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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/m^2.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 $L/m^2.j$ 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	Aminotetzarole
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	Sanning Electron Microscopy
SH	Sulfhydryl
UF	Ultrafiltration
WHO	World Health Organization
WTP	Water Treatment Plant

LIST OF NOMENCLATURES

^{o}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 (Burdușel 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 theses 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-$AgNO_3$ 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 $AgNO_3$ 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 $AgNO_3$ 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-$AgNO_3$ nanohybrid membranes were then characterized on their surface morphologies and functional groups alterations which were resulted from the addition of different concentration of $AgNO_3$ 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 $AgNO_3$ concentration on the PSF-PEI-$AgNO_3$ 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.