POLYSULFONE-TITANIUM DIOXIDE ULTRAFILTRATION MEMBRANE WITH ENHANCED FOULING RESISTANCE FOR HUMIC ACID REMOVAL

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Dedicated to my beloved parents

(Abd Hamid bin Saad and Nurain binti Badri),

Brothers and sister

(*Abdullah, Nur Asyikin, Abdul Aziz, Abdul Rasid,*

Abdul Halim and Abdul Rahman)

who gave me inspiration, encouragement and endless support

throughout the success of my study.

May this thesis be an inspiration and guidance in the future.

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ABSTRACT

This study is aimed to prepare polysulfone ultrafiltration (PSF UF) membranes with enhanced fouling resistance for humic acid (HA) removal separations. The effect of the addition 2 wt. % of titanium dioxide (TiO_2) in the dope formulation on the membrane performance and membrane morphology has been studied. Two types of UF membranes, i.e. PSF membranes with and without addition of TiO_2 were prepared via a simple dry/wet phase inversion technique. The membranes were characterized using contact angle goniometer, x-ray diffractometer (XRD), differential scanning calorimeter (DSC), thermal gravitational analysis (TGA), field emission scanning electron microscopy (FESEM), ultrafiltration (UF) membrane system, molecular weight cut off (MWCO) and anti-fouling measurement. The separation performances of these membranes were evaluated using humic acid solution. The presence of TiO_2 showed significant improvement in the properties of membranes such as hydrophilicity, thermal stabilities, mechanical properties, permeation and antifouling. Based on these aspects, the PSF membrane with TiO_2 was chosen for further investigation by varying the air gap in the range of 0 – 13 cm. Results showed that the membrane prepared from zero air gap during hollow fiber spinning displayed the best performance in terms of water permeation and HA removal. This membrane was further used to investigate the effect of the physicochemical environment (pH and ionic strength) on HA rejection. pH and ionic strength of the feed solution played a significant impact on the HA removal since both of these factors would influence the solute-solute and solute-membrane interactions. A promising result was achieved with the average filtrate flux coupled with higher removal of HA around 10.5 x 10^{-6} m^3/m^2.s and 97 %, respectively at pH 3 with 0.1 M ionic strength. This study indicated that membranes with the presence of TiO_2 and fabricated from zero air gap exhibited the highest permeability coefficient, high humic acid removal, moderate high flux and significant enhancement of anti-fouling ability. Thus, this membrane is suitable to be used in surface water treatment with the optimal pH and ionic strength was 3 and 0.1 M NaCl to obtain the higher HA removal. This research is believed to contribute to the advancement in using membrane technology for water treatment.

ABSTRAK

Kajian ini bertujuan untuk menyediakan membran polisulfona (PSF) ultraturasan dengan mempertingkatkan daya tahan kotoran untuk penyingkiran asid humik. Kesan penambahan 2 % berat titanium oksida (TiO_2) dalam formulasi dop pada prestasi dan morfologi membran telah dipelajari. Dua jenis membran ultraturasan i.e. membran PSF dengan dan tanpa TiO_2 telah dihasilkan melalui teknik kering/basah fasa terbalik. Membran telah dicirikan menggunakan goniometer sudut sentuh, pembelauan x-ray (XRD), kalorimeter pengimbasan pembeza (DSC), analisis termogravimetrik (TGA), mikroskopi imbasan electron pandang pemancaran (FESEM), sistem membran ultraturasan, nilai pemintasan jisim molekul dan pengukuran kotoran. Prestasi pemisahan membran telah dinilai menggunakan larutan asid humik. Kehadiran TiO_2 menunjukkan peningkatan berkesan dalam ciri membran seperti hidrofilik, kestabilan terma, sifat-sifat mekanikal, penelapan dan anti kotoran. Berdasarkan aspek ini, membran PSF dengan TiO_2 telah dipilih untuk kajian seterusnya dengan mempelbagaikan sela udara dalam lingkungan 0 – 13 cm. Keputusan menunjukkan membran yang disediakan dengan sela udara sifar pada pemintalan gentian geronggang mempamerkan prestasi terbaik dalam penelapan air dan penyingkiran asid humik. Membran ini selanjutnya digunakan bagi mengkaji kesan sekitaran fizikal-kimia larutan (pH dan kekuatan ion) terhadap pemisahan asid humik. pH dan kekuatan ionik larutan suapan memberikan impak yang signifikan keatas penyingkiran asid humik kerana kedua-dua faktor ini boleh mempengaruhi interaksi antara zat terlarut-zat terlarut dan zat terlarut-membran. Keputusan yang memberangsangkan telah dicapai dengan fluks turasan purata menggabungkan dengan penyingkiran asid humik yang tertinggi lingkungan 10.5×10^{-6} $m^3/m^2.s$ dan 97 % pada pH 3 dengan kekuatan ionik 0.1 M. Kajian ini menunjukkan bahawa membran dengan kehadiran TiO_2 dan difabrikasi dari sela udara sifar mempamerkan pekali kebolehtelapan yang tertinggi, penyingkiran asid humik yang tinggi, fluks sederhana tinggi dan peningkatan kebolehan anti kotoran. Maka, membran ini adalah sesuai digunakan dalam rawatan air permukaan dengan pH optimum dan kekuatan ionik ialah 3 dan 0.1 M NaCl supaya mendapatkan penyingkiran asid humik yang lebih tinggi. Kajian ini dipercayai mampu menyumbang kepada kemajuan teknologi membran untuk rawatan air.

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LIST OF ABBREVIATIONS

ABS	-	Absorbance
AFM	-	Atomic force microscope
CFV	-	Cross-flow velocity
COD	-	Chemical oxygen demand
Da	-	Dalton
DBPs	-	Disinfection By Products
DER	-	Dope extrusion rate
DOC	-	Dissolved Organic Carbon
DOM	-	Dissolved Organic Matter
DSC	-	Differential scanning calorimeter
FESEM	-	Field emission scanning electron microscope
FTIR	-	Fourier transform infrared
GAC	-	Granular Activated Carbon
GFC	-	Gel Filtration Chromatography
HAAs	-	Haloacetic Acids
HPO	-	Hydrophobic
HPI	-	Hydrophilic
HPSEC	-	High Pressure Size Exclusion Chromatography
HS	-	Humic Substances
IC	-	Inorganic carbon
NOM	-	Natural Organic Matter
MCL	-	Maximum contaminant level
MF	-	Microfiltration
MW	-	Molecular Weight
MWCO	-	Molecular weight cut off
NF	-	Nanofiltration
NTU	-	Nefelometric Turbidity Unit

PAC	-	Powdered Activated Carbon
PEI	-	Polyetherimide
PES	-	Polyethersulfone
POC	-	Particulate Organic Carbon
PSF	-	Polysulfone
PEG	-	Polyethylene glycol
PES	-	Polyethersulfone
PP	-	Polypropylene
PVDF	-	Polyvinylidenefluoride
PVP	-	Polyvinylpyrrolidone
PWF	-	Pure water flux
RC	-	Regenerated Cellulose
RO	-	Reverse Osmosis
SOCs	-	Synthetic Organic Compounds
SS	-	Suspended solid
SUVA	-	Specific UV Absorbance
TC	-	Total carbon
TDS	-	Total dissolved solid
TGA	-	Thermal gravitational analysis
THMs	-	Trihalomethanes
THMFP	-	Trihalomethanes Formation Potential
TiO_2	-	Titanium Dioxide
TMP	-	Trans-membrane pressure
TPI	-	Transphilic
TOC	-	Total organic carbon
TDS	-	Total dissolved solid
UF	-	Ultrafiltration
USEPA	-	US Environment Protection Agency
UV_{254}	-	Ultraviolet Absorbance at 254 nm

LIST OF SYMBOLS

A	-	Membrane surface area (m^2)
A_{sp}	-	The spinneret cross section (m^2)
Cf	-	Concentration of solute in the fluid at the feed ($mol.m^{-3}$)
Cp	-	Concentration of solute in the permeate solution ($mol.m^{-3}$)
d_i	-	Inside diameter of the hollow fiber membrane (m)
d_o	-	Outside diameter of the hollow fiber membrane (m)
d_p	-	Diameter of the particle deposited (m)
J	-	Flux, or flow rate through the membrane ($m^3\ m^{-2}\ s^{-1}$)
$Jpwp$	-	Pure water permeability ($m3.m^{-2}.s^{-1}$ or $m.s^{-1}$)
l	-	Membrane effective length (m)
M	-	Molecular weight ($g.mol^{-1}$)
ρ	-	Density of liquid ($kg.m^{-3}$)
ΔP	-	Transmembrane pressure (Pa)
P_f	-	Feed pressure (bar)
r_m	-	Mean pore radius (nm)
R	-	Solute rejection (%)
R_c	-	Cake Specific Resistances (m^{-1})
R_m	-	Hydraulic Resistances of the clean membrane (m^{-1})
R_{cp}	-	Resistances by concentration polarization (m^{-1})
R_{cl}	-	Resistances by cake layer (m^{-1})
R_a	-	Resistances by adsorbed layer (m^{-1})
T	-	Temperature (^oC)
Δx	-	Membrane effective thickness (m)
V_f	-	Spin line final velocity (ms^{-1})
V_o	-	Spin line initial velocity (ms^{-1})
V	-	Permeate volume (m^3)

w_1	-	Weight of the wet membrane (g)
w_2	-	Weight of the dry membrane (g)

Greek letters

η	-	Solution viscosity ($N.s.m^{-2}$)
μ	-	Solvent viscosity (water viscosity at 25^{o}C, 0.894×10^{-3} $kg.m^{-1}.s^{-1}$)
π	-	Osmotic pressure by concentration polarization

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CHAPTER 1

INTRODUCTION

1.1 Background of the Research

In most countries, water is available everywhere. Unfortunately, ninety-seven percent of the world's total water is seawater while the remaining three percent is fresh water and two-thirds of this fresh water is locked in glaciers, ice or snow, leaving only one percent of the world's total water available for direct human consumption (Ratajczak, 2007). Unfortunately, a large portion of water resources, including surface water and groundwater, has been extensively contaminated by uncontrolled disposal of hazardous waste. In contrast, the quality of drinking water continues to be a major public health concern throughout the world has accelerated the legislation of more stringent regulations for drinking water. Thus, a new advanced technology processing low quality or saline waters has been in great demand for water supplies and complying with stringent regulation such as membrane technology. Membrane technology can provide continuos operation and stable water quality with the potential to remove targeted contaminants in one stage.

Membrane technology is widely accepted as a means of producing various qualities of water from surface water, well water, brackish water and seawater. Application of membrane filtration for water treatment, which includes microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) receiving more attention since it is an outstanding process for the removal of particles, turbidity, microorganisms of natural and waste waters (Mulder, 1991). In the United States alone, the growing demand for membrane treatment technology such as reverse osmosis (RO), microfiltration and ultrafiltration, in all water treatment applications rose 6.5 percent annually starting in 1994, reaching $305 million in the year 2001 (Vial and Doussau, 2002), and considerable further growth has been seen since. The use of membranes has been somewhat limited due to high capital costs, although in recent years the cost of membrane systems has decreased substantially. Laine *et al*. (2000) reported that between 1992 and 2000, a 50 % decrease in cost was observed, with further decreases in cost observed since. This decrease in cost has been mainly attributed to two factors, namely, an increase in membrane surface area per module and an increase in mass production of these membrane modules. As a result of the decreased cost, the use of these systems has seen increased usage over the past 20 years, to become a very attractive and feasible alternative to conventional drinking water treatment.

In water and wastewater treatment, membrane treatment technology application as an advanced physical process for clarification and disinfection is established and rapidly gaining popularity (Gai *et al.*, 2008; Zularisam *et al.*, 2006). Microfiltration (MF) and ultrafiltration (UF) membranes widely applied in the field of drinking water treatment associated with their advantages including superior water quality, easier control of operation, lower cost and maintenance (Fu *et al.*, 2008; Lee *et al*., 2004). MF or UF were employed to remove microparticles and macromolecules including inorganic particles, organic colloids and dissolved organic matter. MF and UF systems were particulate filters and unlike nanofiltration (NF) and reverse osmosis (RO), they do not remove dissolved constituents. This treatment aspect makes them more suitable for use as a replacement to conventional filters. The cost of low pressure membranes systems is also a major driver for increased membrane application compared with conventional treatment technologies. Every year, the capital cost of MF and UF systems has decreased as economies of scale and a competitive market force innovative developments. Generally, low pressure membrane facilities are one half to one third the cost of an NF or RO facility (Farahbakhsh *et al.,* 2004). In addition, the implementation of innovative backwash or cleaning strategies has reduced operational cost, by reducing the degree of fouling that occurs on the surface and inside the pores of the membranes.

Nevertheless, one of the major problems arising in membrane separation is membrane fouling. Membrane fouling can cause a significant reduction in productivity. Productivity decline is defined as flux decrease with time of operation due to an increase of hydraulic resistance. In fact, productivity decline will increase operation and maintenance cost, and shortens the membrane life (Fu *et al.*, 2008; Zularisam *et al.*, 2006). NOM is often claimed as an important factor for both reversible and reversible fouling in water filtration. In particular, NOM is a complex mix of particulate and soluble components that presents in natural water, not only does it affects the odor, color and taste of water, it forms complexes with heavy metals and pesticides and also reacts with chlorine to form carcinogenic disinfection by-products (DBPs) (Zularisam *et al.*, 2006, Kim *et al.,* 2008). DBPs are carcinogens; direct exposure can lead to cancers, miscarriages and nervous system complications.

Among hydrophobic polymers, polytetrafluoroethylene (PTFE), polivinylideneflouride (PVDF), polypropylene (PP), polysulfone (PSF), and polyethersulfone (PES), PSF is so far, the polymer that generally easy to be used for the preparation of asymmetric membranes by the phase inversion method using water as a coagulant (Ahmad *et al.,* 2005). As PSF can be dissolved in common solvent perfectly such as N-methyl-2-pyrrolidone (NMP) and N,N-dimethylacetamide (DMAc), it is an excellent material for the preparation of hollow fiber membranes by a phase inversion method (Stropnik *et al.,* 2005). PSF is a well known polymeric material due to its commercial availability, ease of processing and favourable selectivity-permeability characteristics. It is one of the polymers that are thermally stable, possess good chemical resistance, and are resistant to most corrosive chemicals and organic compounds. Hence, PSF has been a subject of active research in polymer science and has received increasing attention for various membrane separation applications mostly for microfiltration and ultrafiltration (Kaiser and Stropnik, 2000). The main drawback of a PSF membrane is its hydrophobicity, which often resulted in serious fouling when applied to water treatment and separation of bio-products (Qin *et al.,* 2003). In order to increase the usefulness of the membrane, a hydrophobic polymer has been modified by the addition of nanoparticles due to their convenient operations, mild conditions, good and stable performances (Li *et al.,* 2009; Yang *et al.,* 2007). Therefore, it has been applied to a variety problem of environmental interest in addition to water and air purification.

1.2 Problem Statement

Membrane technology is an attractive option for drinking water production to provide better drinking water quality (Jerman *et al.*, 2007). Nevertheless, one of the major problems arising in membrane filtration is membrane fouling by natural organic matter (NOM). Membrane fouling can cause a reduction in productivity. Membrane fouling is usually induced by pore blocking and pore plugging inside the membrane pores and cake layer formation on the membrane surface due to the NOM adsorption, aggregation and deposition (Fu *et al.,* 2008). A humic substance is the predominant species of natural organic matter (NOM) and generally is divided into humic acid (HA), fulvic acid (FA) and humin (Hong and Elimelech, 1997; Yuan and Zydney, 1999a). Humic acid is a fraction of humic substances composed of a long chain molecular molecule, which is high in molecular weight, dark brown in colour and soluble in alkaline conditions (Fu *et al.,* 2008). Membrane fouling by humic substances is influenced by the characteristics of humic substances, the operation conditions, the chemical composition of the feed water and membrane properties (Cho *et al.,* 2000). Understanding of these factors is essential for better control of membrane fouling by humic acids and other types of natural organic matter.

Based on the membrane characteristics, it is considered that morphology, charge and hydrophilicity of membrane surface have a relationship with membrane fouling (Yuan and Zydney, 1999b). Nabe *et al.* (1997) modified the surface of polysulfone UF membranes to be hydrophilic using several methods and found out that the modified membranes had better performance during protein microfiltration and also better recovery after membrane cleaning. Lee *et al.* (2004) investigated the membrane fouling in MF and UF process by four types of membrane. They concluded that the shapes and size of molecules and roughness of a membrane are presumably important influential factors in affecting flux decline. The MF membranes exhibited greater surface roughness was more prone to fouling than the UF membranes. Weis *et al.* (2005) observed the influence of morphology, hydrophilicity and charge upon the long-term performance of UF membranes. They found that for membranes of similar hydrophobicity with different surface roughnesses, flux decline was found to be more significant for the rougher membranes. For the system studied, the rougher hydrophilic regenerated cellulose membrane had a greater tendency to resist adhesion than the smoother hydrophilic regenerated cellulose membrane. However, hydrophobic PES membrane exhibited greater tendency to resist adhesion compared to hydrophilic regenerated cellulose membrane. Therefore, both hydrophobicity and roughness were found to be linked to fouling tendency over the long term operation.

Since hydrophobicity and the surface roughness of the membrane plays a key role in membrane fouling, hydrophilic modification of polymeric membranes surface can be one of the fouling improvement methods. The presence of finely dispersed inorganic particles in polymeric matrix has proven to be very useful in improving membrane performance. Among various metal oxide nanoparticles, TiO_2 had received the most attention because of it enhancement properties such as high permselectivity, good hydrophilicity and excellent fouling resistance (Yang *et al.,* 2005; Bae and Tak, 2005; Cao *et al.,* 2006: Li *et al.,* 2009). To further improve membranes surface modification by finely dispersed TiO_2 particles in the polymer matrix, selection of the appropriate doping of TiO_2 filler or by immobilizing TiO_2 on surfaces are the most addressed efforts. In this research, the produced hollow fiber asymmetric membrane will then be compared between PSF/TiO_2 membranes to pristine membranes on hydrophilicity effects and fouling behaviour of humic acid using UF membrane system.

In order to obtain the hollow fiber asymmetric membrane with various characteristics such as pore size, porosity, roughness and nodular structure size, membranes were prepared via phase inversion process by varying the spinning parameters such as air gap. The air gap length during spinning affects the performance of final fibers and this has been studied by a number of researchers. Khayet (2003) demonstrated that an increased in the air gap length resulted in tighter fibers with lower permeability and increased retentivity because of an increased in the degree of orientation due to the added weight of the fiber below and the extended polymer chains. Similarly, Khulbe *et al.* (2004) observed that the separation of polyethylene glycol (PEG) of different molecular weight increased with an increased in the air gap. Fu *et al.* (2008) stated that the air gap influenced the roughness of the membrane outer surface. Thus, a study of the effect of air gap length was conducted in order to produce PSF/TiO_2 asymmetric hollow fiber ultrafiltration membranes for higher removal of humic acid and low fouling in surface water.

Feed water characteristics were known to have an effect on organic removal in UF membrane processes (Brigante *et al.,* 2009; Dong *et al.,* 2006; Yuan and Zydney, 1999a). Therefore, it is necessary to study the transport properties of humic acid through UF membrane under different physicochemical environment. Since the transportation of solute through the membrane does not only depend on size, other factors such as solute-solute and solute-membrane interactions, salt concentrations, ionic strength, permeate flux and system hydrodynamics were also identified as strong factors which influenced the solute transportation through the membranes. These physicochemical interactions occur between the membrane and solutes in the form of electrostatic charge, hydrophobic or even charge transfer. Thus, physicochemical parameters such as pH value and ionic strength need to be further investigated to achieve higher throughput of product.

1.3 Objectives of the Research

Based on the above-mentioned problem statements, the objectives of the research were:

1. To fabricate the ultrafiltration membrane with different dope formulation and air gap length for humic acid removal.
2. To characterize the membranes in terms of structural and physical properties and separation performance for humic acid removal in natural waters.

3. To investigate the effects of different pH and ionic strength in the humic acid removal through fabricated ultrafiltration membrane.

1.4 Scopes of the Research

In order to achieve the above-mentioned objectives, the following scopes of study were outlined:

1. Preparation of ternary dope solution with two polymer composition which are 18 wt. % PSF/2 wt. % TiO_2/DMAc/PVP (with TiO_2) and 18 wt. % PSF/DMAc/PVP (without TiO_2).
2. Fabrication of PSF/TiO_2 membrane with different air gap which are 0, 5 and 13 cm.
3. Characterizing the cross sections and the surfaces of the membranes using field emission scanning electron microscopy (FESEM) and atomic force microscope (AFM), water permeability and contact angle measurement.
4. Determination of molecular weight cut off (MWCO) of the fabricated membrane using a series of protein with different molecular weight cut off.
5. Evaluating the performance of UF membrane system was measured through permeability of the membranes as a function of time and rejections for the humic acid in terms of ultraviolet absorbance (UV_{254}).
6. Studying the feed solution with different pH and ionic strength. Humic rejection using fabricated membrane was carried out at pH 3, 5, 7 and 10. The effect of ionic strength was performed at 0.001 M, 0.01 M and 0.1 M sodium chloride concentration.

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