



Faculty of Engineering

Incorporation of Silver Nitrate (AgNO_3) in Polysulfone-Polyethyleneimine (PSF-PEI) Membrane for Enhanced Antibacterial Properties Against *Escherichia coli* (*E. coli*)

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Incorporation of Silver Nitrate (AgNO_3) in Polysulfone-Polyethyleneimine
(PSF-PEI) Membrane for Enhanced Antibacterial Properties Against
Escherichia coli (*E. coli*)

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DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Malaysia Sarawak. Except where due acknowledgements have been made, the work is that of the author alone. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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ABSTRACT

The Polysulfone-Polyethyleneimine (PSF-PEI) hybrid membranes were successfully synthesized via wet-phase inversion method with the varying concentration of silver nitrate (AgNO_3). The objective of this research is to characterize and evaluate the performance of antibacterial membrane under various concentrations of AgNO_3 , ranging from 0.5 to 2.0 wt.%. The membrane surface morphologies were examined by using SEM and it was observed that the cross-sections of fabricated membranes showed spongy-like structure. The FTIR analysis has also illustrated some slight adjustment in the spectra due to the presence of AgNO_3 . The performance of the fabricated membranes was evaluated with regards to their porosity, membrane flux, and antibacterial activity in terms of *E. coli* inhibition. Based on the results, it was observed that the highest water flux of 22.2537 L/m².h was illustrated by CM C membrane (with 1.0 wt.% of AgNO_3), while further increment of AgNO_3 amount showed a decrement trend in water flux. The highest porosity of 70.9% was also demonstrated by CM C membrane, which could further support the high water flux findings as exhibited by this membrane. The antibacterial properties were examined using *E. coli* and the antibacterial activity was observed through the inhibition zone diameter. The best antibacterial properties were exhibited by CM E membrane (with 2.0 wt.% of AgNO_3), which was the highest available amount of AgNO_3 among all membrane samples. Hence, it was concluded that the incorporation of AgNO_3 has contributed to the membrane enhancement in terms of water permeability and antibacterial capability which are highly preferable for various industrial applications.

Keywords: Polysulfone, polyethyleneimine, silver nitrate, hybrid membrane, antibacterial properties.

Penggabungan Nitrat Perak (AgNO_3) Dalam Membran Polysulfona-Polietilenaimina (PSF-PEI) untuk Sifat Antibakteria yang Ditingkatkan Terhadap *Escherichia coli* (*E. coli*)

ABSTRAK

Membran hibrid Polysulfona-Polietilenaimina (PSF-PEI) berjaya disintesis melalui kaedah penyongsangan fasa basah dengan kepekatan perak nitrat yang berbeza-beza (AgNO_3). Objektif penyelidikan ini adalah untuk mencirikan dan menilai prestasi membran antibakteria dalam pelbagai kepekatan AgNO_3 , antara 0.5 hingga 2.0 wt.%. Morfologi permukaan membran diperiksa dengan menggunakan SEM dan diperhatikan bahawa keratan rentas membran yang dibuat menunjukkan struktur seperti span. Analisis FTIR juga menggambarkan sedikit penyesuaian dalam spektrum kerana kehadiran AgNO_3 . Prestasi membran fabrikasi dinilai berdasarkan keliangan, fluks membran, dan aktiviti antibakteria dari segi penghambatan *E. coli*. Berdasarkan hasilnya, diperhatikan bahawa fluks air tertinggi 22.2537 L/m².j digambarkan oleh membran CM C (dengan 1.0 wt.% AgNO_3), sementara kenaikan jumlah AgNO_3 selanjutnya menunjukkan tren penurunan dalam aliran air. Keliangan tertinggi 70.9% juga ditunjukkan oleh membran CM C, yang dapat menyokong penemuan aliran air yang tinggi seperti yang ditunjukkan oleh membran ini. Sifat antibakteria diperiksa menggunakan *E. coli* dan aktiviti antibakteria diperhatikan melalui diameter zona penghambatan. Sifat antibakteria terbaik ditunjukkan oleh membran CM E (dengan 2.0% berat AgNO_3), yang merupakan jumlah AgNO_3 tertinggi yang terdapat di antara semua sampel membran. Oleh itu, disimpulkan bahawa penggabungan AgNO_3 telah menyumbang kepada peningkatan membran dari segi kebolehtelapan air dan keupayaan antibakteria yang sangat disukai untuk pelbagai aplikasi industri.

Kata kunci: Polisulfona, polietilenaimina, perak nitrat, membran hibrid, ciri-ciri antibakteria

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LIST OF ABBREVIATIONS

AC	Activated Carbon
AgCl	Silver Chloride
AgNO ₃	Silver Nitrate
AgNP	Silver Nanoparticles
ANOVA	Analysis of Variance
ATZ	Aminotetrazole
FTIR	Fourier Transform Infrared
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
MWCO	Molecular Weight Cut Off
NMP	N-Methyl-2-Pyrrolidone
PDA	Polydopamine
PEM	Polyelectrolytes Multilayer
PES	Polyethersulfone
PSF	Polysulfone
PVDF	Polyvinylidene Fluoride
RO	Reverse Osmosis
ROS	Reactive Oxidation Species
SEM	Scanning Electron Microscopy
SH	Sulfhydryl
UF	Ultrafiltration
WHO	World Health Organization
WTP	Water Treatment Plant

LIST OF NOMENCLATURES

°C	Degree Celcius
CFU/ml	Colony-Forming Unit/Millilitre
cm	Centimetre
g	Gram
L/cap.day	Litre Per Capacity Per Day
L/m ² .h	Litre Per Metre Square. Hour
ml	Millilitre
MLD	Million Litre Per Day
mm	Millimetre
nm	Nanometre
ppm	Parts Per Million
s	Second
wt. %	Weight Percentage

CHAPTER 1

INTRODUCTION

1.1 Introduction

Water is an essential element in our daily life as it is the backbone, not just human beings but also to all life on Earth, due to its versatile usage and applications for various purpose such as for daily household purpose, industrial, agricultural, and domestic applications. Water scarcity and the impact of human activities on water availability is one of the major concerns nowadays and it has been a major obstacle in water and wastewater treatment industry since decades ago.

For instance, water which have not been treated carefully, i.e. a river that contains a lot of contaminants such as chemicals, grease, and oils are harmful to the human body and causes severe water pollution. Water pollution occurs when the energy and other materials are released into the water; thus, contaminating the quality of water for the consumers. The technology development is one of the factors of water pollution. Water pollution is caused by organic and inorganic industrial wastes and effluent discharge into the rivers. Hence, humans may be infected by diseases such as malaria, cholera, and typhoid whereas the life of aquatic species life will get destroyed.

Most of the countries such as Malaysia, Germany, and England tend to use chlorine for water treatment before supplying to the consumer. Generally, chlorine is used to disinfect the *Escherichia coli* (*E. coli*) that are usually found in the water due to the excretion of the feces from animals and human beings which can be caused diarrhoea if it enters into the body intestine (Carson et al., 2001). However, prolonged usage of chlorine may cause skin irritation especially for those who have sensitive skin (Kanikowska et al., 2017).

To date, there are several researches conducted for the purpose of reducing the colloidal and microbial burden of source waters as well as to ensure the water security and its cleanliness for daily usage (Basri, 2010). These studies are targeted on the effort of researching cost-effective alternative water treatment system with high treatment efficiency which could replace the existing conventional method by using chlorine, which somehow possess some imperfections (Kanikowska et al., 2017).

The water treatment system comprises of four stages which are preliminary treatment, primary treatment, secondary treatment and tertiary treatment (Tyne et al., 1992a). Preliminary treatment is the removal of course solids and other large materials found in wastewater; primary treatment is the removal portion of the suspended solids and organic water from wastewater; secondary treatment is the removal of biodegradable organic matter and suspended solids; tertiary treatment is the removal of residual suspended solids, usually by granular medium filtration or micro screens (Tyne et al., 1992b).

The process of membrane filtration and separation is known as tertiary treatment. Among all of the disinfection treatments such as chlorination, reverse osmosis (RO) system, ion-exchanged, and activated carbon adsorption, membrane filtration and separation units has appeared as one of the best methods for water filtration due to lower cost and their flexibility and selectivity when integrated with other processes (Juang et al., 2007). Besides, membrane filtration and separation could be highly preferable due to its adjustable properties based on the desired applications or targeted pollutants to be removed. Therefore, the membrane technology has been developed alongside with the advancement of recent technology.

In water treatment, membrane filtration processes are used as a solid or liquid separation technology. In this case, water is readier to be transported through the membrane than solids which are both suspended and dissolved. The efficiency to remove

macromolecules and suspended matter can be assisted with the use of biological or chemical agents that act as a coagulant and bind the material together. The tertiary water filtration such as adsorption of heavy metal by using activated carbon is easy to install and furthermore it is efficient to remove certain organics, chlorine and to be redone. Moreover, there are some integration technique of membrane with nanomaterials which are aimed to improve the separation efficiency.

According to past research, the addition of silver in the membrane also helps as an antimicrobial agent on unwanted substances can cause severe diseases such as *Poliomyelitis* and *Meningitis* to humans (Tyne et al., 1992c). Silver nanoparticles or also known as nano-silver (n-Ag) have been used in various fields such as food packaging, clothing and especially in the medical field due to its greater antimicrobial properties as compared to other metals (Burduşel et al., 2018). Nano-silver (n-Ag) is preferably used because it is conductive and chemically stable. The size of these n-Ag particles is less than 100 nm. Besides, previous study showed that n-Ag could inhibit the growth of *E. coli* (Ashmore et al., 2018). Therefore, n-Ag is one of the best choices despite its higher manufacturing costs.

With the advancement of membrane technology nowadays, a lot of studies had been performed with nanoparticles embedment in order to improve the membrane performance. Nanoparticles such as copper and silver could be used to embed on the membrane surface to enhance the antibacterial properties. According to a study by Michael Perez (2012), the higher concentration of silver nitrate affects the growth of *E. coli*. It has been proven when only 0.65% *E. coli* could survive with a concentration of silver nitrate of 2500 ug/L within 24 hours. Jung et al. (2008) claimed that silver particles are proficient to bind to the functional group of the sulphur, destabilize proteins and chemicals in terms of transport and metabolic pathway, other than reducing reactive oxidation species (ROS) that assault proteins and make harmful lasting of the structure and the function of DNA molecules, and

additionally, framing pits and gaps on the cellular surface with coordinate communication between microscopic organism cells and the silver nano-particles, turning to cellular membrane destabilization, cytoplasmic material break and morphological integrity loss.

Therefore, this research is made as an effort to broaden the potential of the fabricated membranes with various concentrations of nano-silver (n-Ag) as an additive for enhanced membrane performance against *E. coli*. The employment of hybrid membranes which consist of two types of polymers, i.e. polyethyleneimine (PEI) and Polysulfone (PSF) has appeared as potential alternative polymer combinations in comparison to past research. PSF had been widely used in membrane studies due to its low cost and availability. However, due to its solubility; it has high hydrophobicity. Therefore, N-Methyl-2-Pyrrolidone(NMP) had been used as a solvent and PEI is selected as an additive polymer to increase the membrane hydrophilicity. Hence, the incorporation of n-Ag in PSF-PEI membranes is highly desired due to the synergistic effects between PSF and PEI with n-Ag as antibacterial agents.

1.2 Problem statement

Membrane technology is one of the best techniques in producing good water quality. However, membrane imperfections are common issues in the development of membrane. Despite its environment-friendly nature and lower production costs, this technology suffers from bacterial effects and also hydrophobicity problems (Miyoshi et al., 2015). Besides, previous membrane technology had a problem with the separation efficiency due to the small membrane pores and the passage of big size particles through the membranes. Therefore, it would increase the pumping power of the small pore size membrane which in turn reduce the water permeability. The membrane performance and efficiency could be severely affected if these issues are not solved.

The major concern of this study is to resolve these issues by improving the membrane performances with enhanced separation efficiency. Hence, the research problem will develop a cost-effective low-pressure nanoparticle immobilized membrane that has similar filtration capacities of other high-pressure membranes such as ultrafiltration systems. The introduction of nanohybrid membranes has appeared as one of the popular approaches to enhance the membrane filtration performance and properties. The integration between two types of polymers which are equipped with distinct properties are highly recommended to overcome the hydrophobicity issue in membrane. It is well-known that nano-silver (n-Ag) are potential antibacterial agent for *E. coli* disinfection in water. The embedment of n-Ag is targeted for bacteria inhibition in membrane, too.

Hence, the study of PSF-PEI membrane with balanced hydrophobic-hydrophilic nature and the embedment of various n-Ag concentrations as antibacterial agents should be given more attention in the effort of researching membranes with better properties and performances in terms of antifouling and antibacterial control.

1.3 Hypothesis

The incorporation of AgNO_3 in PSF-PEI membranes is aimed to enhance the membrane performance in terms of various properties such as the water permeability, membrane porosity, antifouling and antibacterial abilities. The major contribution of this research is attributed to the excellent antibacterial properties originated from the AgNO_3 which could provide further performance enhancement in PSF-PEI nanohybrid membranes. The employment of AgNO_3 as the nanohybrid materials is aimed at enhancing the antibacterial performance of membrane due to its well-known bacterial inhibition ability in the elimination and reduction of various kinds of microbes or bacteria. The purpose of the addition of AgNO_3 as the nanohybrid functional materials in membrane development is to

enhance the membrane surface functionality due to its increased surface area with nano-size materials while simultaneously with enhanced antibacterial ability, which could significantly benefit the filtration performance of PSF-PEI membranes especially in wastewater treatment industry with severe bio-fouling issues. By utilizing AgNO_3 in PSF-PEI membranes development, the PSF-PEI- AgNO_3 nanohybrid membranes are targeted for improved membrane permeability with high water flux, membrane porosity, excellent antifouling and antibacterial properties. Hence, this research is aimed at contributing some extended findings towards the membrane development with AgNO_3 as the antibacterial agent against *E. coli*.

1.4 Objectives

This research is developed based on several important objectives towards the enhancement of PSF-PEI membrane development with the incorporation of AgNO_3 as the antibacterial agents for *E. coli* inhibition in membrane. The main objectives of this study are shown as following:

- i. To synthesize the antibacterial hybrid PSF-PEI membranes via wet phase inversion with incorporation of various AgNO_3 concentrations.
- ii. To investigate the PSF-PEI- AgNO_3 hybrid membranes in terms of surface morphology, elemental compositions and functional group alterations via Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Diffraction Analysis (XRD).
- iii. To evaluate the filtration performance of PSF-PEI- AgNO_3 hybrid membranes via performance testing in terms of pure water flux, membrane porosity and antibacterial properties against *E. coli*.

1.5 Scope of study

There are three major scopes for this study; i.e. the synthesis of PSF-PEI-AgNO₃ nanohybrid membranes, characterization of the developed nanohybrid membranes and the evaluation on membrane performance in terms of various properties via different testing.

Firstly, in the stage of membrane synthesis with PSF-PEI as the based polymers and the incorporation of AgNO₃ as the nanohybrid materials, the simple wet-phase inversion method was applied by utilizing N-methyl-2-pyrrolidone (NMP) as solvent, while powdered activated carbon (PAC) was used as additives in membranes. In this phase of membrane development, the main parameter for the experimental design was focused on the concentration effects of AgNO₃ towards the membrane performance and it was varied from 0.5 to 2.0 wt.%. The concentration of other additives and solvent were remained as constant for all experimental sets.

Secondly, the synthesized PSF-PEI-AgNO₃ nanohybrid membranes were then characterized on their surface morphologies and functional groups alterations which were resulted from the addition of different concentration of AgNO₃ in membranes. These characterizations were observed through Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Diffraction Analysis (XRD).

Finally, the membrane overall performance was evaluated according to the membrane permeability and pure water flux, membrane porosity, antifouling study and antibacterial properties against *E. coli*. Hence, the effects of various AgNO₃ concentration on the PSF-PEI-AgNO₃ membrane performance enhancement could be determined based on the performance evaluation study and significant contribution of the research on the relevant field could be identified.

CHAPTER 2

LITERATURE REVIEW

2.1 Domestic wastewater

Domestic wastewater is also known as sewage wastewater coming from many types of sources such as kitchen and bathroom, commercial institution and industrial institutions. Wastewater contains contaminated things that are very harmful to society such as malaria, Hepatitis A and diarrhea. The composition and quality of the domestic wastewater will be dependent on the daily and seasonal basis changes, with the average strength per capita water usage.

As from the perspective of physical properties, domestic wastewater is typically characterised as a grey colour mixture with musty odour and contains little amount of solid. These solid compounds could be a mixture of faeces, oil and grease, soap and detergents, sand and grit, etc. These solids can be categorized as suspended solids or dissolved solids. Amongst these solid components, suspended solids could be removed through activated sludge process while dissolved solids could be treated via chemical treatment or biological (*Domestic Wastewater Sources and Its Characteristics*, 2020).

In terms of chemically description, domestic wastewater consists of 70% of organic and 30% of inorganic compounds as well as various gases. Organic compounds are composed primarily of carbohydrates (25%), proteins (65%) and fats (10%), which reflects the diet of the people. On the other hand, inorganic components may be originated from compounds such as heavy metals, nitrogen, phosphorus, pH, sulphur, chlorides, alkalinity, toxic compounds, etc. However, since wastewater contains a higher portion of dissolved solids than suspended, about 85 to 90% of the total inorganic component is dissolved and

about 55 to 60% of the total organic component is dissolved. The common gases dissolved in wastewater are oxygen, nitrogen and carbon dioxide, while the other gases such as methane, hydrogen sulphide and ammonia are resulted from the organic matter decomposition in the wastewater.

Biologically, there is a lot of microorganisms present in wastewater such as bacteria, fungi, protozoa, and algae, plants, and animals. As for plants compounds, it could consist of ferns, mosses, seed plants and liverworts while animals refer to invertebrates and vertebrates. The wastewater treatment is particularly essential for the removal of Protista which includes bacteria, algae, and protozoa. Additionally, domestic wastewater might contain pathogenic microorganisms which are originated from humans with infectious disease. Generally, the faecal coliforms present in raw wastewater yields the concentration between several hundred thousand to tens of million per 100 ml of sample.

Therefore, the wastewater must undergo a proper treatment before it can be delivered to the users by collecting and transporting via a various network of piping and pump stations to the municipal treatment plant. There are several types of water treatment methods which are well-established and commonly reported in the literature. One of the most effective water treatment methods is with membrane filtration technology. Membrane filtration has appeared to be a promising technique to ensure a highly efficient filtration process with high contaminants removal ability. Recent advancement has been focusing on the membrane properties alteration and enhancement via various modification techniques and the utilization of different functional materials which could considerably improve the membrane performances significantly.

2.2 Overview on Membrane Separation Processes

Membrane separation is the process at microscopic level due to the presence of driving force such as pressure which allows transport of selective components through a selective barrier between two phases (Mulder, 1996). The membrane separation performance or efficiencies are very much dependent on the membrane structural properties. Generally, there are two principal types of membranes, i.e. isotropic and anisotropic membranes. Isotropic membranes consist of microporous membrane, nonporous dense membrane and electrically charged membranes while anisotropic membranes signify to Loeb-Sourirajan membranes and TFC membrane (Baker, 2004).

In membrane separation processes, there are several components which are of utmost importance as they could affect the separation efficiency significantly. First and foremost, membrane materials are one of the important criteria to enhance the membrane structural properties and strength. There is a wide range of materials such as organic or inorganic polymers, mixed matrix or composites (Ng et al., 2014). The examples of commonly used membrane materials are Polysulfone (PSF), Polyethersulfone (PES), Cellulose acetate (CA), Polyvinylidene fluoride (PVDF), and polyamide (PA) (Pendergast & Hoek, 2011). The material selection is conducted based on the desired application and customized functionality in the membrane properties such as physical, chemical, thermal and mechanical strength.

The formation of good quality membrane is very much dependent on the solvent selection, too. Lau et al. (1991) and Zhao et al. (2011) have obtained that some of the common solvents which are utilized in membrane fabrication are dimethylacetamide (DMAc), N-Methyl-2-Pyrrolidone (NMP), dimethylformamide (DMF), N,N-dimethylpropyleneurea (DMPU) and dimethylsulfoxide (DMSO). The selection of good

solvent is based on the high dissolution rate towards the membrane polymers to ensure homogeneous casting solution for membrane fabrication purpose.

Apart from that, membrane fabrication technique is also one of the essential components in the development of high-quality membranes. The fabrication methods which have been reportedly applied in membrane fabrication field, i.e. phase inversion which consists of immersion precipitation, thermally induced phase separation, evaporation-induced phase separation and vapor-induced phase separation, interfacial polymerization, stretching, track-etching, and electrospinning (Lalia et al., 2013a). The utilization of different fabrication techniques is selected based on the desired membrane applications.

Additionally, the membrane fabrication conditions are equally important to develop high quality membranes. Several factors could cause impacts on the separation efficiency. For instance, the polymer concentration, types of solvent, coagulation bath temperature and additives, etc. The polymer concentration and coagulation bath temperature appear to be the most effective factors, owing to the significant influence on membrane morphology and phase separation mechanism (Akbari & Yegani, 2012). The increment in polymer concentration would help to promote the solute rejection capability due to the formation of less porous structure (Sani et al., 2014). Besides, the coagulation bath temperature would enhance the thermodynamic stability of the polymer at higher temperature by reducing the polymer precipitation rate. Some additives were reported as good pore former and surface modifier in membrane formation process as well (Loh & Wang, 2012).

Membrane technology is known to be an advanced approach in a broad range of industries such as in water and wastewater treatment industries desalination, separation and purification processes as well as other industries like pharmaceutical industry, chemical processing industry, food industry, etc. (Van der Bruggen et al., 2008). The development of

membrane processes starts off with the microfiltration, followed by the process of ultrafiltration, membrane distillation, pervaporation, reverse osmosis and nanofiltration (Strathmann et al., 2006).

2.2.1 Development of Membrane Filtration Technology

Membrane separation process has been well-known as effective filtration technology in recent era. Table 2.1 has summarized the historical development of membrane.

Table 2.1: Historical Development of Membrane

Year	Membrane Development
1748	Semipermeable animal membranes (microporous and hydrophilic)
1803	Reuss Electro-Osmosis
1855	Fick Diffusion Collodion Membrane (first synthetic membrane)
1861	Graham Dialysis
1887	Van't Hoff Osmotic Pressure
1889	Nernst-Planck Electrolyte Transport Einstein Osmotic Pressure Henderson membrane potential
1892	Rubbery Membranes (homogeneous and hydrophobic)
1905	Donnan Membrane Equilibrium
1907	Sollner Anomalous Membrane Nitrocellulose Membrane (Graded Pore Size)
1911	Pressure Retard-Osmosis Asymmetric Cellulose Acetate Membrane
1920	Microfiltration
1930	Ultrafiltration
1950	Haemodialysis
1960	Electrodialysis Reverse Osmosis
1962	Asymmetric Membrane Schmid Pore Model

Table 2.1 continued

1965	Lonsdale Solution-Diffusion Model Composite Membrane
1970	Composite Membrane Teorell Ionic Membrane
1980	Gas Separation Membrane Distillation
1990	Pervaporation
2000-2020	Nanofiltration Membrane Bioreactors Membrane Contactors

A membrane is most commonly known as a thin film of material with selective permeability. Membrane separation efficiency is evaluated based on permeability. Membrane filtration is an essential alternative to many industrial processes due to its environmental sustainability and cost-effectiveness than other filtration technologies. The membrane itself is crucial for the process. The first commercial membranes were made of cellulose acetate which the temperatures had to be maintained below 30 °C and the pH ranges were between 3 to 6. These constraints have restricted the membrane usage due to the disadvantages of couldn't undergo heat disinfection or be acid or alkali detergents cleaning. Then during the 1970s polymeric membranes with polyamides were made but it was low tolerant to chlorine. It is estimated over 150 organic polymers have been known to be investigated for membrane applications. Membrane filtration consists of four main types which are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) as shown in Table 2.2. The driving force for these materials would then lead to the pressure-driven membrane processes.

It is reported that various membrane processes have been found in industrial applications instead of wastewater treatment such as the food industry, biotechnology, medical field, chemical industry, and energy field. In membrane filtration, a portion of fluid known as permeates (filtrate) passes through the membrane, while other retentive

(constituents) are retented by the membrane and retained in the concentrated stream. The membrane filtration mechanism is shown in Figure 2.1.

Table 2.2: Comparing Four Membrane Processes (Mulder, 2012 and Fane et al., 2011)

	Reverse osmosis	Nanofiltration	Ultrafiltration	Microfiltration
Membrane	Asymmetrical	Asymmetrical	Asymmetrical	Symmetrical Asymmetrical
Pore size (μm)	< 0.002	< 0.002	0.2 – 0.02	4-0.02
Operating pressure (bar)	15-150	5-35	1-10	<2
Membrane materials	-film composite polyamide Thin, cellulose acetate	Thin-film composite polyamide, cellulose acetate, other materials	Polymeric, some inorganic	Polymeric, inorganic
Membrane module	Tubular, spiral wound, plate and frame	Tubular, spiral wound, plate and frame	Tubular, hollow fiber, spiral wound, plate and frame	Tubular, hollow fiber
Water permeability ($\text{l m}^{-2}\text{h}^{-1}\text{bar}^{-1}$)	0.5-10	5-50	20-500	>500
MWCO (Da)	>10	>100	1000-300 000	Not applicable
Contaminant filtered	Dissolved ions, small molecules	Di- and multivalent ions, natural organic matter, small organic molecules	Polymeric, some inorganic	Polymeric, inorganic

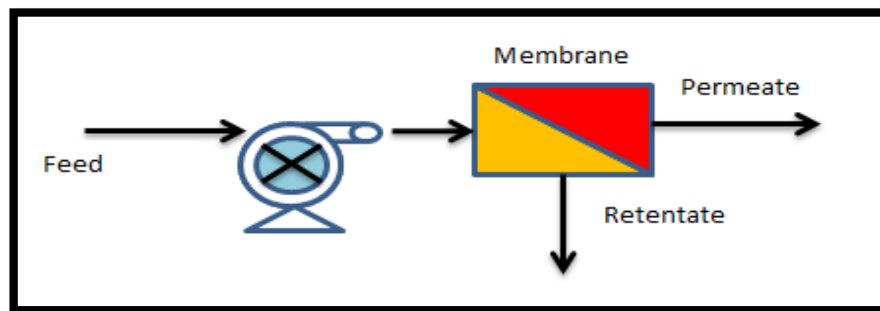


Figure 2.1: Mechanism of Membrane Filtration

Membrane filtration technology is a good advancement of technology compared to chlorination because they are usually continuous and comparatively has low energy utilization. Besides, it has a modular design and no phase changes of contaminants are required. Membrane filtration also gives a small temperature change and got a minimum of moving parts. The most important thing is it uses physical separation of contaminants compared to chlorination which uses chlorine to kill the bacteria.

Membranes are usually made up of polymer and ceramic materials. In order to obtain the best membrane separation performance, some properties such as the permeability of pure water, size of the pore, molecular weight cut off (MWCO), hydrophobicity, hydrophilicity, the charge of surface or pore, the roughness of the membrane surface and also the chemical stability must be analysed. Table 2.3 demonstrates the examples of the polymeric membrane and ceramic membranes materials.

Table 2.3: Examples of Polymeric and Ceramic Membranes.

Polymeric membranes	Ceramic membranes
Polysulfone	Alumina
Polyethersulfone	Titania
Polyphenylsulfone	Zirconia
Polyvinylidene fluoride (PVDF)	ATZ mix
Polypropylene (PP)	
Polyethylene (PE)	
Cellulose and cellulose acetates (CA)	
Polyamide (PA)	
Polyacrylonitrile (PAN)	
Polytetrafluoroethylene (PTFE)	
Polycarbonate (PC)	
Polymethylmethacrylate	

2.3 Membrane Fabrication Materials

There are several important materials needed for the fabrication of membranes. Among all, the most important materials are the types of polymers and solvents used. The right combination of polymers and solvents are relatively important and highly recommended to ensure a homogeneous dope solution which could lead to great membrane properties. In this section, there are several types of materials which are commonly reported in the literature.

2.3.1 Polysulfone (PSF)

PSF membrane is a commonly used material for UF membrane application due to its versatile chemical and mechanical properties (Eren et al., 2015). It is widely from the fabrication of artificial kidneys for blood purification to waster and water treatment as well as food and beverage processing. It has excellent characteristics such as favourable selectivity-permeability, good mechanical strength, thermal characteristics, and chemical properties (Park et al., 2016). PSF is amorphous thermoplastics and is stable at high temperatures (Ho et al., 2013). Figure 2.2 shows the chemical structure of PSF.

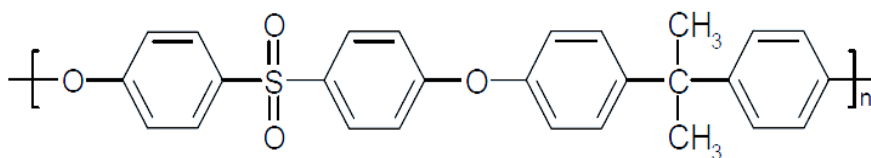


Figure 2.2: Chemical Structure of Pulysulfone (El-hibri, 2001)

PSF is excellent polymer with high chemical, thermal and mechanical stability and could tolerate high pH range (Lalia et al., 2013b). The only disadvantage is the hydrophobic nature of PSF polymer, causing them to be prone to have fouling issues. Hence, the development of PSF nanocomposite membranes had received great attention by incorporation with some metal NPs such as Co, Ni and Ag (Phelane et al., 2014). To date, there were also several studies which had investigated the incorporation of silver into PSF membranes.

2.3.2 Polyethyleneimine (PEI)

Polyethyleneimine (PEI) is a weak base, aliphatic and nontoxic synthetic polymer. It is polycationic due to the presence of primary, secondary, and tertiary amino groups. It also has a strong permeability. PEI can be used as a stabilizing agent for nanoparticles formation such as metal or metal oxide nanoparticles (Jamal et al., 2015). It is a branched chain polymer and to be used to modify membrane surface and can be incorporated on the membrane surface to use as a ligand or to supply coupling sites for different ligand immobilization. PEI has properties such as chemical reactivity and the capability of selectively adsorbing biological macromolecules (Morimoto et al., 1995). The chemical structure of PEI is shown in Figure 2.3.

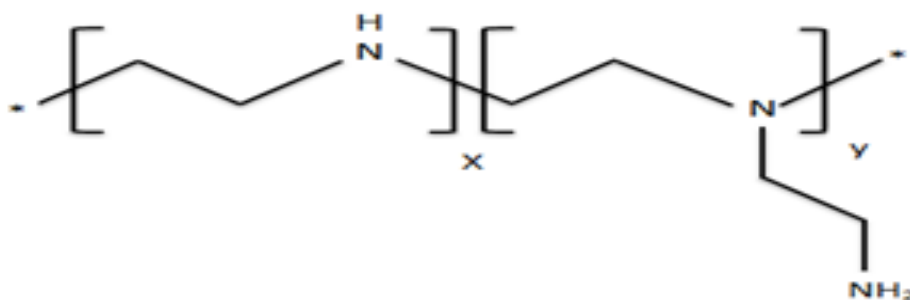


Figure 2.3: Chemical Structure of Polyethyleneimine (Ouradi et al., 2014)

2.3.3 Activated carbon

Activated carbon is well-known and has been broadly applied as effective adsorbent for the water and wastewater treatment in organic and inorganic pollutants removal (Bhatnagar et al., 2013). The properties of AC are high porosity, large surface area, well developed internal pore structure consisting of micro-, meso- and macropores, variable characteristics of surface chemistry and a high degree of surface reactivity. AC is not only used as adsorbent but also acts as catalyst for different purposes for pollutants removal and chemical purification or recovery. It tends to be expensive than other adsorbents due to high production costs (Dias et al., 2007a). AC is also commonly known as carbon-based materials and can be produced from a wide range of enriched carbonaceous materials such as wood, coal, lignite and coconut shell. Variable amounts of atoms, known as heteroatoms, can be found in AC such as oxygen, hydrogen, sulphur, and nitrogen in the form of functional groups or chemical bonding which affects carbon surface chemistry (Bhatnagar et al., 2013).

The adsorption process of AC depends on the properties of adsorbate itself such as molecular size, solubility, pKa and nature of substituents. The molecular size can affect the accessibility of the adsorbate to the carbon pores, solubility controls the degree of hydrophobic interactions between the adsorbate and the carbon surface and pKa determines controls the dissociation of the adsorbate (Dias et al., 2007b). The incorporation of AC into the polymeric membranes could add value to the existing membrane properties by providing adsorptive functions towards the membrane filtration properties which could further enhance the separation efficiency of the existing membranes.

2.3.4 N-Methyl-2-Pyrrolidone (NMP)

N-Methyl-2-Pyrrolidone is a nitrogen heterocyclic compound which is non-toxic, stable and recyclable efficient selective solvent. It is an organic compound consisting of 5-membered lactam as shown in Figure 2.4. It is a colorless liquid, although impure samples can appear yellow. It is miscible with the water and with the most common organic solvents. It is also included in the class of dipolar aprotic solvents such as dimethyl formamide and dimethyl sulfoxide. According to Mahdi Pourafshari Chenar et al. (2013), NMP was the best solvent to be mixed with Polysulfone-based nanocomposite membranes with different types of solvents such as DMAc, NMP, and THF, which differ in term of their abilities to dissolve polysulfone.

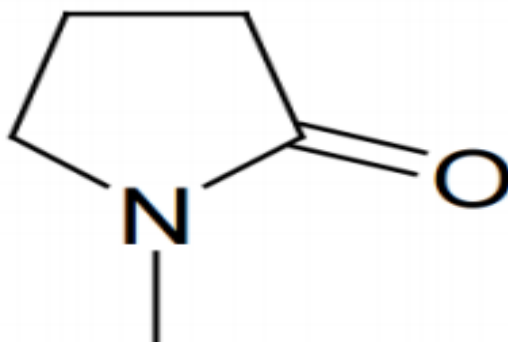


Figure 2.4: Chemical Structure of NMP (States et al., 2015)

Table 2.4: Properties of NMP

Molecular formula	C ₅ H ₉ NO
Molecular weight	99.134
Melting point	-23.60 °C
Boling point	202 °C
Flash point	890 °C
Viscosity	1.796
Ignition temperature	245 °C

2.4 Membrane Fabrication Methods

There are many techniques for membrane fabrication as reported in the literature. One of the conventional and well-established method is phase inversion, which is an immersion precipitation process. This membrane fabrication technique was first introduced by Loeb and Sourirajan during 1960s on the synthesis of asymmetric and symmetric commercial membranes (Holda et al., 2013). These fabricated membranes are commonly applied on several applications such as water and wastewater treatment (Zhao et al., 2007).

In phase inversion, it is a thermodynamic process, which converts the polymer dope solutions from liquid phase into porous solid state when solidification occurred after some period (Holda et al., 2013). There are two types of demixing process in this phase inversion process, which could result in different membrane structural properties. An instantaneous demixing which occurred in a faster rate would produce a highly porous structure with abundance of macrovoids while a delayed demixing process which converts into membrane at a slower rate could produce finger-like with spongy bottom structure layer as well as denser and thicker skin layer of membrane (Ma et al., 2011).

Apart from the types of demixing processes, the formation of membrane structures is dependent on many factors and these factors could highly affect the resulted membrane structures and performance. These factors could be the casting speed, temperature, demixing time, types of polymers, composition of dope solution, the coagulation bath condition and so forth. The inconsistencies during the membrane fabrication process could lead to the failure of obtaining membrane with good quality. Though the manual fabrication methods is lack of consistencies and accuracies, there are still many researches focusing on the effort to enhance the membrane performances in terms of external and internal properties such as

surface morphologies, membrane permeability, hydrophilicity, porosity and antifouling ability (Chakrabarty et al., 2008).

2.5 Membrane Modification Methods

As aforementioned, it is of great importance to improve the membrane properties and performances and one of the recent advances to is by performing membrane modification. It is also targeted to customize the desired membrane properties according to specific requirements in various industrial applications. Generally, membrane modification approaches can be divided into two major categories, namely grafting polymerization (which includes UV-grafting, interfacial polymerization) and nanomaterials incorporation. The following sections will be a brief description on the nanomaterial's incorporation as the modification technique.

2.5.1 Grafting Polymerization

Grafting polymerization covers a wide range of modification techniques, i.e. UV-grafting, electron beam irradiation, layer-by-layer deposition and plasma treatment. All these grafting methods are broadly applied in order to obtain enhanced membrane qualities and performances in various industrial applications. UV-grafting polymerization is the surface modification performed by the chemical bonding between membrane surface and the active layer without penetration into the bulk polymer. For instance, the UV-initiated graft polymerization used for the production of high flux positively charged NF membranes was successfully conducted (Deng et al., 2011). Besides, there were also literature on photo-grafting at different functionalization conditions such as MWCO of the base membrane, monomer concentration, cross linker fraction, UV irradiation intensity and time in the study by Zhong et al. (2012). In one of the recent researches, UV induced graft polymerization on a commercial polyamide nanofiltration membrane was achieved by varying monomer

concentrations and incorporation of carboxylated-MWCNTs (COOH-MWCNTs) (Vatanpour et al., 2019).

Additionally, electron beam irradiation is also one of the common techniques for membrane modification via the high-energy electron beam irradiation in penetrating into polymer layer. In this process, it could trigger the formation of active sites on the polymer and no special additives were required during the irradiation process. Some of the literature has reported on nylon-66 membranes which act as a typical semi crystalline polymer and subsequently could be crosslinked by EB irradiation to form NF membranes (Linggawati et al., 2009), and further improvements on the membrane performance such as excellent removal of neutral solutes and improved rejection of divalent ions were also reported (Linggawati et al., 2012). Another study by Xu et al. (2014) also proved that EB irradiation on a PSF support demonstrated high efficiency in removing hexavalent chromium, Cr (VI) ions which were mutagenic and carcinogenic (Xu et al., 2014). Recently, the fouling resistance capacity and filtration performances of commercial PVDF/PVP membrane was investigated based on the impact of electron beam irradiation in presence of zwitterions on the modification route (Nguyen et al., 2019).

On top of that, layer-by-layer (LBL) process is also one of the grafting methods for membranes modification. One of the recent researches for composite nanofiltration membranes development is via the LBL process inspired by the mussel adhesion mechanism, plant polyphenol tannic acid (TA) with abundant catechol groups and hydrophilic Jeffamine (JA) containing amino groups (Guo et al., 2020). Some of the literature also demonstrated the development of NF membranes with greater performance stability and higher salt selectivity by LbL method via modification of polyelectrolyte bilayers on the PES membranes (Ng et al., 2014). Besides, the introduction of two crosslinking methods, namely

amine coupling and silane coupling, were applied in LbL assembled NF membranes (Saeki et al., 2013).

Moreover, plasma treatment is also an effective way to modify membrane for surface hydrophilicity and wettability enhancement. One of the recent study has proposed microwave plasma of oxygen under fixed plasma conditions in order to control membrane porosity level for water treatment application (Naz et al., 2020). It is an advantageous method for membrane physicochemical properties alteration without changing the bulk properties. One of the recent study demonstrated that Ar/O₂ plasma treatment as a greener alternative of CNT functionalized membranes for selective removal of contaminants from water (Ali et al., 2020). There was also a study reported on the surface wettability modification of poly (vinylidene fluoride) copolymer films and membranes by plasma treatment, which has successfully decreased the mean surface roughness of membranes (Correia et al., 2019).

Despite the advance in membrane development nowadays, there are still some limitations to achieve greater membrane characteristics. Common challenges or issues are the production of membrane with enhanced antifouling properties and simultaneously high permeability rate as well as good physical and chemical properties. A variety of membrane modifications methods are introduced for this purpose, including interfacial or grafting polymerization and nanomaterials incorporation (Mohammad et al., 2015). The enhancement of membrane structural properties could be done by performing modifications such as the employment of additives like organic materials which includes hydrophilic or amphiphilic polymers and inorganic nanomaterials (Ahmad et al., 2013). Hence, there is stillroom of improvement in the development or invention of new fabrication or modification techniques to ensure more progressive membrane production with excellent performances.

2.5.2 Nanomaterials Incorporation

Nanomaterials have attained considerable attention in recent decade due to their outstanding properties in terms of antimicrobial photoemission and catalytic activity. The integration between membrane technology and nanotechnologies has gained tremendous interest in the recent decades for various purposes (Pendergast & Hoek, 2011). The incorporation of nanomaterials in membrane fabrication is aimed in producing excellent membrane qualities in terms of permeability, rejection capability and fouling propensity in addition to excellent physical properties such as mechanical and thermal stabilities.

Recently, there are many reviews or researches, which have employed the embedment of metal/metal oxide nanomaterials into polymeric membrane fabrication. This is mainly attributed to the flexibility to alter and customize the targeted quality of membranes under various field of applications such as water and wastewater treatment purposes (Yin & Deng, 2015). Besides, the most recent developments and shortcomings of metal nanocomposite PSF and PES membranes had been reviewed for wastewater treatment (Richards et al., 2012). The membranes embedded with NPs had performed well in terms of fouling reduction (Kochkodan & Hilal, 2014; Lau et al., 2012; Richards et al., 2012). The usage of inorganic nanomaterials has been widely practiced in various industries due to its non-toxic advantage (Hajipour et al., 2012). Besides, there are many types of nanomaterials which are reportedly used in membrane fabrication, for instance, silica, titanium dioxide, silver, polyaniline, zinc oxide and some other combination of nanomaterials.

The following sections are discussing on some of the past researches on different types of nanomaterials and followed by the specific literature on the silver nanomaterials.

Silica or silicon dioxides are metal oxides equipped with great abrasion resistance, large surface area, great chemical properties and thermal stability as well as good electrical insulation. Silica could be embedded in membranes via IP technique as per reported in the study of novel synthesis of polyamide nanocomposite membranes (Jadav & Singh, 2009). A few studies were reported on the impregnation of SiO₂ NPs in membrane fabrication via various approaches and polymers such as the incorporation of silica for the enhancement of tensile strength and surface hydrophilicity due to the presence of hydroxide radicals and improve membrane fouling resistance (Ng et al., 2013), the novel synthesis of composite SiO₂ NF membrane for oily wastewater desalination (Jin et al., 2012), the application of amino-functionalized silica with polyetherimide in TFC nanofiltration membrane (Namvar-Mahboub & Pakizeh, 2013), the production of NF membrane with polypiperazine-amide and silica on a PES support (Hu et al., 2012), while another nanomaterial being applied in TFN membrane was MCM-41 silica, a type of mesoporous silica developed (Yin et al., 2012).

Besides, titanium dioxide (TiO₂) is a versatile nanomaterials with excellent photocatalytic effect and hydrophilic properties (Kim et al., 2005) and had gained rising attention in membrane applications. The pioneer development of PES/TiO₂ composite membranes was investigated with the employment of Rutile TiO₂ in PES membranes (Wu et al., 2008). There were also several studies by then such as TiO₂ embedment in PVDF membranes via different approaches (Li et al., 2009), the preparation of PVDF membranes with the polyacrylic acid (PAA) functionalized TiO₂ through in situ grafting polymerization (Madaeni et al., 2011), the PVA/PES/TiO₂ thin film nanocomposites membranes (Pourjafar et al., 2012), TiO₂/PES-blended membranes for water flux improvement and excellent antifouling properties (Vatanpour et al., 2012), the production of PVDF/ TiO₂ mixed matrix membrane via in situ colloidal precipitation technique (Teow et al., 2012), the development

of PA-TFN membranes with aminosilanised TiO_2 NPs (Rajaeian et al., 2013), functionalization of TiO_2 membranes with immobilized laccase also received rising attention due to its excellent bio-catalytic performance (Hou et al., 2014).

Zinc Oxide (ZnO) are nanoparticles with versatile physico-chemical properties with great thermal, mechanical and chemical stability as well as great photo stability (Kołodziejczak-Radzimska & Jesionowski, 2014). Owing to its low toxicity, biocompatibility and biodegradability, it has great potential in biomedicine and in pro-ecological systems. The piezoelectric and pyroelectric properties of ZnO are also suitable to use in sensors, converters, energy generators and photo-catalyst for hydrogen production (Vaseem et al., 2010). Besides, there is also some remarkable enhancement obtained from the usage of ZnO in membrane application such as the study of membranes with ZnO exhibited high reusability with satisfactory permeation rate although after repeatable utilization (Rajabi et al., 2015), ZnO-membrane research with the introduction of RSM to determine significant parameters during the ZnO-membrane preparation process (Ahmad et al., 2016) and PSF membranes impregnated with photocatalytic nanomaterials (TiO_2 , Mn- TiO_2 and ZnO) for humic acid removal (Ng et al., 2016).

On the other hand, there are also some other nanomaterials such as Polyaniline (PANI) which is also used as polymeric additives in membrane industry (Teli et al., 2012) due to its conductive properties with high chemical durability. Several studies reported on the application of PANI such as oligomers and nanospheres in PSF nanocomposite membrane (Zhao et al., 2011) and the preparation of PES/PANI membranes via optimization approach, RSM (Razali et al., 2013). Some other nanomaterials which were employed in membrane applications are synergistic $\text{TiO}_2/\text{Al}_2\text{O}_3$ for hydrophilic composite membrane (Mendret et al., 2013), integrated polyaniline and iron oxide (III) $[\text{PANI}/\text{Fe}_3\text{O}_4]$ prepared by in situ chemical oxidative polymerization (Daraei et al., 2013), hydrous manganese dioxide

in PES membrane fabrication (Jamshidi Gohari et al., 2014). Moreover, there are also other variety of nanomaterials introduced for membrane application such as electrospun nanofiber (Bui et al., 2011), functionalized multi-walled carbon nanotubes (Vatanpour et al., 2014), halloysite nanotubes (Zhu et al., 2014), surface functionalization of graphene oxide (Mahmoud et al., 2014), and GO-nanohybrids (TiO₂-GO, SiO₂-GO and Ag-GO) served as excellent nanofillers with enhanced distribution in the membrane matrices in desalination and water purification process (Ali et al., 2016; Hegab & Zou, 2015). With the utilization of these functionalized nanomaterials in membrane fabrication, it could lead to a major improvement of membrane performance can be achieved soon.

2.6 Membrane Incorporation with Silver Nanomaterials

Silver (Ag) nanomaterials is non-toxic which is environmentally friendly, chemically stable and well known for its superb antibacterial capacity. The great antibacterial ability exhibited by Ag ions could be demonstrated via a broad spectrum of antimicrobial activities which could damage the bacterial cells and interrupt the electron transport chain (Mollahosseini & Rahimpour, 2013). The application of Ag nanomaterials offers a potential alternative in solving bio-fouling issues in membranes industry.

The pioneer development of Ag nanomaterials in membrane fabrication was initiated by Taurozzi et al. (2008) in the investigation of the effects of fabrication conditions such as nanofillers incorporation route and porosities onto the membrane's performance (Taurozzi et al., 2008). This study was then further extended by Zodrow and co-researchers (2009) with the employment of Ag nanomaterials in PSF membranes and the membranes have excellent antiviral properties against *E. coli* K12 and *P. mendocina* KR1 (Zodrow et al., 2009). Furthermore, there was a study on Ag nanoparticles incorporation in an acrylamide layer grafted on a PES hollow fibre membranes, have proven that Ag nanoparticles has great

antibacterial capability (Sawada et al., 2012). Additionally, the synthesized PSF-Ag membranes could be applied in protein and carbohydrate filtration tests (Koseoglu-Imer et al., 2013). The study by Andrade et al. (2015) had shown the comparison between direct dispersion of Ag nanomaterials into casting solutions the in-situ synthesis of Ag (Andrade et al., 2015). Apart from that, there were also researches which reported on the integration between Ag with other materials which could further amplify the antimicrobial quality of Ag nanomaterials (Huang et al., 2016).

In consequences to the significant contribution and versatile properties originated from the silver nanomaterials, there is variety of researches expanded from the previous development. These research works which involved the usage of silver nanomaterials in membrane applications such as the following are developed: Anisotropic silver immobilized PSF-based membranes for sulfate rejection (Little Flower et al., 2019), the usage of silver-nanoparticles in nanocomposite membranes for pervaporation of ethanol–water mixture (Selim et al., 2019), the integrated silica-silver nanoparticles hollow fiber membranes for pharmaceutical wastewater treatment (Behboudi et al., 2018), silver-deposited polyamide layer of thin film composite membranes by plasma-enhanced magnetron sputtering for effective antifouling strategies (Hirsch et al., 2019).

In the recent development of silver nanomaterials incorporated membranes for the enhancement of antibacterial effects, there are significant contribution on the bacterial response according to exposure of varied sized silver nanomaterials reported for *Pseudomonas aeruginosa* PAO1 (PAO1) with the application of spherical silver nanoparticles and fibrous silver nanorods (Lu et al., 2020). Besides, there are several studies focusing on the impact of antibacterial effect reported as following: enhancement of bactericide activity of silver nanoparticles/silver ion exchanged zeolites in cellulose acetate

nanofiltration composite membranes (Beisl et al., 2019), the new greener alternative silver nanoparticles (AgNPs) on commercialized polycarbonate membrane for the enhancement of antibacterial effect (Sackey et al., 2020), the integrated of UV irradiation in the sterilization of silver-functionalized PVA membranes to maintain their antibacterial functionality (Chen et al., 2020).

As aforementioned, there are many on-going researches with the application of either solely Ag nanomaterials or the integration of Ag with other functional materials as the continual efforts in achieving significant advancement in terms of the membrane structural properties as well as the membrane performances.

2.7 Silver for Antibacterial Applications

Silver are well known for its great antibacterial properties and are highly favorable in many types of applications with regards to bactericidal or biofouling issues. In this section, brief introduction on the common usage of silver ions and silver nanoparticles in terms of antibacterial properties towards *E. coli* were presented.

2.7.1 Silver ions

Silver has been used as a prevention of disease for many countries. It is the most antimicrobial of all metals compared to other metals which are mercury, copper, and lead. The excellent antimicrobial properties exhibited by silver and most silver compounds is attributed to the oligodynamic effect and are toxic for most of the bactericidal components such as bacteria, algae, and fungi in vitro. The antibacterial activity of silver is highly dependent on the silver ions, in which the antibacterial effectiveness is based on the ability of the biologically active silver ion (Ag^+) to irreversibly destruct the key enzyme systems in pathogens' cell membranes. Besides, the antibacterial performance of these silver ions could

be further enhanced under the presence of an electric field due to the impact of silver released into the bacteria culture. Table 2.3 shows literature of diversity of microorganisms inactivated by silver ions and/or nanoparticles.

Table 2.5: Survey of Literature on Microorganisms Inactivated by Silver Ions and Nanoparticles.

Microbe type	Microbe species	Form of Ag	Reference
Bacteria	<i>Eschericia coli</i> (<i>E. coli</i>)	Ag ⁺ ions	(Jung et al., 2008) (Berger et al., 1976)
		AgNPs	(Morones et al., 2005) (Kv1 & Vec, 2006)
		Ag – activated carbon fibers	(Rehabilitation et al., 1998)
		AgNP – granular activated carbon	(Bandyopadhyaya et al., 2008)
		AgNP rice paper plant stem	(Zeng et al., 2007)
		AgNP ceramic beads	(Gong et al., 2007)
		AgBR NP polymer composite	(Vigneshwaran et al., 2007)
		Ag ⁺ ions in ceramics	(Loher et al., 2008)
		Polyethersulfone membranes with AgNPs in multilayer	(Diagne et al., 2012)

2.7.2 Silver nanoparticles (AgNPs)

Silver nanoparticles are crystalline particles of Ag metal with at least one dimension between 1 to 100 nm. Silver nanoparticles measurements are typically measured 25 nm. AgNPs can have a spherical prism, cubic or rod-shaped morphologies. AgNPs are the noble metal nanoparticles that have been studied extensively due to its various biological properties. Due to the properties of silver at the nano level, nanosilver is currently used by an increasing number of consumers and in medical products. AgNPs are non-ionic and have no history of being harmful to the environment and aquatic life (Akter et al., 2018).

2.7.3 Antibacterial mechanism of silver nanoparticles towards *E. coli*

AgNPs can be synthesized through two types of approaches which are chemical approaches and biological approaches (Chauhan et al., 2013). Synthesis of AgNPs by bacteria; *E. coli* are known as biological approaches. Silver is a non-toxic, safe inorganic antibacterial agent used for centuries and it has the capability of killing different types of diseases caused by microorganisms. The remarkably strong antimicrobial activity is the major reason for the recent increase in the development of products that contain nanosilver. The antibacterial activity of silver nanoparticles is most effective against *E. coli*. The mechanism of growth inhibition is related to the formation of free radicals from the surface of the silver. According to Beenarjee et al. (2004), the AgNPs inhibit antimicrobial activities against *E. coli* by injecting AgNO₃ solution into a petri dish containing agar and *E. coli*.

2.7.4 Bactericidal Action of Silver Ions/Nanoparticles

The antibacterial action of silver nanoparticles could be explained based on several types of mechanism. Generally, the most common mechanisms which are reported in the literature are as follows: the uptake of free silver ions followed by disruption of ATP production and DNA replication, generation of reactive oxygen species (ROS) and direct cell membrane damage (Marambio & Hoek, 2010). These are some of the common antibacterial mechanisms reported thus far in the literature.

In the first stage of silver ions uptake, these silver ions could interact with the thiol groups which are commonly found in many important enzymes and resulted in the deactivation of these enzymes. It would then affect the uncoupling of respiration from ATP synthesis when the silver ions encounter enzymes of the respiratory chain reaction (Prabhu & Poulose, 2012). The silver ions which were bounded with transport proteins could induce proton motive force collapse due

to the proton leakage. Moreover, DNA mutation frequencies increased during polymerase chain reaction (Marambio & Hoek, 2010).

Apart from that, the reactive oxygen species (ROS) which were produced from the metabolism of respiring organisms could result in oxidative stress and the formation of free radicals have the ability to attack membrane lipids and damage the bacterial cell (Marambio-Jones & Hoek, 2010; Prabhu & Poulouse, 2012). This phenomenon was also attributed by the impairment of respiratory chain enzymes through direct interaction of silver ions with thiol groups or through photo catalytically.

Additionally, silver nanoparticles or ions could accumulate onto the membrane cell surface or through the penetration into the bactericidal cells, which could result in structural changes in the cell membrane and induced the formation of pits on the cell surface. It was also known that the interaction between bactericidal cell and silver nanoparticles was due to the presence of electron static attraction. This was due to the negative charge originated from the cell membrane which was attracted towards positive charge silver. The permeability of bactericidal cell membrane would then increase when silver nanoparticles were attached to the bactericidal cell membrane (Marambio-Jones & Hoek, 2010).

2.7.5 Advantages of Antibacterial Membrane

Owing to the excellent antibacterial properties as illustrated by silver nanomaterials, it was highly preferable to embed Ag nanomaterials into the membrane structures in order to achieve greater enhancement in terms of membranes' antibacterial capability especially for industries which faced biofouling issues. As aforementioned, the silver antibacterial mechanism could assist in the disruption of bactericidal cell wall membrane which could then enhance the antibacterial efficiency. Therefore, the immobilization of these antibacterial agents into polymeric membrane structures could give a positive impact on the membrane

performance in terms of biofouling control, which could provide dual functions in terms of filtration and disinfection purpose, simultaneously (Basri et al., 2011).

2.8 Summary

As a major resource, the amount of water that can be supplied to the customer depends on water treatment plant capacity available in the state. Water treatment methods are selected based on the types of impurities or contaminants which are to be removed. The conventional water treatment method focuses on the removal of heavy metal while other methods are explored for the removal of other impurities. Membrane technology has appeared as one of the potential water treatment method due to the advantage of being flexible in terms of targeted filtrates. The membrane filtration performance was highly dependent on the membrane structural properties as well as the functional additives that are incorporated into the membrane.

In this study, the functional materials which are immobilized into the PSF membrane structures is silver nitrate nanoparticles. The purpose of this material selection is possibly attributed to its superior antibacterial capability which could serve as antibacterial agent in the membrane filtration process. The varying concentrations of silver nitrate was manipulated in order to evaluate its effects onto the membrane performances in terms of membrane permeability and antibacterial properties. Additionally, the additional of functional materials such as PEI and AC is aimed to improve the membrane hydrophilicity and adsorptive functionalities. Hence, it is highly recommended to perform the investigation on the silver nitrate concentration effects towards the membrane performances enhancement in various aspects.

CHAPTER 3

METHODOLOGY

3.1 Introduction

The experimental procedures and methodology for this study were presented in this chapter. The membrane fabrication procedures for this study was also discussed. The equipment used in the characterization of the membrane with several characterization analyses was stated and the procedures for the membrane performance testing was described in detail.

3.2 Materials

Polysulfone (PSF) pellets with an average of M_w^* of 35,000 and polyethyleneimine (PEI) branched solution (50 wt.% H_2O) (PEI) with an average of M_w^* of 25,000 respectively supplied by Sigma-Aldrich (USA) were used as polymers for membrane synthesis. The solvent used for membrane fabrication was N-Methyl-2-Pyrrolidone (NMP), which was supplied by Sigma-Aldrich (USA). Palm kernel activated carbon (PAC) in powder form which served as adsorbent was added as an additive in this study. The nanohybrid materials were formed using silver nitrate ($AgNO_3$, 98%), sodium hydroxide (NaOH, 0.1M) and ethanol solutions, which were obtained from Merck. The utilization of Luria-Bertani broth and agar acquired from Sigma-Aldrich were used to grow and culture bacteria for membrane antibacterial properties' characterization.

3.3 Experimental Design

The experimental design for this project was depicted in Figure 3.1. This study would focus on the investigation of the effects of silver nitrate ($AgNO_3$) addition in membrane morphology and the evaluation of synthesized membrane in the aspects of antibacterial

properties and water flux. The flow of the experimental methodology was represented in Figure 3.1.

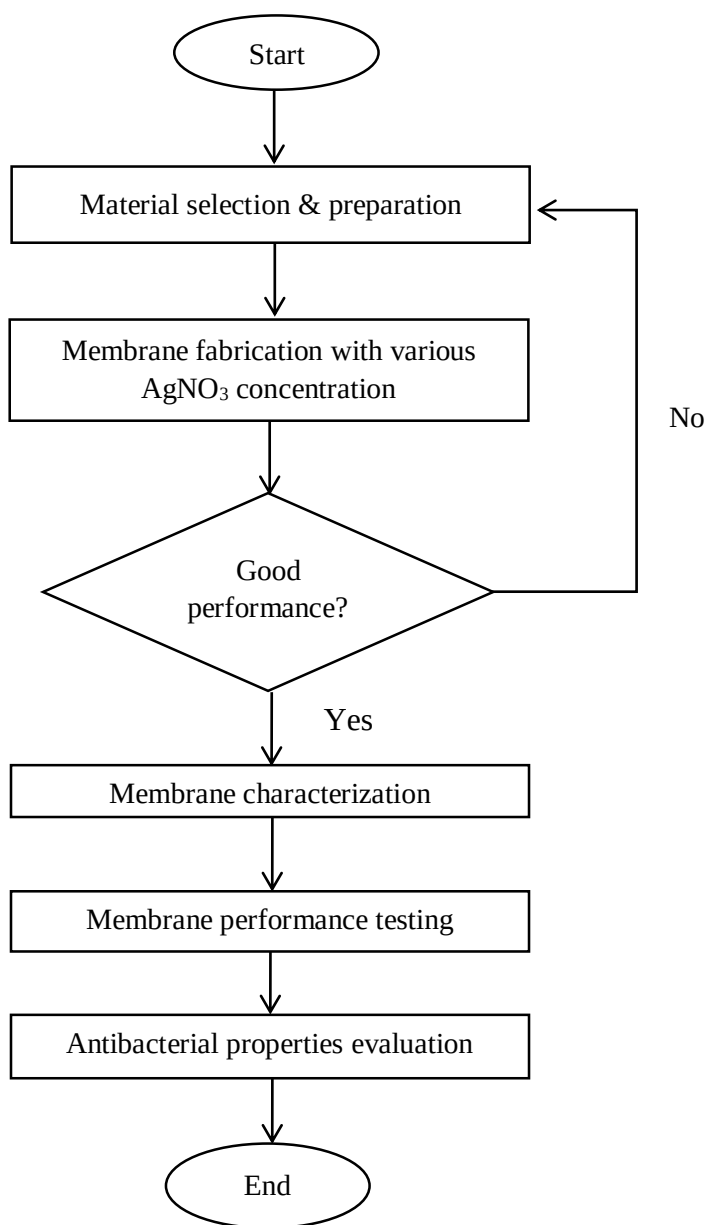


Figure 3.1: Flowchart for Experimental Procedures

3.4 Preparation of Membranes

The PSF-PEI nanohybrid membranes in the form of flat sheet were prepared by using phase inversion technique with the incorporation of AgNO_3 as the functional nanomaterials as well as other additives such as PEI and PAC. The combination of these functional additives was targeted to further enhance the membrane performance with respect of water flux, membrane porosity and the antibacterial capability towards *E. coli*.

3.4.1 Membrane Fabrication and Casting

The major goal of this study was the investigation of the best composition of the antibacterial hybrid membrane, with the incorporation of silver nitrate (AgNO_3) ranging from 0.5 to 2.0 wt.% in the hybrid membrane structures. The main polymers selected for fabrication of membrane were polysulfone (PSF) with an additional polymer of polyethyleneimine (PEI) at 0.3 wt.% to provide hydrophilicity properties in the fabricated membranes. Besides, the solvent used to dissolve the polymers was N-Methyl-2-Pyrrolidone (NMP) and 0.5 wt.% of powdered activated carbon (PAC) was used as an additive which acted as adsorbent. The polymer (PSF) to solvent (NMP) ratio was set at 15:85 and the nanomaterials (AgNO_3) percentage were varied in the range of 0.5 to 2.0 wt.% during the membrane fabrication as shown in Table 3.1. All the composition for each set of membrane were stated in Table 3.1 and the detailed calculation was presented in Appendix A.

Table 3.1: Composition of Membrane

Type of membrane	Composition (wt.%)				
	AgNO ₃	PSF	PEI	NMP	PAC
CM A	-	15.0	-	85.0	-
CM B	0.5	15.0	0.3	83.7	0.5
CM C	1.0	15.0	0.3	83.2	0.5
CM D	1.5	15.0	0.3	82.7	0.5
CM E	2.0	15.0	0.3	82.2	0.5
CM F	-	15.0	0.3	84.2	0.5

Before the dope solution was prepared, the PSF polymer and the adsorbent, powdered activated carbon (PAC) were put into an oven (Brand: Panasonic MOV Laboratory Oven) to remove the moisture content for 24 hours. In this stage, a flat sheet form of the PSF membrane was fabricated through a wet phase inversion method. Around 15.0 g of PSF was mixed with NMP (85.0 ml) in a 250 ml beaker as shown in Table 3.1 to obtain a pure PSF membrane solution without any additives, which was denoted as CM A. The mixture was then mechanically blended for 8 hours to form a homogenous solution at 60 °C as shown in Figure 3.3. The lid of the container was kept closed with aluminium foil to prevent the solvent evaporation during the stirring process of polymer solution.

Apart from that, for other composite membranes (CM B to CM E) with the variation of AgNO₃ as the major effects onto the membrane performance, after mixing of PSF and NMP, the other materials such as AgNO₃, PEI, and PAC were added into the solution according to the amount as tabulated in Table 3.1. The concentration of PEI and PAC were kept constant and only the amount of AgNO₃ was varied from 0.5 to 2.0 wt.% with slight adjustment on the amount of NMP to dissolve the nanohybrid materials. Besides, there was

also a control set of membrane with the presence of PEI and PAC but without any AgNO_3 addition in the membrane mixture (CM F).

Next, the homogeneous membrane dope solution was casted on a 210 mm x 297 mm glass plate with a casting blade. The membrane was left under evaporation for one minute and the membrane with glass plate was immersed in a water bath at room temperature to ensure a complete phase separation. After that, the flat sheet membrane was rinsed for three times in the coagulation bath (2.5 litres of distilled water) in order to remove the solvent and was dried at room temperature for a day; 24 hours. Figure 3.2 shows the fabricated membrane in the form of a flat sheet on a glass plate after the phase inversion occurred.

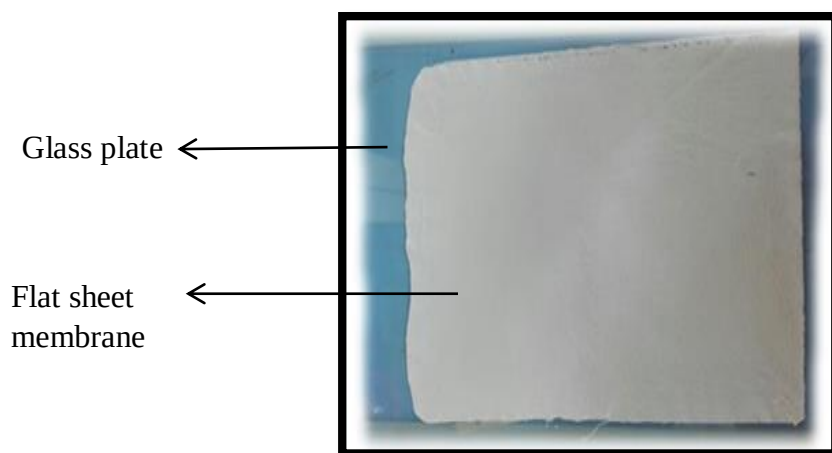


Figure 3.2: Fabricated Membrane

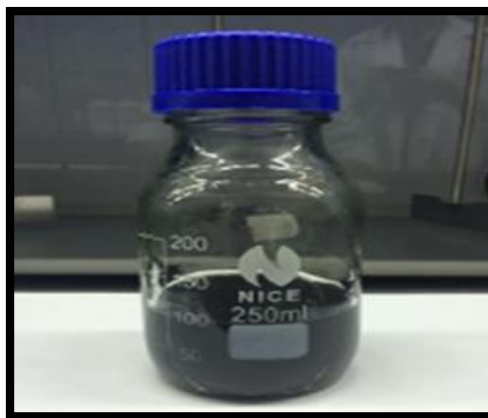


Figure 3.3: Membrane Dope Solution

3.4.2 Post treatment

After the completion of phase inversion process, the fabricated membranes were then placed in a container containing ethanol for post-treatment. In this phase, the excess solvent on the surface of membrane could be removed. Then, the synthesized membranes could dry at room temperature for 1 day. After that, the membrane which was cut at the size of 44.5 mm (radius) as shown in Figure 3.4 were ready to be tested with several characterization and performance testing.

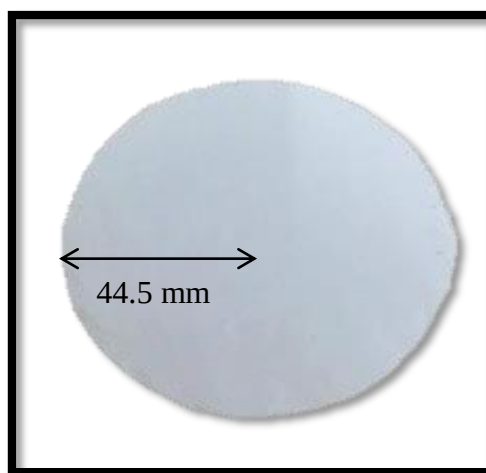


Figure 3.4: Size of Membrane for Characterization and Testing

3.5 Membrane Characterization

Once the PSF/PEI/NMP/AgNO₃/PAC membranes had been fabricated, they were characterized by using Fourier Transfer Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) analyses.

3.5.1 Fourier Transform Infrared (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) (Bunker Equinox 50) examination was utilized to determine the presence of functional groups in the nanohybrid membranes

containing a diverse measures of silver loadings. A small portion of the composite membranes (1 cm x 1 cm) were required in this analysis. The FTIR spectrum was analysed in the range 4000 to 400 cm^{-1} with 40 scans for each sample and 4 cm^{-1} resolutions. The wavelength transmittance value represents the functional groups in the membranes.

3.5.2 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is an imaging technique used to determine the membranes' surface and cross-sectional structural morphology, which utilizes a high-energy beam of electrons in the production of a raster scan pattern. During the scanning analysis, the interaction between electrons with the atoms from the sample could produce signals on the samples' information in terms surface and cross-section morphologies.

The surface and cross-section morphology of the prepared membranes were examined by using SEM, supplied by JEOL, Japan (Model JSM-6390LA) operating at 15 kV. The composite membrane samples which were cut to a size of approximately 1 cm^2 were then immersed in liquid nitrogen for one minute and fractured cryogenically to provide even surface breakage on the membrane samples.

The cracked membrane samples were then attached to a sample holder followed by a coating process with a thin layer of gold under vacuum for 20 seconds using an Auto Fine Coater (JOEL JFC 1600, Japan). The top surface and the cross-sectional morphology were then evaluated. The average pore size of the membrane surface was manually measured from the SEM analysis.

3.5.3 X-ray diffraction (XRD)

X-ray diffraction is an all-around analytical technique to scan crystalline solids, which include metals, ceramics, geological materials, organics, polymers and electronic

materials. Depending on the desired measurement such materials may be single crystals, sheets, powders, fibers, multilayer thin films, or erratic shapes. X-ray diffractometers are of two types: single-crystal and powder. Single crystal diffractometers are normally used to find the molecular structure of new materials. Powder diffractometers are usually used for phase detection, quantitative phase analysis and used for many applications, including texture and stress analysis, grazing incidence diffraction, variable-temperature studies and reflectometry. The theoretical basis of X-Ray diffraction is on Bragg's Equation; Equation 3.1.

$$n\lambda = 2d \sin \theta \quad \text{Equation 3.1}$$

where, n is (an integer 1, 2, 3, etc) known as the order of reflection, d is the distance between successive planes and θ is the glancing angle (the angle between the direction of the incident beam and the planes) and λ is the wavelength. Constructive interference occurs and diffracted intensity is obtained when the path length in the crystal ($2d \sin \theta$) is a multiple of the wavelength. Overall, the d -spacing is a function of the angles (α , β , γ) and lattice parameters (a , b , c) defining the unit cell, and the Miller indices (h , k , l) denote a particular reflection.

X-ray diffraction analysis of the membrane was done by X-ray diffractometer equipment (Model Philips PW 1710, UKM) with a Cobalt target at 40 kV in $(10-80)^\circ 2\theta$ values. Adsorbent sample was prepared by compressing in the cassette sample holder without any adhesive substances.

3.5.4 BET (Membrane's Surface Area)

The Brunauer, Emmett and Teller (BET) (Autosorb iQ-MP, UNIMAS) gas adsorption theory is generally used to determine surface area in high specific surface materials. The method depends upon finding the volume of a gas required to form a unimolecular adsorbed layer (monolayer) on the solid. These days the S-shaped BET isotherm is extensively applied and the BET; Equation 3.2 can be tested by writing it in the linear form as:

$$\frac{p}{V(p_0 - p)} = \frac{1}{V_m c} \cdot \frac{c - 1}{V_m c} \cdot \frac{p}{p_0} \quad \text{Equation 3.2}$$

Where V is the volume of gas adsorbed under pressure p , p_0 is the saturated vapour pressure at the same temperature. V_m is the volume of gas adsorbed when the surface is covered with a monolayer and c is a constant for a given adsorbate. So a plot of $\frac{P}{V(P_0 - P)}$ versus $\frac{P}{P_0}$ gives a straight line with slope equal to and intercept as $\frac{1}{V_m}$. Hence, from the slope and intercept the two constants V_m and c can be calculated. The former is the volume of the gas necessary to form a monolayer and is used.

To calculate the specific surface area of the adsorbent using molecular area a_m , the average area occupied by a molecule of the adsorbate in the completed monolayer.

The specific surface area can be calculated by using the following relationship Equation 3.3;

$$S_{BET} = a_m \cdot N \cdot V_m \quad \text{Equation 3.3}$$

Where N is Avogadro's number.

If the monolayer capacity is expressed in volume of gas adsorbed (reduced to NTP) per gram of the adsorbent, and a_m is expressed in nm^2 per molecule, then Equation 3.4.

$$S_{BET} = \frac{V_m}{22400} \cdot N \cdot a_m 10^{-19} \text{m}^2 \text{g}^{-1} \quad \text{Equation 3.4}$$

According to the classical BET method, the specific surface area of the adsorbent is regularly measured by adsorption of nitrogen at 77K using molecular area a_m of nitrogen as 0.162 nm^2 and the BET surface area (SBET) of the adsorbent was conducted using a surface area analyzer.

3.6 Membrane Performance Testing

There were three analyses conducted for the nanocomposite membrane performance evaluation. These performance testing were pure water flux analysis, porosity, and halo zone method for the antibacterial characterization. For the water flux and porosity analysis, the membrane was cut into a circular shape with a surface area of 13.4 cm^2 while for the halo zone method of those composite membranes in term of antibacterial properties, the surface area of the membrane was cut to 3.14 cm^2 as shown in Figure 3.4.

3.6.1 Pure water flux

The synthesize membrane performance was characterized by measuring the pure water flux. The pure water flux was tested with an ultrafiltration set up using a laboratory scale dead-end system, Stirred Ultrafiltration Cell (Model 8050, Millipore Corp., Bedford, MA) at room temperature with a 50 ml-internal volume under an active membrane surface area of 13.4 cm^2 . In this test, the membranes with different concentrations of silver nitrate were examined to obtain the best-performing membrane under different composition.

Firstly, the membrane with a radius of 44.5 mm was immersed in the deionized water prior to the filtration process for 5 minutes. Then, the membrane was positioned between two steel plates, which was then sealed with an O-ring. The feed solution for the pure water flux test was deionized water and it was stirred using a magnetic stirrer which was placed within the membrane stirred cell system. The membranes' pure water flux was measured at a 10-minute filtration and compacted at 2 bars. The membrane permeates flux was measured continuously with the collection of permeate at regular volume intervals. These experiments were conducted at room temperature under a 2-bar pressure which was supplied by the compressed gas. The membranes' pure water flux was determined using the Equation 3.5 below:

$$\text{Flux, } J_0 = \frac{\text{Volume of water permeation (V)}}{\text{Membrane area (A)} \times \text{Permeation time (t)}} = \frac{V}{A \Delta t} \quad \text{Equation 3.5}$$

Where,

J_0 is the pure water flux (L/m².h)

V is the volume of water permeated (L)

A is the membrane area (m²)

Δt is the permeation time (h)

3.6.2 Porosity

In order to determine the porosity of the synthesized membranes, these membranes which have been cut into the size of 2 cm² were soaked in the de-ionized water for 24 hours. Then, the weight of the wet membrane was recorded after the adhering water on the membrane's surface was wiped. After that, the membranes were left for drying in an oven at 75 °C for 24 hours in order to obtain the dry weight. The thickness of the membrane was

measured by using a digital calliper and it was to be used in the calculation of the membrane's porosity. The porosity of the membrane could be calculated with gravimetric method using Equation 3.6 as below:

$$\varepsilon(\%) = \frac{w_w - w_d}{A \cdot \delta \cdot \rho} \times 100\% \quad \text{Equation 3.6}$$

Where, ε is the porosity of membrane, A is the membrane's area (cm^2), δ is the membrane's thickness (cm) and ρ is pure water density (0.998 g/cm^3).

3.7 Evaluation on Membrane Antibacterial Properties

The fabricated membranes were then evaluated for their antibacterial properties by using disk diffusion method and counting the viable cell technique. Firstly, the bacteria culture media were prepared with Lura Bertani (LB) stock powder and bacteriological agar. Around 5 grams of bacteriological agar and 25 grams of LB stock were blended into 1000 ml of deionized water. The blend was then sanitized in an autoclave at a temperature of 121°C for 20 minutes. After the sanitization procedure of agar solution, the mixture was cooled to room temperature for about 30 minutes prior filling it into the petri dishes. Lastly, the petri dishes were stored in the refrigerator prior the usage for further antibacterial activity experiments.

3.7.1 Disk Diffusion Method

In this method, the cotton swab was immersed into the *E. coli* solution before the cells were spread homogeneously onto the agar plates. After that, the agar plates were utilized immediately for the antibacterial performance tests. The sterilized composite membranes were then placed on the LB agar and underwent 24 hours of incubation at 37°C . The inhibition zone on the membrane surface was then observed for the antibacterial activity

indication after the incubation process. The inhibition zone was measured by the difference of the membrane area and area of the ring formed around the sample as demonstrated in Figure 3.5.

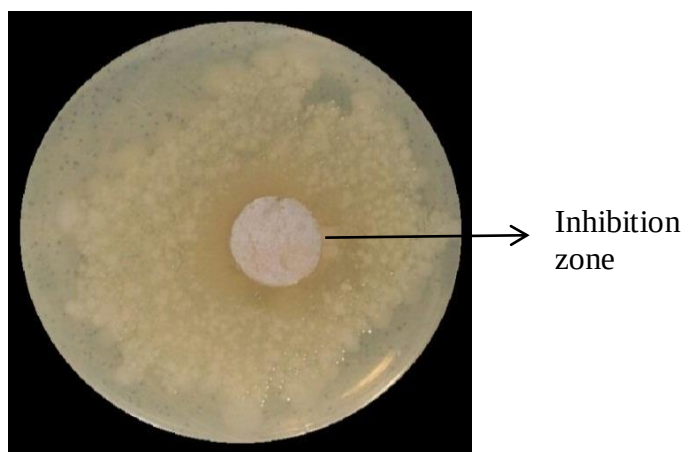


Figure 3.5: Inhibition Zone Method

3.7.2 Cell Counting and Viability Technique

The dilution of *E. coli* was performed using the standard dilution method, in which the 1 ml of *E. coli* arrangement was diluted with a 9 ml LB stock media. The dilution factor selected for this analysis was 1000. The membranes were cut with 2 cm x 4.5 cm, as shown in Figure 3.5, and were autoclaved for 20 minutes. At that point, each of the membrane was added to 4 ml of diluted *E. coli* arrangement in specific bottles. Another control set was prepared by using 4 ml of the diluted *E. coli* solution. Both of the control and E-coli membrane sample solutions were then incubated at room temperature for 4 hours. After the incubation process, a small quantity of 0.3 ml from each sample solutions and control solution was spread homogeneously onto the LB broth culture medium plate. These culture plates were then undergone another incubation process at 37 °C for 24 hours. The colonies number on the agar plates were identified by the plate count method. The colony forming unit was then calculated based on the number of colonies formed per the plated volume by

using Equation 3.7, while the *E. coli* inhibition percentage was calculated by utilizing Equation 3.8.

$$\frac{\text{cfu}}{\text{ml}} = \frac{\text{No. of colony formed}}{\text{Volume plated (ml)}} \times \text{Dilution factor} \quad \text{Equation 3.7}$$

$$E. coli \text{ inhibition (\%)} = \frac{\text{No. of colony in control plate} - \text{No. of colony in sample plate}}{\text{No. of colony in control plate}} \times 100 \quad \text{Equation 3.8}$$

CHAPTER 4

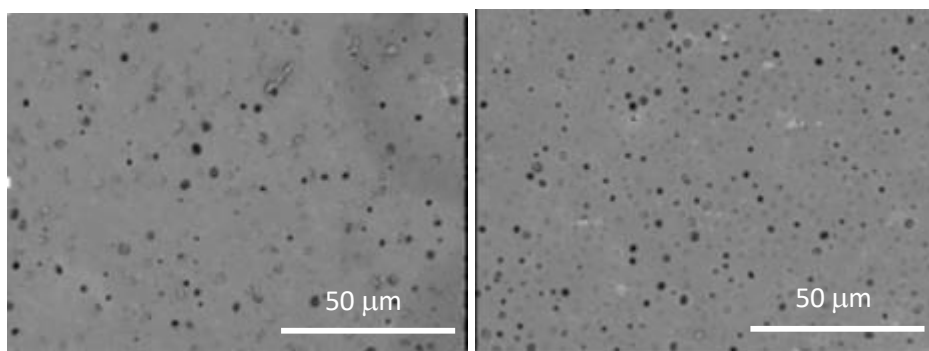
RESULTS AND DISCUSSION

This chapter discusses the membrane characterization and membrane performances with the effect of silver nitrate (AgNO_3) under varying concentrations in order to find the best performed membranes with good antibacterial properties and high water flux. In this section, the topics covered were membrane morphology examination with SEM analysis, the determination of functional groups present in membrane with FTIR analysis, membrane water flux performance testing, and lastly the evaluation of membrane antibacterial properties with regards to the effects of various AgNO_3 concentrations onto the membrane overall performances.

4.1 Membrane morphology

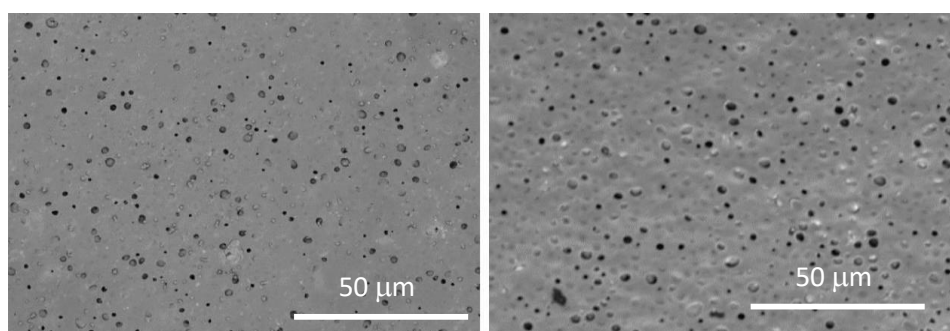
The microscopic cross section morphologies of the prepared membranes were examined by a scanning electron microscope (SEM) (FEI Quanta 200, USA). For the SEM measurement, the samples were cracked with liquid nitrogen in order to get the membrane cross-sectional area. After sputtering with gold, the microscopic cross section morphologies of the membranes were observed with the SEM.

The membrane surface and cross section morphologies were observed by SEM in order to investigate the effect of silver ions presence onto the membrane morphologies. Figure 4.1 shows the membrane surface for each sample (CM A to CM F).



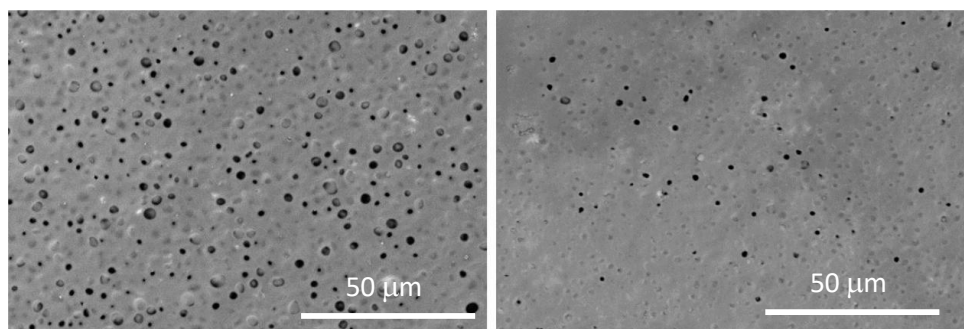
(a) CM A

(b) CM B



(c) CM C

(d) CM D



(e) CM E

(f) CM F

Figure 4.1: SEM Image for Surface Morphology (1500 Magnification, 50 μm) (a) Pure PSF Membrane, (b) 0.5 wt.% Silver Content, (c) 1.0 wt.% Silver Content, (d) 1.5 wt.% Silver Content, (e) 2.0 wt.% Silver Content and (f) 0 wt.% Silver Content

The membrane surface morphology for CM A to CM F were illustrated in Figure 4.1 (a) to (f). As observed from Figure 4.1, the pores formed on the membrane were not uniform and some large pores were found on the membrane surfaces. The measured values of the average pore size were taken manually from the SEM analysis and were shown in Table 4.1. It was observed that no significant difference in membrane pore size distribution when silver concentration increased from 0 to 2.0 wt.% as illustrated in Figure 4.1 (f to b). However, the number of pore formation had been enhanced with the addition of silver and PEI into the PSF membrane in Figure 4.1 (b to f) compared to CM A. This finding was in accordance with the study by Ananth et al. (2012) for the addition of PEI into polyethersulfone membranes (Ananth et al., 2012). The membrane surface exhibited by CM F as shown in Figure 4.1 (f), without any addition of silver content also exhibited hoarser surface morphology which was in line with the previous study conducted by Fan et al. (2008) and Meng et al. (2015) on the pure PSF membranes.

Besides, it was obvious that all membranes showed similar flat surfaces without obvious silver particles aggregation on the surface as observed from Figure 4.1. This means that silver nitrate was homogeneously dispersed into the membrane dope solution. The appearance of few uneven white spots on the surface in Figure 4.1 (b, c, d, e & f) could be due to some possible contaminant deposition as per reported and observed by Jyothi et al. (2014). The silver nitrate additive could also affect the surface hydrophilicity and viscosity of the casting solution which might in turn affect the surface morphology according to Yu et al. (2013).

Apart from the similar findings as aforementioned, there were also some other researches from literature which obtained similar findings. In the study conducted by Koseoglu-Imer et al. (2013), surface roughness value of pure PSF membrane decreased from

15.7 to 9.7, 10.1 and 14.2 nm according to AgNP ratios (0.25:0.5:1.0 wt,%, respectively) after the addition of AgNP. According to Mehrparvar et al. (2014), the rough surface tends to make deposits due to the increase in time interaction between particles and surface roughness. The surface roughness can cause easier adhesion of microorganisms and lead rapid colonization on the membrane surface as well as bio fouling (Dolina et al., 2015). The reduction of surface roughness with the addition of AgNP could somehow improve the membrane external properties. Hence, the addition of silver to the composite membranes became smoother compared to CM A and CM F and the addition of silver ions could definitely give positive impacts towards the membrane external and internal properties.

Table 4.1: Average Value for Pore Size of Composite Membrane

Composite membrane	Average value for pore size
CM A	2.24 ± 0.1
CM B	3.13 ± 0.1
CM C	3.18 ± 0.1
CM D	4.15 ± 0.1
CM E	3.26 ± 0.1
CM F	2.18 ± 0.1

On the other hand, the cross-section morphologies changes in the composite membrane are shown in Figure 4.2. All the composite membrane exhibited the typical symmetric structure with sponge-like pores. The addition of a different amounts of silver ions in the composite membrane showed small changes in the cross-section morphology as illustrated in Figure 4.2. Pure PSF membrane morphology showed no dispersed formation of macro voids on the cross section of the membrane as observed from Figure 4.2 (a). However, as antibacterial agents' contents increased to 2.0 wt.% (CM E), the macro voids clearly shown in Figure 4.2 (d and e). As the silver increased (from 0 to 1.5 wt.%), the

membrane became denser but when the silver added was 2.0 wt.% macro void still formed but it turned out to be micro void. Similar observations were obtained from Panda & De (2014) where observed cross section morphology of composite membranes displayed macro voids at the bottom as the additive percentage increased (Panda & De, 2014) and Vahid et al. (2015) found macro voids were expanded in number and size by increasing the amount of silver (Vahid, 2015) .

In the finding of Ananth et al. (2012), one of the causes of the sponge-like structure was hydrophilic of PEI absorbed water and extensive diffusion occurred from intra molecular hydrogen bonding non-solvent and functional groups of the membrane during phase separation. The same symmetric structure was reported for PSF/NMP membrane made by water vapor phase separation (Park et al., 1999). As silver concentration in composite membranes increased, the viscosity of the casting solution also increased due to increased nanoparticle/polymer ratio. The viscosity of casting solution plays a major part in phase inversion because it affects the solvent-nonsolvent exchange rate as well as the morphology of the membranes (Sile-Yuksel et al., 2014).

In brief, both membranes with silver and without silver content showed a similar symmetric sponge-like structure. These findings indicated that the addition of silver did not affect much of the membrane structure of cross section. However, compared to the pure PSF membrane, the pores of the modified PSF membrane seemed to become wider which would enhance the membrane flux.

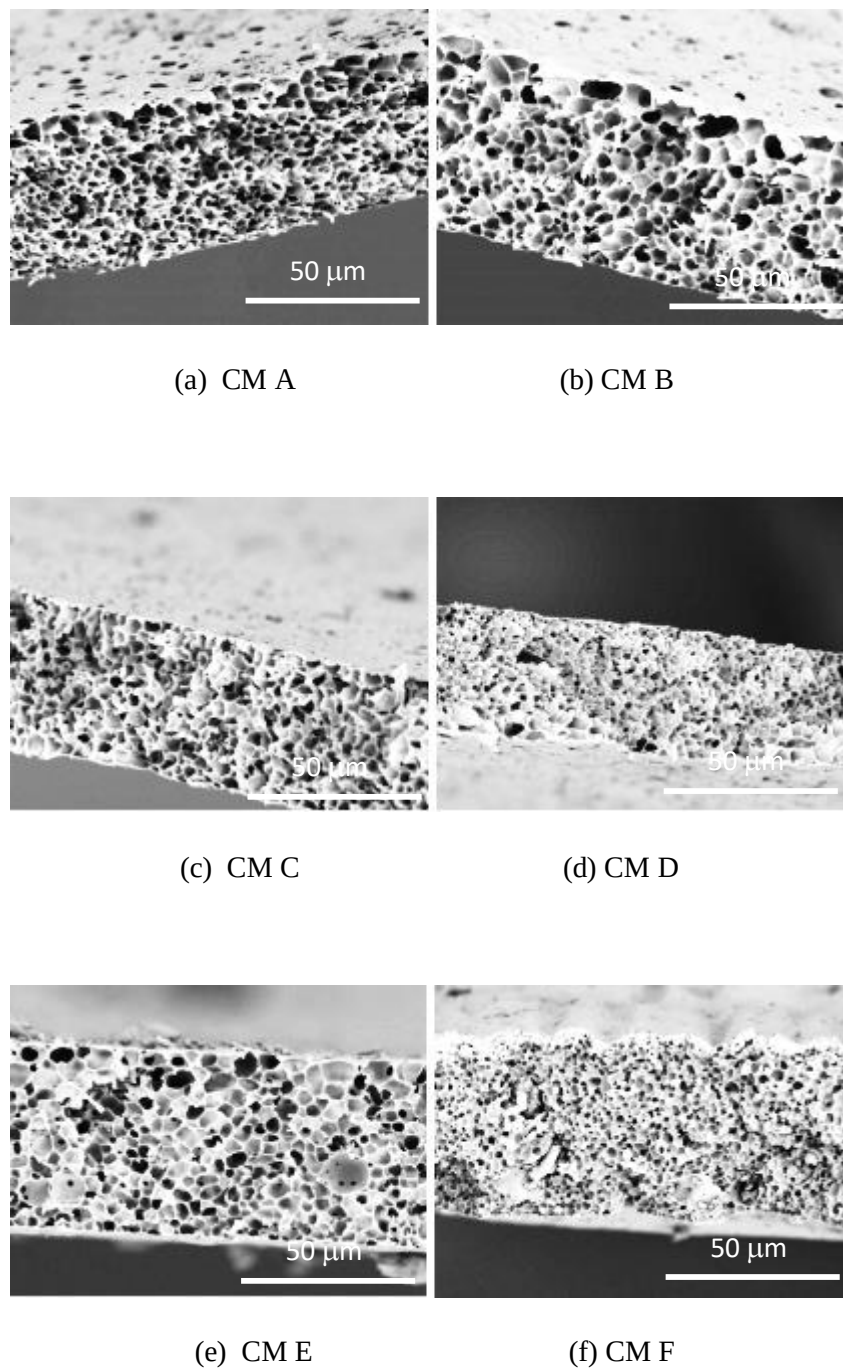


Figure 4.2: SEM Image for Cross Section Morphology (1500 Magnification, 50 μm)
 (a) Pure PSF Membrane, (b) 0.5 wt.% Silver Content, (c) 1.0 wt.% Silver Content,
 (d) 1.5 wt.% Silver Content, (e) 2.0 wt.% Silver Content and (f) 0 wt.% Silver
 Content

4.2 FTIR Analysis

The functional changes in the composite membranes were evaluated by using FTIR analysis. Figure 4.3 shows the FTIR spectra of sample CM A, CM E and CM F. The obvious changes of the peak were clearly shown in the membrane sample CM A, CM E and CM F, since different materials were present as mentioned in Table 3.1. As aforementioned, CM A was used as a reference for comparison with the other samples. From the spectra of CM A, CM E and CM F, it was clearly shown that the peak of 873.75 cm^{-1} corresponding to the presence of C-H aromatic out-plane deformation was observed (Meng et al., 2015).

As for the presence of silver nanoparticles, it was not shown obviously in the FTIR spectra due to the existence at a lower wave number which is around $400\text{ to }600\text{ cm}^{-1}$, in which the FTIR analysis conducted in this study could only observe until the wavenumber of 750 cm^{-1} . The existence of silver could fall beyond 750 cm^{-1} as per observed in Figure 4.3. This observation could be further supported by previous study which has proven the presence of silver peaks within the wavenumber of $400\text{ to }550\text{ cm}^{-1}$ (Narasimha, 2013). Therefore, it could be concluded for the high possibility of silver nanoparticles presence in the membranes incorporated with silver.

As shown in Figure 4.3, CM A exhibited O=S=O stretching at 1294.24 cm^{-1} from the strong absorption of the sulfonyl group existed in pure polysulfone membrane. After the additional of PEI, the sample of CM E and CM F showed a sharper peak at 1623 cm^{-1} (C=O stretching). This observation complied with the study of Goa et al. (2014) who found the amide group after PEI cross linking with the PES membrane. Both CM E and CM F showed strong absorption peaks at 1585.49 cm^{-1} that associated with N-H bond, 2310.72 cm^{-1} corresponding to NH^+ asymmetric stretching vibration compared to CM A due to the

addition of PEI into the composite membranes. The result obtained from Ananth et al. (2012) showed the same observation with the addition of PEI.

The summary of the bonds and functional groups existed in the CM A, CM E and CM F was tabulated in Table 4.2. All these three FTIR spectra has demonstrated the slight difference in terms of the pure PSF membrane without any silver loading, the silver-loaded membranes and the PSF/PEI membranes without any silver loading. Based on the findings, there was no obvious or significant alterations observed from the peaks. Although no significant difference was observed amongst these samples, the specific functional groups from each material was listed accordingly as per Table 4.2.

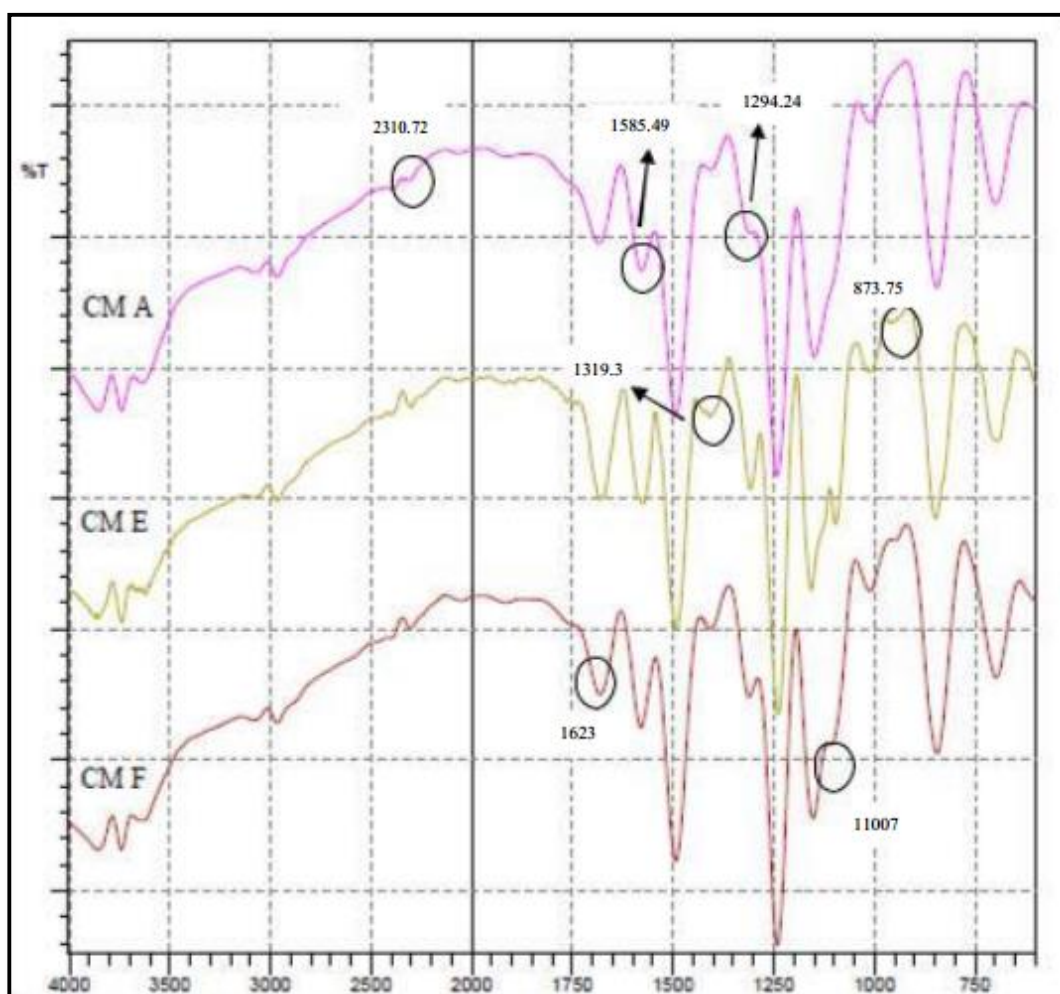


Figure 4.3: FTIR Result for CM A (Pure PSF), CM E (2.0 wt.% of Silver Content) and CM F (PSF/NMP/PEI/AC, 0 wt.% of Silver Content)

Table 4.2: Bonds Exist in CM A, CM E and CM F

Wavelength (cm ⁻¹)	Bond
873.75	C-H aromatic
1100.00	Strong C-O stretching
1294.24	Symmetric stretching vibration O=S=O
1319.31	C-N stretching
1585.49	N-H bond
1623.00	C=O Stretching
2310.72	NH ⁺ asymmetric vibration

On the other hand, all composite membranes with silver loadings which were demonstrated in Figure 4.4 had similar spectrum characteristics since they were comprised among the same materials which were PSF/PEI/NMP/AgNO₃/AC. The peaks between 2900 cm⁻¹ and 3100 cm⁻¹ were represented as aromatic and aliphatic C-H stretching vibration (Meng et al., 2015; Vatanpour et al., 2015). All membranes exhibited a C-O-C vibration bond at peak 1240.23 cm⁻¹. The peak of 2912.52 cm⁻¹ indicated the presence of C-H symmetric vibration that was responsible for alkyl groups (Mondal & Mandal, 2014). The characteristic band at 692.44 cm⁻¹ indicated –NH wagging vibration (Ananth et al., 2012).

The peaks at 1149.57 and 1294.24 cm⁻¹ represented symmetric stretching vibration of the O=S=O group of PSF membrane. As shown in Figure 4.4, both peaks at 1149.57 cm⁻¹ and 1294.24 cm⁻¹ became sharper with the increase of silver concentration (Eren et al., 2015). Absorption peaks at 1000 to 1100 cm⁻¹ indicated strong C-O stretching (Gultekinoglu et al., 2015). The fingerprint region observed at the range of 800 to 1100 cm⁻¹ were proven to be the presence of silver nitrate as per reported by Thirunavoukkarasu et al. (2013). Table 4.3 shows the summary of the functional groups presence in the silver loaded membranes which were denoted as CM B to CM E.

Table 4.3: Bonds Exist in the Silver Loaded Membrane

Wavelength (cm^{-1})	Bond
692.44	-NH wagging vibration
873.75	C-H aromatic
1149.57	Symmetric stretching vibration O=S=O
1585.49	N-H bond
2912.543	C-H symmetric vibration

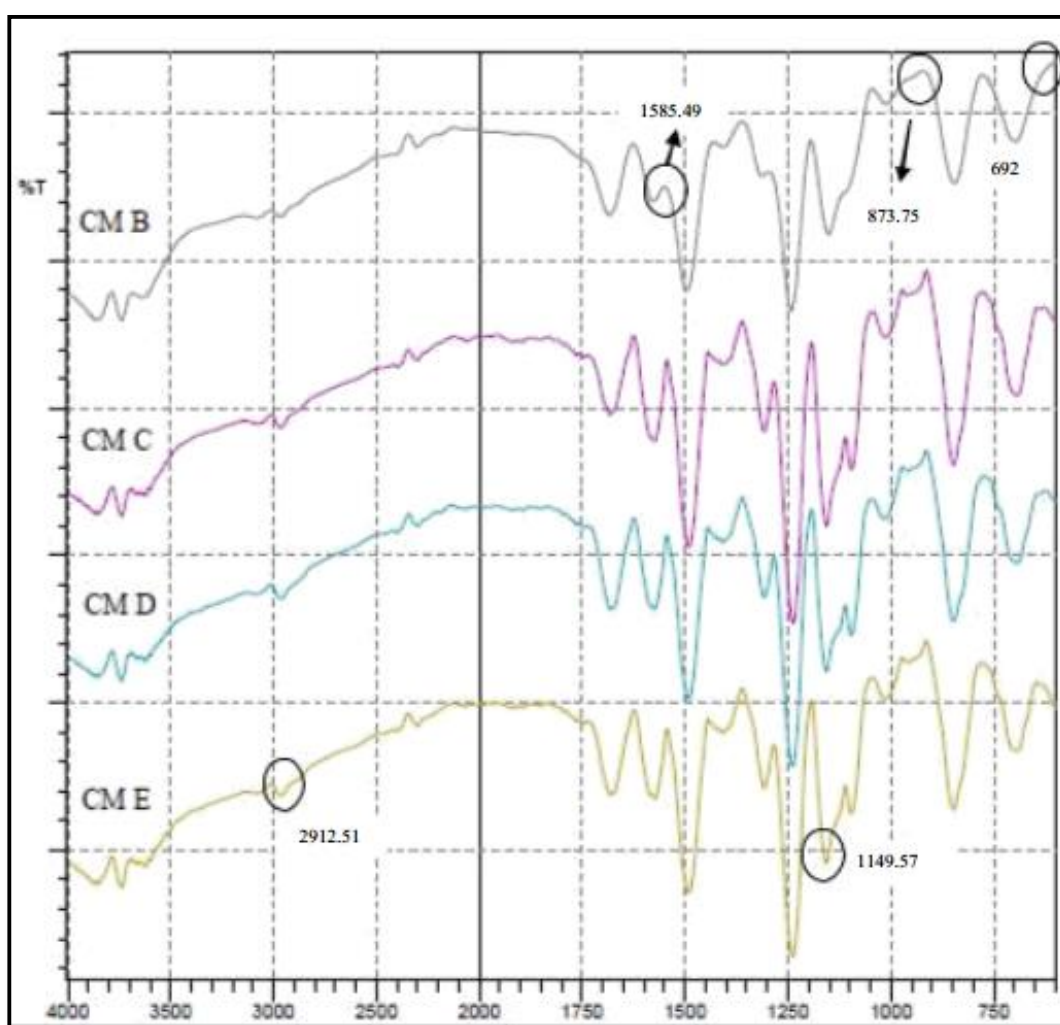


Figure 4.4: FTIR Result for CM B (0.5 wt.% Silver Content), CM C (1.0 wt.% Silver Content), CM D (1.5 wt.% Silver Content) and CM E (2.0 wt.% Silver Content)

4.3 XRD Analysis

Generally, XRD analysis was used to evaluate the filtration performance of membrane based on the presence of various silver amount with constant PEI and PAC on the synthesized membranes (CM B to CM F). Figure 4.5 demonstrated the crystalline or amorphous nature of the PEI and PAC content in PSF membranes as well as the existence of silver content. It was postulated that the membrane water flux should increase proportionately when the increment of silver content in the PSF membranes.

According to the XRD diffraction patterns in Figure 4.5, the peaks appeared at 2θ of 15° has proven the presence of PEI (Zhao et al., 2016), while the peaks of 11° to 13° have illustrated the existence of amorphous carbon (PAC) for CM B to CM F membranes. On the other hand, no obvious peaks were observed at this position for sample CM A. These findings have proven the presence of both PEI and PAC in all the samples except CM A, in which the results were in accordance with other reported studies with amorphous carbon materials (Ionita et al., 2016). Additionally, the major component which could control the water filtration performance in this study was the silver content which was supposed to be observed at the peaks of 38° , 45° , 65° and 75° (Shameli et al., 2012). However, owing to the little amount of silver content incorporated in membranes CM B to CM E, the peaks sharpening was not obvious as per demonstrated in Figure 4.5.

On the other hand, the XRD spectra of PSF was exhibited by broad diffraction peaks at the 2θ of 17° to 20° which indicated the amorphous structure of PSF for all these membrane samples. The observed peaks at this range were in accordance to literature with PSF nanocomposite membranes (Badrinezhad et al., 2018). The addition of PAC to the PSF membranes did not alter the 2θ values of both PAC and PSF. The silver peaks were somehow sharpened gradually with the increment of silver content as per observed in CM B to CM E

with the amount from 0.5% to 2.0%, which indicated the successful incorporation of silver into the PSF matrix. It might cause a slight structure alteration in the PSF membranes with the gradual increment of silver composition, resulting in a more amorphous PSF-composite material. These alterations could assist in reducing the instabilities of PSF polymer chains which led to significant properties improvement with synergistic characteristics of both silver and PAC-PEI into the PSF membrane structures as reported by Badrinezhad et al. (2018). Therefore, the broader peaks observed from the XRD with higher silver amount should contribute to a greater filtration performance with the enhanced structural properties.

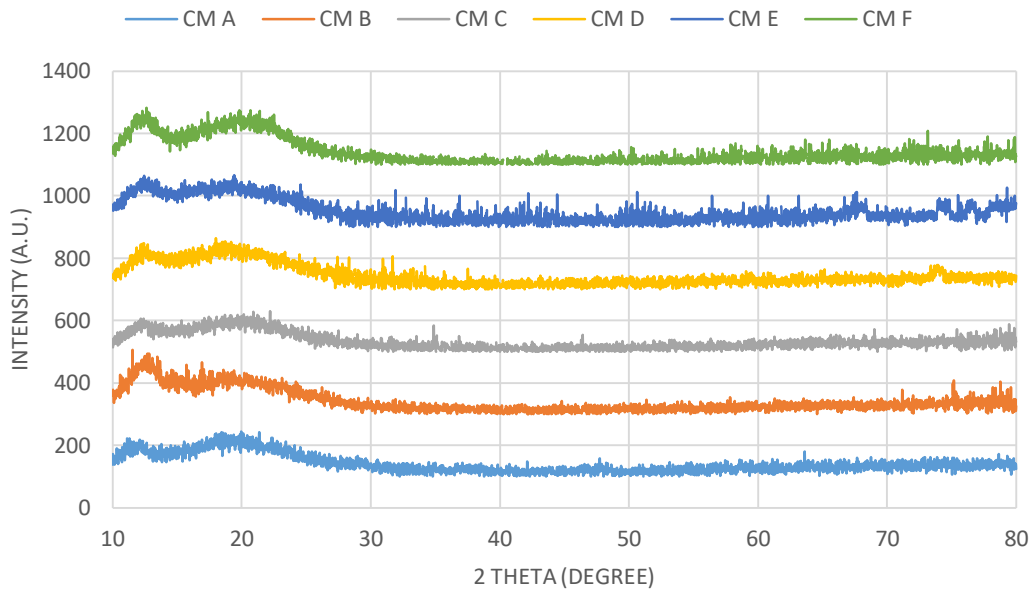


Figure 4.5: XRD Analysis for Membranes CM A to CM F

4.4 BET Analysis

The effects of silver nanoparticles concentration on the surface areas (BET) of PSF-PEI-AgNO₃ nanohybrid membranes are shown in Table 4.4. Based on the observations, CM F membrane which are incorporated with PAC and PEI but no silver content has the highest surface area, followed by the control membrane (CM A) with a slight decrement of surface area compared to CM F. On the other hand, a gradual decrement was observed on the surface areas of all nanohybrid membranes with the increment of silver content in the membranes. It was notable that the surface area gradually decreased from 1216.38 to 678.94 m²/g with increasing silver concentration from 0.5 to 2 wt.%. It was shown that the addition of silver into membranes had decreased the surface area. However, it did not impose negative impacts towards the membrane flux performance but has further improved the membrane water flux, which were further discussed in next section.

Table 4.4: Surface Area of CM A to CM F Membranes

Membrane	Surface area (m ² /g)
CM A	1216.38 ± 2.11
CM B	937.21 ± 1.37
CM C	856.267 ± 0.02
CM D	731.19 ± 0.83
CM E	678.94 ± 0.21
CM F	1341.17 ± 1.25

4.5 Membrane water flux

In this study, the water flux of the composite membrane with different silver loading was determined by a Stirred Ultrafiltration Cell. The flux was used to express the rate at which water permeated a membrane barrier ($\text{L}/\text{m}^2\cdot\text{h}$). Table 4.5 shows the fluxes for all membranes at 2 bars. It was observed that the pure water fluxes of composite membranes increased rapidly with the increase of silver concentration and then slowly decreased when the concentrations were at the maximum amount.

Table 4.5: Water Flux of the Composite Membrane

Composite membrane	Flux ($\text{L}/\text{m}^2\cdot\text{h}$)
CM A	5.5371
CM B	16.8806
CM C	22.2537
CM D	14.0149
CM E	8.4627
CM F	9.403

According to Table 4.5, from CM A to CM C, it showed increments of pure water flux of $5.5371 \text{ L}/\text{m}^2\cdot\text{h}$, $16.8806 \text{ L}/\text{m}^2\cdot\text{h}$ to $22.2537 \text{ L}/\text{m}^2\cdot\text{h}$ with increasing AgNO_3 concentration (0 wt.%, 0.5 wt.% and 1.0 wt.% respectively). These results present that the addition of silver into a composite membrane provides better water flux performance in comparison with CM A by 67.20% for CM B and 75.11% for CM C (highest water flux). This can be explained by the increase in hydrophilicity of the membranes which could attract water molecule to pass through them (Chen et al., 2012).

Apart from that, the comparison between CM A membrane (pure PSF) and other membranes (CM B to CM F) was made with the addition of activated carbon (AC) as the functional adsorptive materials in the membrane performance evaluation. It was observed

that CM A membrane which was free from AC content showed the lowest water flux among all the samples, while CM F membrane which was free from silver loading has illustrated slightly higher water flux than CM A membrane. This finding has further proven the contribution of AC in the membrane hydrophilicity and its contribution for the membrane hydrophilicity enhancement. The addition of silver loading into the membranes at an optimum amount could further add value to the enhancement of water flux performance, too.

As per reported in Table 4.1, the membrane pore size did exhibit an increment trend when the concentration of AgNO_3 increased until an optimum amount was achieved while a slight decrement was observed as the concentrations kept increasing. Based on the findings in Table 4.1, the average surface area and pore size of silver containing other membranes (CM B, CM C, CM D, and CM E) was greater than CM A, proving that the membrane flux for CM B to CM E was higher than CM A. The larger the pore sizes, the more water can pass through the membranes. This is in accordance to the study by Andrade et al. (2015) which stated that the large pore sizes also can attribute to the increase water flux. The same result was obtained where the fluxes were increased as additive content increased compared to pure PSF membranes by (Zhao et al., 2011). Figure 4.6 shows the trends of water flux for composite membranes (CM A to CM F) with different AgNO_3 concentrations.

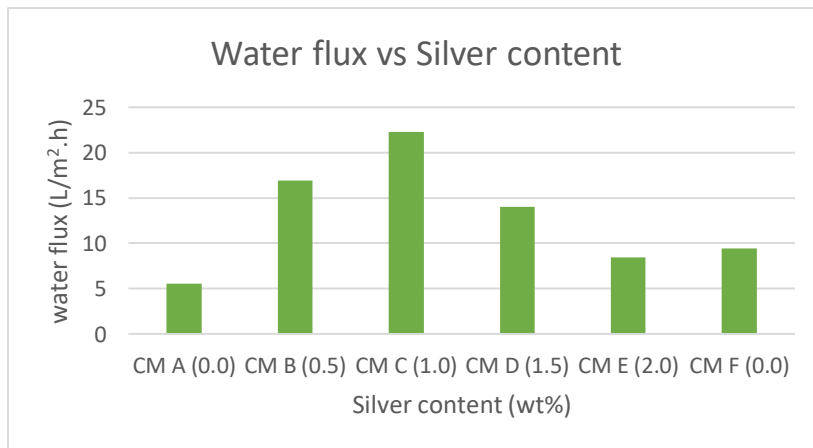


Figure 4.6: Flux Changes of the Composite Membranes (CM A to CM F)

On the other hand, with the further addition of AgNO_3 concentration (1.5 wt.% and 2.0 wt.%), the water flux was then reduced with a value of $14.0149 \text{ L/m}^2\cdot\text{h}$ and $8.4627 \text{ L/m}^2\cdot\text{h}$ respectively. Koseoglu-Imer et al. (2013) and Sawada et al. (2012) showed that by increasing the concentration of silver nanoparticles on the membrane, it resulted in low water flux due to the barrier created by the presence of silver nanoparticles or agglomeration of nanoparticles on the membrane surface.

The agglomeration of the silver occurred due to the formation of a crystalline silver particle in this research which led to low water permeation. This observation agreed with the study of Basri et al. (2010) where the addition of silver nitrate in the dope solution attributed to the high crystallinity of silver nanoparticles. The pure water flux for CM F was higher than CM A due to the addition of PEI which increased the membrane hydrophilicity compared to CM A.

According to the findings obtained, it was notable that the incorporation of lower concentration of AgNO_3 could contribute to the hydrophilicity enhancement due to the presence of sufficient AgNO_3 nanoparticles that trigger the hydrophilic properties within the membrane structures. However, the increment of AgNO_3 concentration could cause saturation onto membrane structures due to the agglomeration of nanoparticles on the membrane surface which indirectly affect the water flux properties of membranes. Therefore, an optimum amount of AgNO_3 was strongly recommended for this study in order to achieve the membrane properties with high hydrophilicity and water flux simultaneously.

4.6 Membrane porosity

Generally, membrane porosity was highly dependent on the mass transfer of the polymer solution during the phase inversion process. Based on the findings as shown in Table 4.6, CM A membrane (pure PSF) had the lowest porosity as compared to other

membrane samples with higher porosity. This scenario was possibly due to the hydrophobic nature of PSF polymer which has delayed the mass transfer between the solvent and non-solvent phase during the phase inversion process and thus led to the formation of less porous membranes. As the content of AgNO₃ increased from 0.5 wt.% to 1.0 wt.%, the porosity of membranes increased tremendously to 70.9%, while a decrement trend was observed when the concentration of AgNO₃ was increased further until 2.0 wt.%. These findings were in accordance with the water flux results and it has further proven the direct correlation between these two properties. It could be explained based on the hydrophilicity effect of the AgNO₃, PEI and AC additives which have greatly enhanced the mass transfer process during phase inversion and resulted in the formation of highly porous membranes. As a result, the highly porous membranes could contribute to higher permeance rate which then led to higher water flux. Therefore, it was concluded that the porosity and water flux of membrane are correlating proportionately in accordance to the concentration of AgNO₃ and other functional additives which has altered the hydrophilicity of the polymer solution.

Table 4.6: Porosity of the Composite Membrane

Composite membrane	Porosity (%)
CM A	6.5
CM B	15.5
CM C	70.9
CM D	46.9
CM E	27.1
CM F	38.8

4.7 Antibacterial properties

The sample membranes were placed in a Petri dish plate containing LB medium that was cultured with leachate containing bacteria. The inhibition of bacterial growth exhibited the ring which represented the performance of the composite membranes. The ability of the

composite membranes to inhibit the growth of bacteria was discussed in this section. The bacteria were not only present in various environments but also identified as one of the most possible bacteria promoting bio fouling, due to the EPS secreted (Zhu et al., 2010).

The diameter of the inhibition zone was tabulated in Table 4.7 by the difference between the area of the ring and area of the sample composite membrane. Diameter of membrane was 17 mm. Figure 4.7 shows the antibacterial properties results for the growth of bacteria. Both CM A and CM F did not show any inhibition effect against the growth of the bacteria due to the absence of silver concentration in Figure 4.7 (a) and (f). This statement was supported by Chen et al. (2012) which stated that the antibacterial activity of the membranes was caused by the antibacterial agent, not from the polymer. In this case, silver acted as an antibacterial agent. The same goes with CM F that was compromised of PSF/PEI/NMP/AC showed no antibacterial activity.

Therefore, it proved that the antibacterial effect of the composite membranes should be due to the silver addition. During the test, silver ions were released from the composite membranes and enriched the LB agar with silver ions. As a result, bacteria were attacked by these silver ions and deteriorated (Koseoglu-Imer et al., 2013). Additionally, the rest of the composite membranes also showed an inhibition zone surrounding the samples. The inhibition zone became clearer and wider as silver content in membranes increased due to more toxic silver ions lost from membranes to the LB medium. It was notable that CM E displayed the largest inhibition zone as it contained the highest silver concentration (2.0wt.%) as shown in Figure 4.7 (e) among all other membrane samples.

In addition, Andrade et al. (2015) stated that most of the silver ions were concentrated on the membrane surface by using the in-situ method. It was important because most of the interactions with the bacteria cells occur on the material's surface. The direct interaction between bacteria cells and the silver nanoparticles might allow the formation of pits on the

cellular surface, which led to the destabilization of cellular membrane and loss of morphological integrity. Therefore, it showed higher antibacterial performance as diffusivity of silver ions is high (Vatanpour et al., 2015). Meanwhile, a composite membrane with silver concentration 0.5 wt.%, 1.0 wt.%, and 1.5 wt.% showed no expressive antibacterial activity as shown in Figure 4.7 (b), (c) and (d). This observation complied with the study in literature as per reported by Andrade et al. (2015).

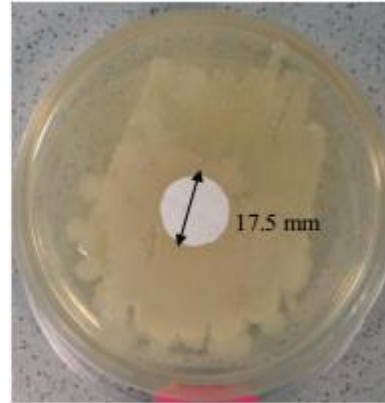
Generally, silver nanoparticles or ions can anchor to the bacterial cell wall and penetrate it resulting structural changes in the cell membrane and induced the formation of pits on the cell surface. Then, silver nanoparticles accumulated on the cell surface (Prabhu & Poulouse, 2012). The interaction between bacterial cell and silver nanoparticles was due to the electron static attraction of negative charge cell membrane with positive charge silver. The permeability of cell membrane increased, and respiration disturbed when silver nanoparticles attached to the bacterial cell membrane (Marambio & Hoek, 2010). Therefore, the excellent antibacterial properties of silver nanoparticles attributed by this antibacterial mechanism had made AgNO_3 appeared to be an essential antibacterial agent amongst all other nanoparticles which are available in the market.

Table 4.7: Diameter of Inhibition Zone

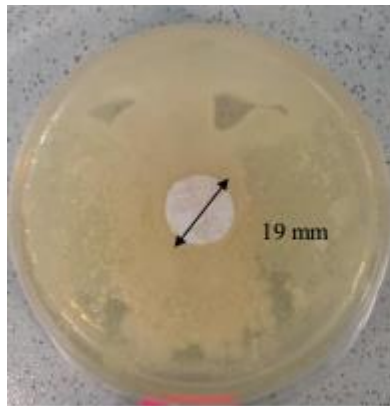
Composite membrane	Diameter (mm)
CM A	17.0
CM B	17.5
CM C	19.0
CM D	21.0
CM E	27.0
CM F	21.0



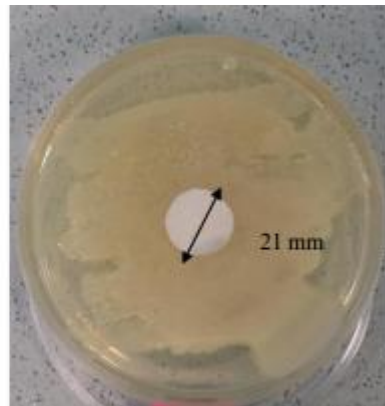
(a) CM A



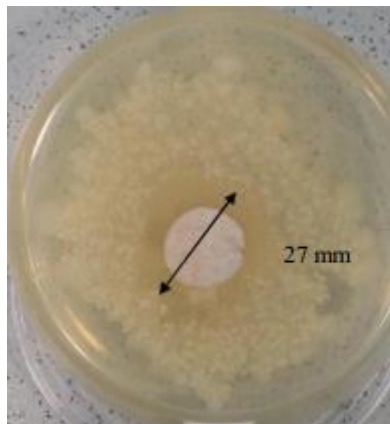
(b) CM B



(c) CM C



(d) CM D



(e) CM E



(f) CM F

Figure 4.7: Inhibition Zone on Agar Plates

4.8 Summary

Generally, the synthesized PSF/PEI/NMP/AgNO₃/AC membranes were evaluated in terms of their physicochemical properties under the effects of varying AgNO₃ concentrations towards the membrane performances. The findings presented in this section were highly favourable due to the encouraging phenomena and results which could make this PSI/PEI/AgNO₃ composite membranes to be outstanding membrane alternatives for the enhancement in terms of water permeability alongside with great antibacterial capability. In this study, it was notable that the addition of various additives such as PEI, AgNO₃ and AC into PSF membranes which were highly hydrophobic in nature could significantly affect the membranes structural performance as well as internal properties enhancement. The improved hydrophilicity originated from the PEI and the adsorptive functions from the AC could definitely add value to the excellent antimicrobial capability which were contributed by AgNO₃. All these synergistic effects among the additive materials could give significant positive impacts onto the membrane performances. Therefore, this study serves as a preliminary investigation on the combination of various functional additives towards the effort of improving the current nanocomposite membrane performances.

CHAPTER 5

CONCLUSION & RECOMMENDATION

5.1 Conclusion

In this research, the Polysulfone-Polyethyleneimine (PSF-PEI) hybrid membranes were successfully synthesized via wet-phase inversion method with the varying concentration of silver nitrate (AgNO_3). Besides, there was some additional functional materials such as activated carbon (AC) which could serve as adsorptive materials in enhancing the membrane separation efficiency. The purpose of the integration between PSF and PEI polymers were aimed to improve and balance between the hydrophilicity and hydrophobicity of membrane surface due to the distinct properties of these two polymers.

The objectives of this research were to synthesize, investigate and evaluate the performance of antibacterial membrane under various concentrations of AgNO_3 , ranging from 0.5 to 2.0 wt.% (CM B to CM E). These membranes were then compared with control membranes, i.e. pure PSF membrane (CM A) and PSF-PEI membrane (CM F) without any silver loadings. It was observed that the membranes incorporated with these functional nanohybrid materials had demonstrated significant enhancement in terms of water flux and antibacterial capability.

Besides, the membrane surface morphologies were examined by using SEM analysis and it was observed that the cross-sectional structures of the synthesized membranes showed spongy-like structures. Moreover, the average pore size measured from the SEM analysis had shown that CM D membrane yield the largest pore size of 4.15 ± 0.1 . On top of that, the FTIR analysis has also illustrated some slight adjustment in the spectra due to the presence of AgNO_3 as per reported in the results. The XRD analysis also proved that the presence of

the additives such as PEI, PAC and silver nitrate in the nanohybrid membranes. BET analysis on the other hand had shown the decrement of surface area with the increment of silver nitrate content but it did not affect the membrane performance.

Furthermore, the performance of these PSF-PEI-AgNO₃ nanohybrid membranes were evaluated with regards to their porosity, membrane flux, and antibacterial activity in terms of *E. coli* inhibition. According to the findings, the highest water flux of 22.2537 L/m².h was achieved by CM C membrane (with 1.0 wt.% of AgNO₃), while further increment of AgNO₃ amount from 1.0 to 2 wt.% had resulted in the decrement of water flux. This phenomenon was possibly attributed to the saturation of AgNO₃ content in the membrane structures which has led to the decreased water flux as shown in the observations. Besides, CM C membrane demonstrated the highest porosity (70.9%) amongst all samples and it was in accordance to the water flux results, which has further proven the direct correlation between these two responses.

Additionally, the antibacterial properties were examined using *E. coli* and the antibacterial activity was observed through the inhibition zone diameter on the PSF-PEI-AgNO₃ nanohybrid membrane surface. Based on the observations, the best antibacterial properties were exhibited by CM E membrane (with 2.0 wt.% of AgNO₃), which was the highest available amount of AgNO₃ in all the experiments. This encouraging observation was mainly due to the abundance amount of silver ions presence in the membrane structures which could disrupt the bactericidal activity of *E. coli* and thus resulted in a larger inhibition zone as per demonstrated in the findings.

Hence, it was concluded that the incorporation of AgNO₃ into the PSF-PEI nanohybrid membranes had contributed to the membrane enhancement in terms of water permeability and antibacterial capability in a great extent. The significant enhancement

obtained was highly preferable in the industrial applications and it was postulated that the synthesized PSF-PEI-AgNO₃ nanohybrid membranes yield an excellent potential in improving the current membrane development strategies and approaches.

5.2 Recommendation

In order to provide a further advancement on the PSF-PEI-AgNO₃ nanohybrid membrane development, there are several recommendations for future studies which are summarized as following:

a. Experiments are conducted with flow system

Dead end system is used as preliminary experiment for the investigations of these PSF-PEI-AgNO₃ nanohybrid membranes. It is highly recommended that crossflow system is applied for the performance testing and characterizations of these nanohybrid membranes in a larger scale which could improve the feasibility for commercialization.

b. Real water samples from industrial applications

In this study, the membrane permeability was only evaluated with pure water. It is suggested that real water sample should be used for the evaluation of applicability and efficiency of these nanohybrid membranes. The real sample could be any water sources from the industrial applications and the purpose is to ensure the prolonged feasibility of these membranes in real-life applications.

c. Combination with other membrane modification techniques

Instead of the conventional phase inversion technique with nanohybrids incorporation, there are other modification techniques which could be suggested as the integration techniques with these nanohybrid membranes such as layer-by-layer grafting method, electron beam irradiation or UV grafting approach.

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APPENDICES

Appendix A: Calculation for amount of PSF, AgNO₃ and NMP needed in membrane fabrication.

The ratio of polymer (PSF) to solvent (NMP) is 15:85 and the percentage of AgNO₃ was varied during membrane fabrication as shown in Table 3.1. The calculation was shown below:

PEI is constant = 0.3 wt. %

PSF is constant = 15.00 wt. %

PAC is constant = 0.5 wt. %

Membrane CM A,

$$100.00 \text{ g} - 0.00 \text{ (AgNO}_3\text{) g} - 15.0 \text{ g (PSF)} - 0.00 \text{ g (PEI)} - 0.50 \text{ g (PAC)} = 85.00 \text{ g (NMP)}$$

Therefore, NMP = 83.70 g

Membrane CM B,

$$100.00 \text{ g} - 0.50 \text{ (AgNO}_3\text{) g} - 15.0 \text{ g (PSF)} - 0.30 \text{ g (PEI)} - 0.50 \text{ g (PAC)} = 83.70 \text{ g (NMP)}$$

Therefore, NMP = 83.70 g

Membrane CM C,

$$100.00 \text{ g} - 0.10 \text{ (AgNO}_3\text{) g} - 15.0 \text{ g (PSF)} - 0.30 \text{ g (PEI)} - 0.50 \text{ g (PAC)} = 83.20 \text{ g (NMP)}$$

Therefore, NMP = 83.20 g

Membrane CM D,

$$100.00 \text{ g} - 1.50 \text{ (AgNO}_3\text{) g} - 15.0 \text{ g (PSF)} - 0.30 \text{ g (PEI)} - 0.50 \text{ g (PAC)} = 82.70 \text{ g (NMP)}$$

Therefore, NMP = 82.70 g

Membrane CM E,

$$100.00 \text{ g} - 2.00 \text{ (AgNO}_3\text{) g} - 15.0 \text{ g (PSF)} - 0.30 \text{ g (PEI)} - 0.50 \text{ g (PAC)} = 82.20 \text{ g (NMP)}$$

Therefore, NMP = 82.20 g

Membrane CM F,

$$100.00 \text{ g} - 0.00 \text{ (AgNO}_3\text{) g} - 15.0 \text{ g (PSF)} - 0.30 \text{ g (PEI)} - 0.50 \text{ g (PAC)} = 84.20 \text{ g (NMP)}$$

Therefore, NMP = 84.20 g

Appendix B: Calculation of pure water flux

Pure water flux was calculated using the Equation 3.1. Since the time taken was constant, so the volume of permeate was taken from the difference of weight of beaker and weight of beaker with permeate, then, the value was divided by value of water density to obtain volume of permeate. Equation B.1 was used to calculate volume of water permeated. The raw data is tabulated in Table B.1.

$$v = \frac{m}{\rho} \quad \text{Equation B.1}$$

Where,

Pressure = 2 bar

Time = 10 min = 0.1667 hour

Effective area = 0.00134 m²

Weight of beaker = 63.44 g

Density of water = 1 g/cm³

Table B.1: Water Flux of Composite Membrane

Composite membrane	Weight of permeate	Volume of permeate	Pure water flux, $J_0 = \frac{V}{A\Delta t}$
CM A			5.5357
CM B	3.77	0.00377	16.881
CM C	4.97	0.00497	22.254
CM D	3.13	0.00313	14.015
CM E	1.89	0.00189	8.463
CM F	2.11	0.00211	9.448

Appendix C: SEM images at different magnification

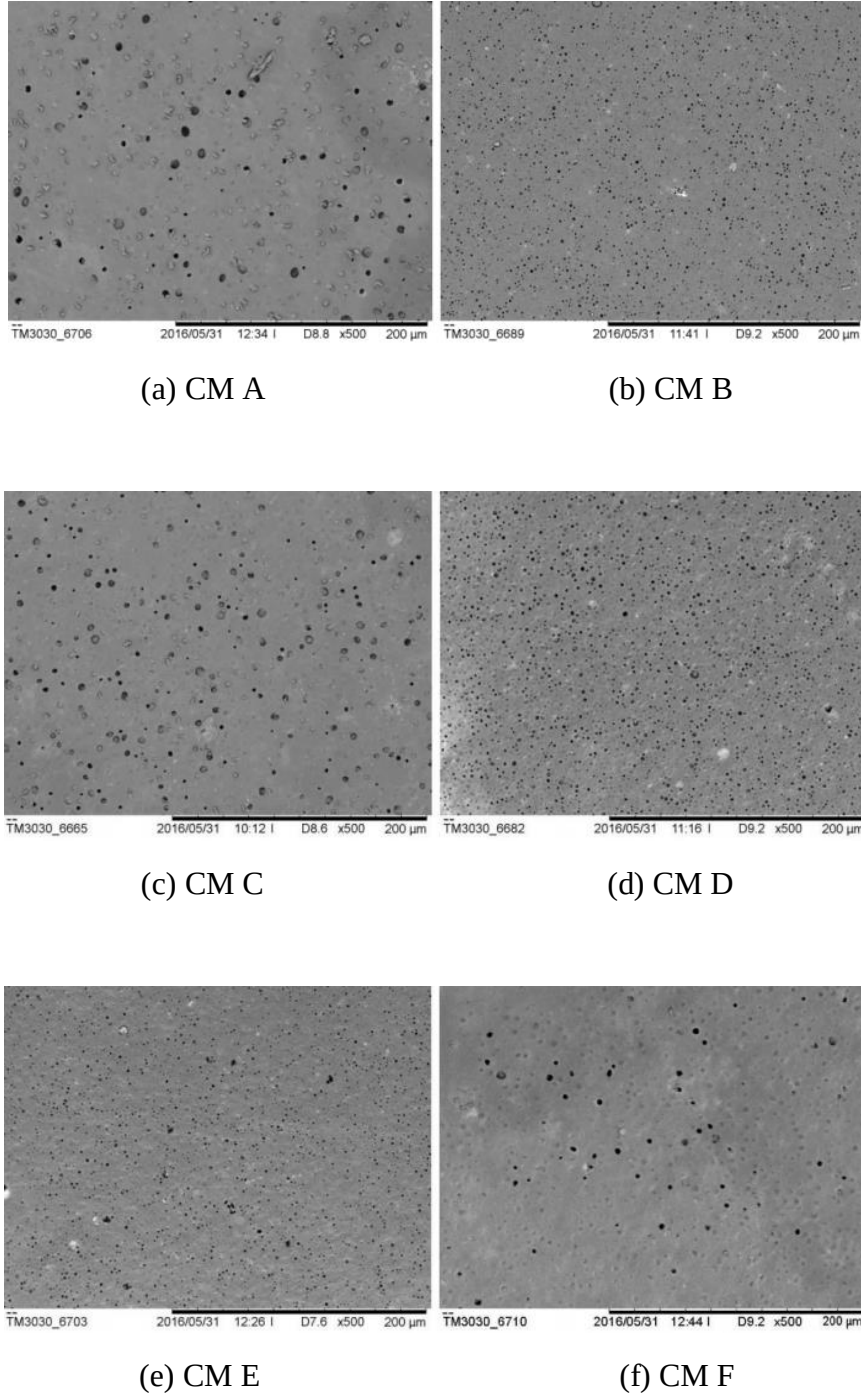
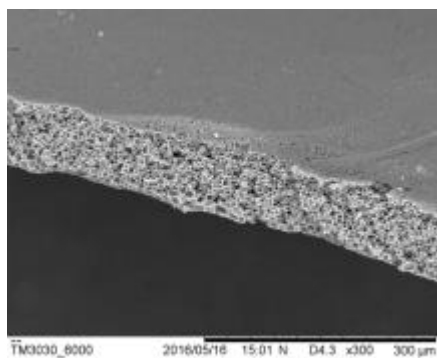
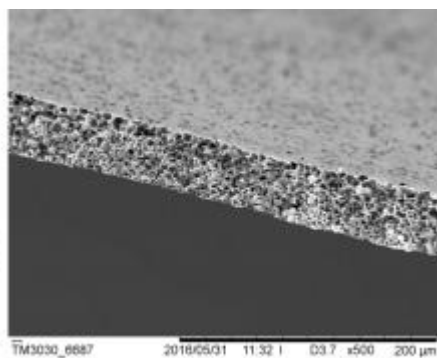


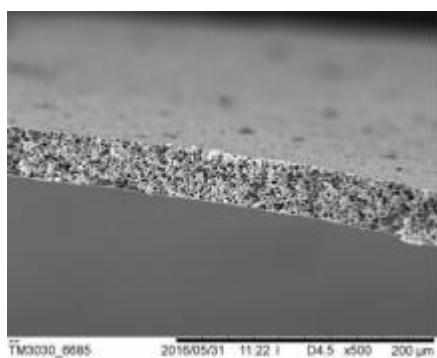
Figure C.1: SEM Image for Surface Morphology (a) Pure PSF Membrane, (b) 0.5 wt.% Silver Content, (c) 1.0 wt.% Silver Content, (d) 1.5 wt.% Silver Content, (e) 2.0 wt.% Silver Content and (f) 0 wt.% Silver Content



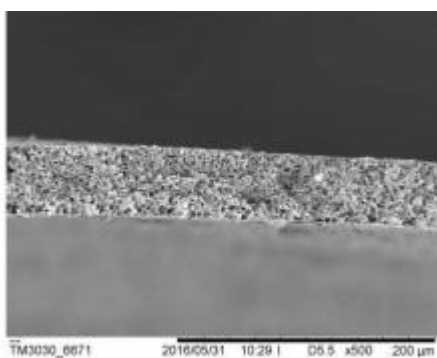
(a) CM A



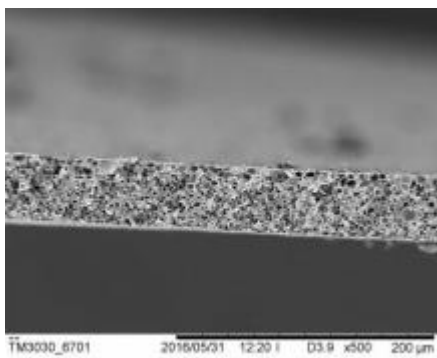
(b) CM B



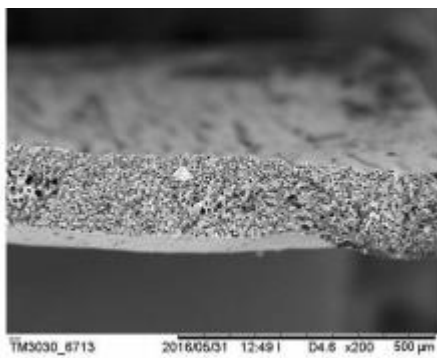
(c) CM C



(d) CM D



(e) CM E



(f) CM F

Figure C.2: SEM Image for Cross Section Morphology (a) Pure PSF Membrane, (b) 0.5 wt.% Silver Content, (c) 1.0 wt.% Silver Content, (d) 1.5 wt.% Silver Content, (e) 2.0 wt.% Silver Content and (f) 0 wt.% Silver Content

Appendix D: Calculation of inhibition zone

Inhibition zone is the difference of the area of the ring formed and area of membrane. Equation D.1 was used to measure the area of the ring and membrane. The diameter of the membrane was kept constant which is 17 mm. The values of the calculation inhibition zone are tabulated in Table D.1

$$A = \frac{\pi d^2}{4} \quad \text{Equation D.1}$$

Table D.1: Inhibition Zone Calculation

Composite membrane	Diameter of inhibition zone (mm)	Area of composite membrane (mm ²)	Area of ring formed (mm ²)	Area of inhibition zone (mm ²)
CM A	17.0	226.98	226.98	0.00
CM B	17.5	226.98	240.53	13.55
CM C	19.0	226.98	283.53	56.55
CM D	21.0	226.98	346.36	119.38
CM E	27.0	226.98	573.56	345.58
CM F	17.0	226.98	226.98	0.00

Appendix E: Raw Materials

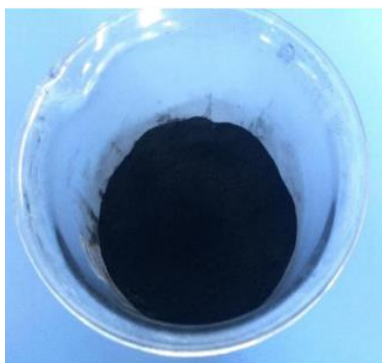


Figure E.1: Activated carbon

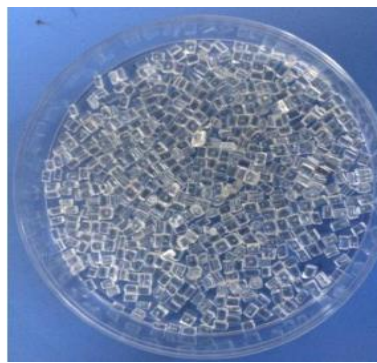


Figure E.2: Polysulfone

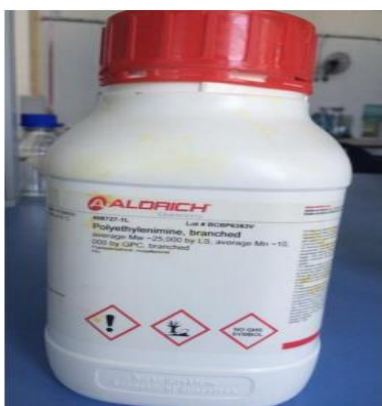


Figure E.3: Polyethyleneimine (PEI)



Figure E.4: Silver nitrate



Figure E.5: N-Methyl-2-Pyrrolidone