CHARACTERIZATION OF POLYVINYLIDENE FLUORIDE HOLLOW FIBER MEMBRANE WITH TITANIUM DIOXIDE FOR WATER TREATMENT

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To my wife, parents, friends and lecturers, thank you very much for the endless love, hope, support and prayer. Thank you so much.

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ABSTRACT

Membrane filtration system is one of the effective ways to remove micro-pollutants such as natural organic matter (NOM) in water treatment process. The surface of the membrane is, however, easily fouled by the deposition of NOM, thereby decreasing flux and separation performances. Thus, in this study, a series of polyvinylidene fluoride/titanium dioxide (PVDF/TiO_2) hollow fiber membranes with different TiO_2 loadings ranging from 0-3 wt.% were prepared via phase inversion method. The result shows that morphology of membrane layer becomes denser and thicker with the addition of TiO_2. The increase of TiO_2 loadings ranging from 0 to 2 wt.% resulted in the increase of membrane pore size from 142 to 155 nm with increase surface roughness from 20.2 to 23.98 nm. However with further increase of TiO_2 loading the pore size and surface roughness decreased to 152 and 19.33 nm respectively. The mechanical strength of membrane showed slight improvement from 3.01 MPa to 3.41 MPa as TiO_2 loading increased from 0 to 2 wt.% before reducing to 3.06 MPa with further increase of 3 wt.% TiO_2. Water contact angle demonstrated that with increase TiO_2 loading from 0 to 2 wt.% the contact angle was lowered slightly from 79^o to 74^o. At 2 wt.% TiO_2 loading, the highest peak values achieved were 37.86 L/m^2h for polymer organic solution flux and 39.04 L/m^2h for pure water flux. Membrane with 2 wt.% of TiO_2 loadings gives the highest rejection for all molecular weights of PVP. 14 % flux reduction were achieved at 2 wt.% TiO_2 loadings for pure water flux after organic polymer rejection test from 38.64 L/m^2h to 33.11 L/m^2h. Based on this study, it was found that membranes with 2 wt.% addition of TiO_2 were excellent in mitigating fouling particularly in reducing fouling resistance and increasing the rate of rejection.

ABSTRAK

Sistem penapisan membran merupakan salah satu cara yang berkesan untuk menghilangkan bahan pencemar mikro seperti bahan organik semulajadi (NOM) dalam proses rawatan air. Walaubagaimanapun, pemendapan NOM pada permukaan membran mengakibatkan kerosakan pada membran dan memberi kesan penurunan fluks dan prestasi pemisahan. Oleh demikian, satu siri membran serat berongga polivinililiden fluorida/titanium dioksida (PVDF/TiO_2) telah disediakan melalui kaedah fasa songsang dengan muatan TiO_2 berbeza pada julat 0 hingga 3 wt.%. Keputusan menunjukkan morfologi lapisan membran menjadi padat dan tebal dengan kehadiran TiO_2. Peningkatan muatan TiO_2 pada julat dari 0 hingga 2wt.% menyebabkan peningkatan pada saiz liang membran daripada 142 kepada 155 nm, dengan peningkatan permukaan kasar daripada 20.2 kepada 23.98 nm. Walaubagaimanapun, penambahan muatan TiO_2 menyebabkan saiz liang dan permukaan kasar berkurang kepada 152 nm dan 19.33 nm. Kekuatan mekanikal membran pula menunjukkan sedikit peningkatan daripada 3.01 MPa kepada 3.41 MPa apabila muatan TiO_2 ditambah daripada 0 hingga 2 wt% sebelum pengurangan kepada 3.06 MPa apabila penambahan 3 wt% TiO_2. Sudut sentuhan air pula menunjukkan peningkatan muatan TiO_2 daripada 0 hingga 2 wt%, sudut sentuhan air membran menunjukkan pengurangan kecil daripada 79^o kepada 74^o. Pada 2 wt.% muatan TiO_2, puncak paling tinggi yang dicapai adalah 37.86 L/m^2j bagi flux larutan polimer organik dan 39.04 L/m^2j bagi flux larutan air tulen. Membran dengan 2 wt.% muatan TiO_2 juga menunjukkan penolakan paling tinggi bagi semua jenis berat molekul PVP. 14 % pengurangan fluks telah dicapai pada 2 wt.% muatan TiO_2 dalam flux air tulen selepas ujian penolakan polimer organik daripada 38.64 L/m^2j kepada 33.11 L/m^2j. Berdasarkan kajian ini, membran dengan 2 wt.% muatan TiO_2 adalah sangat baik dalam mengurangkan kerosakan terutamanya dalam mengurangkan kerosakan membran dan meningkatkan kadar penolakan.

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LIST OF SYMBOLS

%	Percent
^0C	Celcius
E	Porosity
μ	Viscosity
P	Density
ΔP	Transmembrane Pressure
ω_1	Weight of wet membrane
ω_2	Weight of dry membrane
σ_p	Geometric standard division
μ_p	Mean pore size
µm	Micrometer
A	Area
Al_2O_3	Aluminium oxide
ClO_4	Perchlorate
cP	CentiPoises
c_p	Concentration of permeate
c_f	Concentration of feed
Cm	Centimeter
Da	Dalton
D_o	Outer diameter
D_i	Inner diameter
d_p	Pore size membrane
G	Gram
g/mol	Gram per mole
g/ml	Gram per milliliter

H_2O	Water
H	Hour
J	Flux reduction
J_r	Flux rejection of polymer
J_w	Flux pure water
J_i	Flux initial
J_f	Flux final
J_r/J_w	Flux ratio
K	Kelvin
kN	Kilo Newton
L	Liter
LiCI	Lithium chloride
$LiClO_4$	Lithium perchlorate
LiPF6	Lithium hexafluorophospate
Li+	Lithium ion
Ml	Mililiter
Mm	Milimeter
Mg	Miligram
mW	Mili watt
Min	Minute
MPa	Mega Pascal
m^2	Meter square
m^3	Meter cube
m^3/d	Meter cube per day
Nm	Nanometer
N	Number of pores
Ppm	Part per millions
Q	Flow rate
R	Rejections
R_a	Surface roughness
Rpm	Rotor per minute
SiO_2	Silica oxide

TiO_2	Titanium dioxide
T	Time
T_g	Thermogravimetric
V	Volume
wt.%	Percent weight
ZnO	Zinc Oxide

LIST OF ABBREVATIONS

AFM	Atomic force microscopy
BOD	Biological oxygen demand
CA	Cellulose acetate
COD	Chemical oxygen demand
DBP	Disinfection by product
DOM	Dissolve organic matter
DON	Dissolve organic nitrogen
DMAc	N,N-dimethylacetamide
DMF	N,N-dimethylformamide
DMSO	Dimetylsulfoxide
DSC	Differential Scanning Dicalorimetry
GCMS	Gas chromatography mass spectometry
GS	Gas separation
HA	Halocetic acid
HAN	Halocetonitriles
MD	Membrane Distillation
MF	Microfiltration
MWCO	Molecular weight cut-off
NF	Nanofiltration
NMP	N-methylpyrrolydone
NOM	Natural organic matter
PEG	Polyethylene glycol
PES	Polyethersulfone
PMMA	Poly(methyl methacylate)
PP	Polypropylene

PSf	Polysulfone
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
PVP	Polyvinylpyrrolidone
RO	Reverse Osmosis
SEM	Scanning Electron Microscopy
TEP	Triethylphospate
TGA	Thermogravimmetric analysis
THM	Trihalomethane
TOC	Total organic carbon
TSS	Total suspended solid
UF	Ultrafiltration
UV	Ultra-violet
WTP	Water treatment plant

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Drinking water is essential to human life. Drinking water resources are mainly from rivers or water bodies that enter water treatment plant (WTP) before distribution. In the past decade, the WTPs were designed to treat contaminants that exist in water bodies such as natural organic matter (NOM) and ammonia. These compounds are found in the water body or originated from either soil upstream water bodies. Mostly they were from plantation or aquatic plants that flow in water bodies by precipitation, underground flow and flood.

However, there are some problems in existing WTP where the presence of free chlorine content that is used as a disinfectant is found to react with residual NOMs. This reaction process has been found to have a tendency to form disinfection by-products (DBPs) such as trihalomethanes, haloacetic acids and other halogenatic organics. DBPs are carcinogens and direct exposure may lead to cancers, miscarriages and nervous system complications (Zularisam *et al.*, 2006).

Moreover, the increasing soil erosion and flood from unplanned construction and rapid economic development will increase the amount of NOMs which leads to problems in existing WTP (Tian *et al.*, 2009). Certainly, up to date existing WTP are not able to eliminate these DBPs to a satisfactory level, thus an advanced treatment process is needed (Wintgens *et al.,* 2002).

At present, the development of membrane technologies has attracted attention in the field of water treatment process. Microfiltration and ultrafiltration are used when membrane filtration is applied for removal of larger particles. Therefore, in this study, a hydrophilic polyvinylidene fluoride polymer membrane a hollow fiber configuration was investigated. The performance of membrane were analysed with different characterization such as hydrophilicity, mechanical, thermal and flux reduction.

1.2 Problem Statement

Based on the research background, the potential of micropollutants such NOM with various molecular weight cut-off react with chlorine during the chlorination process potentially forming disinfection by-products such as trihalomethanes (THMs), halocetic acids (HAs), and other halogenated organics in current conventional water treatment. THMs, HAs and many other by-products which are potentially hazardous to human body have been detected in the drinking water although at low level concentration.

Among all water treatment technologies, one of the most promising options for pollution separation and purification is membrane technology. Membrane processes are becoming more popular in water treatment because the process can purify water without chemical addition and prevent the formation of toxic DBPs (Rana *et al.,* 2005). The benefits of membrane treatment process have been highlighted as having a small footprint, compact module, low energy consumption, environmental friendliness (Zularisam *et al.,* 2006).

However, membrane fouling is one of the biggest obstacles that constrain the use of membrane in technical or even economical view (Balta *et al.,* 2012). One of the causes is adsorption of organic pollutants into the pores and deposition on the membrane surface that would limit the water transportation across the membrane itself at the same time increasing energy consumption and reducing membrane life (Asatekin *et al.,* 2007). Therefore, a quick measure is needed to further extend the application of membrane-based process for water treatment such as developing hydrophilic, antifouling and high flux performances membrane (Li *et al.,* 2014).

Many attempts have been carried out to adjust membrane surface like surface charge, pore size and hydrophilicity, effectively in order to prevent the adsorption phenomenon and consequently reduce membrane fouling which can improve the membrane performances significantly. The hydrophilicity of membrane can be improvised using various techniques, such blending, chemical grafting, and surface modifications (Li *et al*., 2006). Among these techniques, physical blending with inorganic nanoparticles offers more benefits due to average conditions, excellent performances and appropriate operations.

The nanoparticles normally introduced as an additive to the polymer membranes are SiO_2 (Ochoa *et al*., 2003), Al_2O_3 (Zhang *et al*., 2009), ZnO (Wang *et al*., 2000), and TiO_2 (Li *et al*., 2006). TiO_2 has received the most consideration due to its stability under stiff conditions, commercial availability, and ease of preparation. The effect of other hydrophilic additives, i.e. LiCl and PVP, on the thermodynamic/kinetic relations during the phase inversion process in the preparation of PVDF-based membranes was investigated by Fontananova *et al*. (2006).

Blending modification is the most practical way which can be applied to an industrial scale production. The hydrophilic PVDF membrane with other desirable properties can be obtained simultaneously during the membrane preparation process without any pre-treatment or post treatment procedures, which is usually adopted in chemical grafting or surface grafting. More importantly, most of the blending modification methods focused on the flat sheet PVDF membranes which limit its application in the modification of hollow fiber membrane (Liu *et al*., 2011). Although a large amount of scientific papers have been published, only little information was available in the literature for the blending modification of hollow fiber PVDF membrane with inorganic particles, titanium dioxide.

Several research has been reported for the blending modification of hollow fiber PVDF membrane with titanium dioxide, however this is limited to the application of oily wastewater treatment. Therefore, the current research was conducted to explore the possibility and effectiveness of using inorganic nanoparticle blending with membrane polymer. Modified polyvinylidene fluoride (PVDF) hollow fiber membrane were blended with titanium dioxide nanoparticles which are expected to increase the membranes hydrophilicity and emphasize the antifouling performances using different molecular weight of organic solution which replicate the transport property as NOMs in surface water.

1.3 Objectives of the Study

The main aims of this study are to:

1. To investigate the effects of TiO_2 concentration on the structural and physical properties of the hollow fiber PVDF membranes.

2. To investigate the effect of TiO2 concentration on the improvement of hydrophilicity of the hollow fiber PVDF membranes.

3. To investigate the effect of TiO_2 concentration on the antifouling properties and the separation efficiency of hollow fiber PVDF membranes under various feed molecular cut-off.

1.4 Scope of Study

To achieve the above mentioned objectives, the following scopes of study were designed. These were divided into three stages and briefly elaborated as follows:

1. The effect of titanium dioxide on formation of hollow fiber membrane.

The hollow fiber membrane preparation and fabrication were conducted by formulating membrane materials and dope preparation (polymer, solvent, additives, inorganic nanoparticles). In order to increase the hydrophilicity of membrane, the adding nanoparticles will be explored which is known as blending modification method.

2. Membrane filtration measurement and characterization.

This task involved the characteristics as well as the physico-chemical properties of the fabricated hollow fiber membrane. Polyvinylidene fluoride hollow fiber membrane was characterized using Scanning Electron Microscopy (SEM), contact angles, Differential Scanning Calorimetry (DSC), mechanical strength, porosity as well as pure water flux.

3. Antifouling, separation and hydrophilicity performance

The study involved preparation of hollow fiber module and setting up the membrane testing rig to determine membrane flux, solute rejection and anti-fouling performance. Solute rejection: Polyvinylpyrrolidone (PVP) solution with difference molecular weight cut-off. This involves detection analysis using the total organic compound analyzer (Shidmadzu) (TOC). Antifouling performance was studied based on the membrane flux reduction which to explore the influence of hydrophilic agent (nanoparticles) towards before and after solute rejection flux.

1.5 Significance of Study

The overall rationale and significance of the current research is to explore the formation and development of polyvinylidene fluoride hollow fiber membrane. Configuration of hollow fiber membranes has an extra advantage in the higher packing density whereas selection of synthetic polymer polyvinylidene fluoride has drawn much attraction in comparison with other polymers due for example to good resistance to many acids and alkalines, high tolerance towards oxidants, excellent mechanical properties, outstanding membrane formation, and great thermal stability. Due to the positive outcomes exhibited by hydrophilic membrane ultrafiltration in terms of higher permeates flux and rejection, this membrane is a promising technique for treating micro pollutant produced from surface water. Most of the current work explores the commercially fabricated membranes and flat type configuration membranes.

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