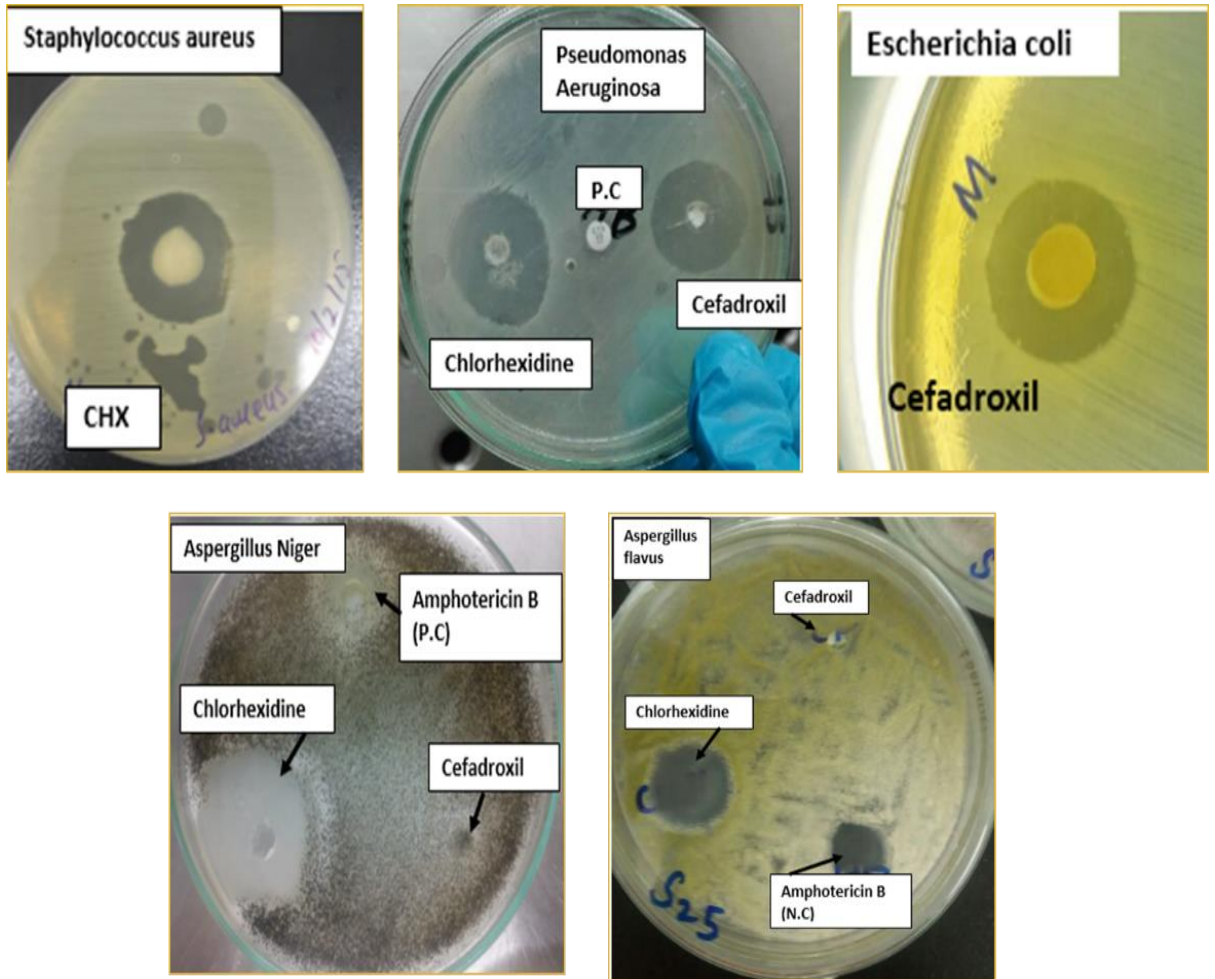
Figure 4.16 shows the presence of zone around positive control (an antibiotic incorporated inside) however no zone was found around the membranes incorporated with Chlorhexidine and Cefadroxil. These incorporated PES membranes indicates that the antibiotics are non-leachable out of the polymer matrix. The non-leachability will allow long-term effective killing of microbial and hence longer life of membrane.



**Figure 4.16 shows the absence zone of inhibition around membranes.**

#### **4.10 ANTI-BACTERIAL AND ANTI-FUNGAL ACTIVITY OF ANTI-MICROBIAL AGENTS:**

Figure 4.17 shows that both Cefadroxil and Chlorhexidine are effective against bacteria such as staphylococcus aureus, pseudomonas Aeruginosa and Escherichia coli as indicated by the presence of zone around them. Only Chlorhexidine is effective against fungus (Aspergillus Niger and aspergillus flavus) as it shows the larger zone around it while Cefadroxil is not anti-fungal because of the absence of zone around it.



**Figure 4.17 shows the presence and absence of zone around anti-microbial agents for bacteria and fungus.**

#### 4.11 ANTI-BACTERIAL TESTING OF MEMBRANES:

After removal of the membranes (with activated side towards bacteria), the clear area shows the inhibition of bacterial growth by modified membranes while bacterial growth was observed at the bottom of PES membranes. For some bacteria, clarity in the bacterial growth at the place where membranes were placed increases with increase in the concentration of anti-bacterial agent as shown in figure 4.18.

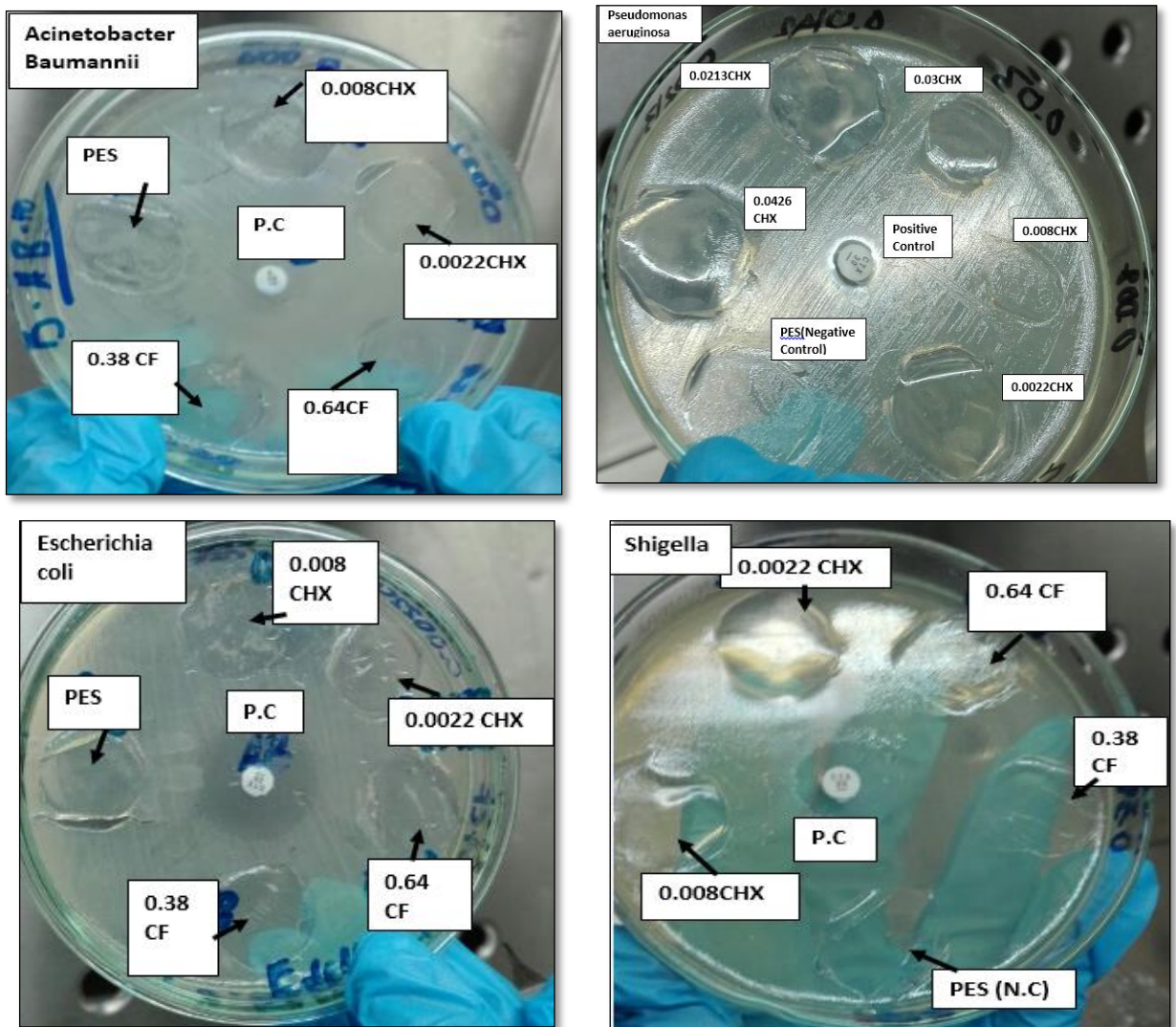


Figure 4.18 shows the anti-bacterial activity of membranes.



#### 4.12 ANTI-FUNGAL TESTING OF MEMBRANES:

After removal of the membranes (with activated side towards fungus), the clear area shows the inhibition of fungul growth by modified membranes while respective growth was observed at the bottom of PES membranes. The inhibition of fungus by membrane incorporated with chlorhexidine is clearly visible in figure 4.19. However fungus growth were observed at bottom of (Cefadroxil incorporated PES) membranes due to absence of anti-fungal activity.

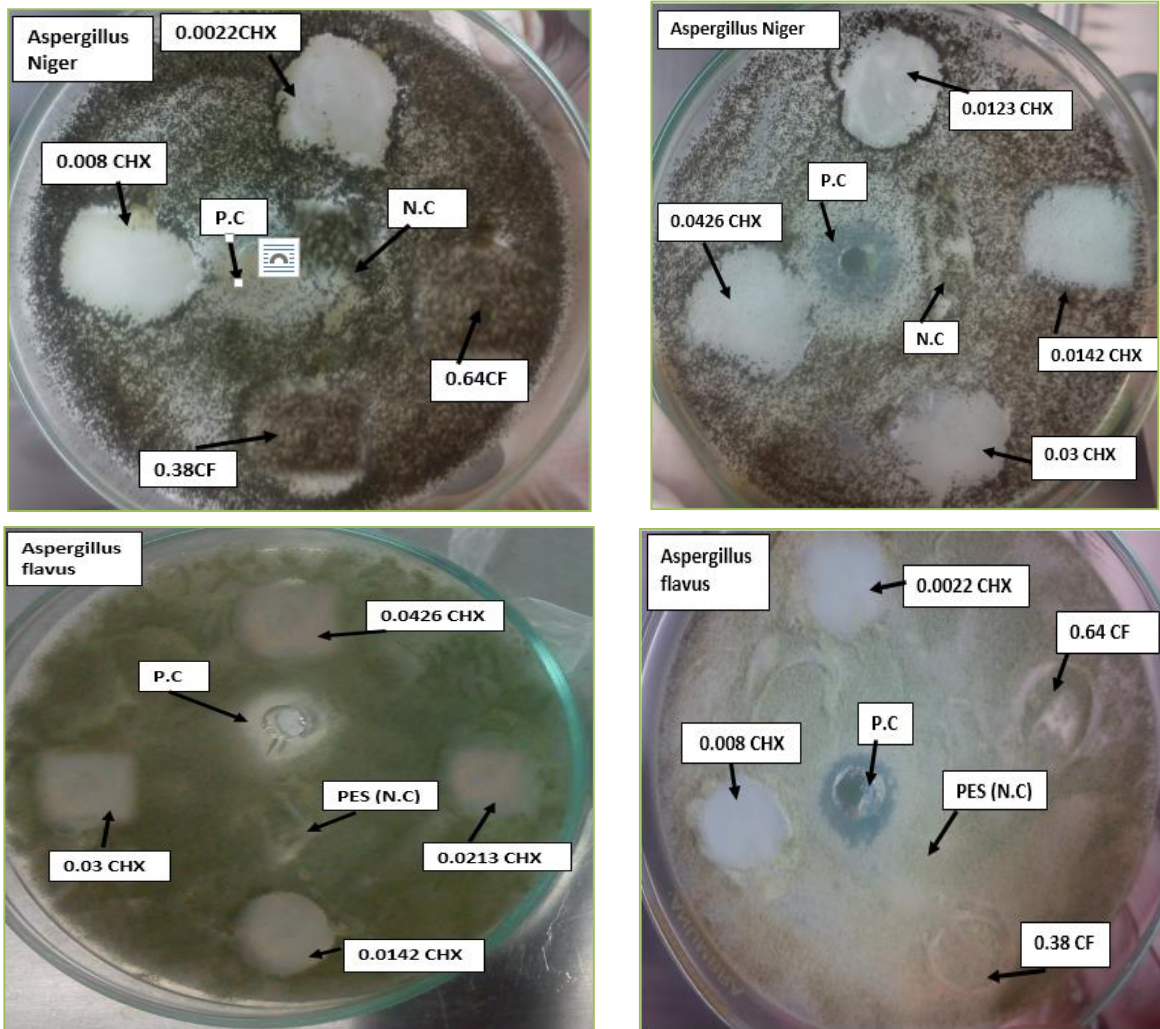


Figure 4.19 shows antifungal activity of chlorhexidine incorporated PES membranes.

#### 4.13 ANTI-FOULING EVALUATION OF SELECTED MEMBRANE:

Percentage reduction in fouling of modified membranes was calculated to be 75% as shown in the following table, which means life of membranes will be enhanced up to 3 times because of addition of Chlorhexidine.

**Table 4: Measurement Fouling Resistance of Membrane**

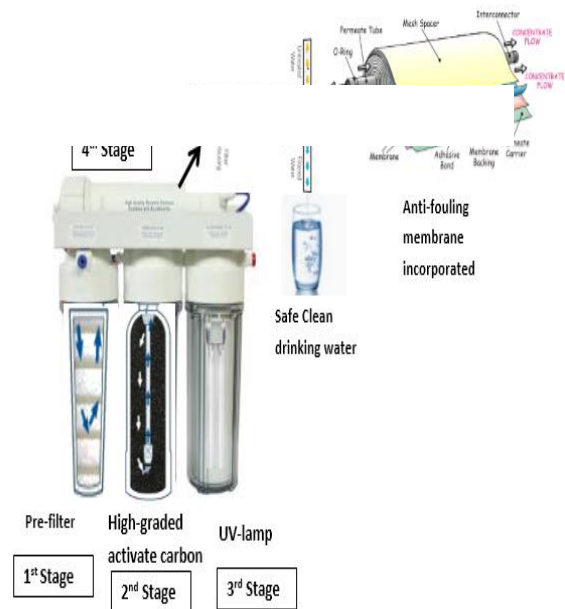
Sample	R <sub>m</sub>	R <sub>t</sub>	R <sub>f</sub> = R <sub>t</sub> -R <sub>m</sub>
PES	0.5	25.87	25.37
0.00852 CHX	1.5	7.5	6.5

$$\% \text{Reduction} = \left[ \frac{R_f(\text{PES}) - R_f(\text{CHX})}{R_f(\text{CHX})} \right] \times 100$$

$$= 75\%$$

#### 4.14 DEVELOPMENT OF MEMBRANE MODULE:

Anti-fouling membrane with highest concentration of Chlorhexidine because of its



**Figure 4.20 Membrane Filtration Module**

better results in anti-microbial tests and fouling tests was implemented within the filtration system by adding fourth stage to the traditional filtration system. The schematic and developed module is shown in figure 4.20.

**4.15 WATER QUALITY TEST:**

Permeate through the membranes was evaluated to see the quality of water being produced. This was compared to normal tap water as shown in following table:

**Table 5 Permeate Quality Testing**

Sample	PH	COD(mg/l)	BOD
PES	8.08	141	84.6
0.00852CHX	7.65	21.76	13.056
0.64CF	8.00	21.76	13.056

An improvement in PH, COD (indication amount of organic matter in permeate) and BOD (indication of microbial present in permeate) was observed.

**7.7408 COST ANALYSIS:**

Price of material of PES membrane and our modified anti-fouling membrane was compared, it was found that increase in price is only 0.6%, therefore it can be said that modified Chlorhexidine membrane provides a very cheap solution to overcome fouling.

***Conventional Membrane of PES***

**Table 6 Cost of PES Membrane**

Name of material	Cost (Rs/g or ml)	Amount Required(gm or ml)	Total cost(Rs.)
NMP	0.316	8	2.528
PES	4.1064	2	8.2128
<b>Total cost</b>			10.7408

10.7408 Rupees per membrane (Size = 25cmx5cm)

Required size for filtration plant = 25cmx50cm

Price = 107.408 Rs per membrane of standard size.

**Anti-fouling membrane:**

**Table 7 Cost CHX Membrane**

NAME OF MATERIAL	COST (Rs/g or ml)	Amount required(gm or ml)	Total cost (Rs)
NMP	0.316	8	2.528
CHX	0.31539	0.0213	6.717*10 <sup>-3</sup>
PES	4.1064	2	8.2128
<b>Total cost</b>			10.74757

10.74757 Rs per membrane (Size = 25cmx5cm)

Required size for filtration plant = 25cmx50cm

Price = 107.4757 Rs per membrane of standard size.

# CONCLUSION:

A novel approach to prevent bio-fouling of membrane has been designed that offers economic and ecological benefits compared to conventional methods.

From above results, following conclusions can be drawn;

1. The membrane surface was featured by high hydrophilicity and decreased roughness with a unique surface pattern.
2. This novel approach to prevent bio-fouling is easy to implement and the module of membrane was prepared successfully, with the significant decrease in cost as compared to commercially available systems.
3. Chlorhexidine is found to be more effective in overcoming fouling than Cefadroxil.
4. Following unique features are improved;
  - Mechanical strength
  - Flux enhancement.
  - Permeate quality due to pore size reduction.
5. In addition the antifouling evaluation shows, that the antifouling property of newly fabricated membranes is enhanced up to 75 percent.

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