

**PVDF-TIO₂ NANOCOMPOSITE MEMBRANE
WITH ANTI-FOULING PROPERTIES FOR OIL
EMULSION REMOVAL**

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PVDF-TiO₂ NANOCOMPOSITE MEMBRANE WITH ANTI-FOULING PROPERTIES FOR OIL EMULSION REMOVAL

by

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LIST OF ABBREVIATIONS

AFM	Atomic force microscope
Al ₂ O ₃	Alumina
APTES	3-aminopropyltriethoxysilane
BSA	Bovine Serum Albumin
CA	Cellulose acetate
CNTs	Carbon nanotubes
COD	Chemical oxygen demand
DMAc	N,N-dimethylacetamide
DMF	N,N-dimethylformamide
DMSO	Dimethylsulfoxide
EPS	Extracellular polymeric substances
EQA	Environmental Quality Act
Fe ₃ O ₄	Ferroxane
FESEM	Field emission scanning electron microscope
FRR	Flux recovery ratio
FTIR	Fourier transform infrared spectroscopy
HDTMS	Hexadecyltrimethoxysilane
HMPA	Hexamethylphosphoramide
HNTs	Halloysite nanotubes
MD	Membrane distillation
MF	Microfiltration
MWCNTs	Multi-walled carbon nanotubes
N ₂	Nitrogen
NF	Nanofiltration
NMP	N-methyl-2-pyrrolidone
PAN	Polyacrylonitrile
PEG	Polyethylene glycol
PEGMA	polyethylene glycol methyl ether methacrylate
PEO	Polyethylene oxide
PES	Polyethersulfone
PSF	Polysulfone
PI	Polyimide

PVDF	Polyvinylidene fluoride
PVP	Polyvinylpyrrolidone
RFR	Relative flux reduction
RO	Reverse osmosis
SiO ₂	Silica
SPES	Sulfonated-polyethersulfone
TEP	Triethylphosphate
TFOA	3,3,4,4,5,5,6,6,7,7,8,8-tridecafluorooctyl acrylate
TiO ₂	Titanium dioxide
TMP	Transmembrane pressure
TMU	Tetramethylurea
TOC	Total organic content
UF	Ultrafiltration
UV	Ultraviolet
XPS	X-ray photoelectron spectroscopy
ZnO	Zinc oxide
ZrO ₂	Zirconia

LIST OF SYMBOLS

		Unit
ε	Membrane Porosity	%
w_1	Weight of the wet membrane	g
w_2	Weight of the dry membrane	g
ρ_p	Specific gravity of the PVDF polymer	g/cm ³
ρ_b	Specific gravity of 2-butanol	g/cm ³
J	Membrane permeation flux	L/m ² .hr
V	Volume of the permeate	L
A	Membrane effective area	m ²
Δt	Time taken to collect 2 mL of the permeate sample	hr
R	Rejection of the solute	%
C_p	Permeate concentration	ppm
C_f	Feed concentration	ppm
J_{w1}	Initial pure water flux	L/m ² .hr
J_{w2}	Pure water flux after the hydraulic cleaning	L/m ² .hr
J_p	Final permeate flux	L/m ² .hr
$\gamma_{SL}, \gamma_{LV}, \gamma_{SV}$	Surface tensions of solid-liquid, liquid-vapor and solid-vapor	-

MEMBRAN KOMPOSIT PVDF-TiO₂ BERSIFAT NGAH-KOTORAN UNTUK PENYINGKIRAN EMULSI MINYAK

ABSTRAK

Polivinilidena fluorida (PVDF) membran yang terdedah kepada kotoran emulsi minyak sukar deibersihkan melalui saluran air pada permukaan membran. Sifat hydrophilic titanium dioksida (TiO₂) akan mengubah kestabilan larutan polimer semasa fasa penyongsangan dan mengubah morfologi membran. Dalam kajian ini, PVDF-TiO₂ membran matriks bercampur yang bersifat pembersihan sinar ultraungu (UV) telah disintesis untuk penyingkiran emulsi minyak mentah dalam keadaan kemasinan yang tinggi. Kesan parameter sintesis membran, iaitu kepekatan polimer, jenis pelarut, jenis dan kepekatan TiO₂, dan kepekatan polietilena glikol (PEG) telah dikaji. Sifat-sifat fizikokimia membran dinilai dan dikaitkan dengan prestasi dan sifat anti-kotoran membran. Saiz liang dan keporosan membran merupakan kesan mendominasi pengotoran oleh emulsi minyak. Dari segi anti-kotoran, parameter sintesis membran optima diperolehi dengan menggunakan 18 % berat kepekatan polimer dengan menggunakan N,N-dimetilasetamid (DMAc) diguna sebagai pelarut dan ditambah dengan 3 % berat P25 TiO₂. Fluks penelapan air yang diperolehi adalah 160.19 ± 11.54 L/m².hr, penolakan emulsi minyak sebanyak 96.27 ± 0.28 % dengan 23.40 ± 1.10 % nisbah pemulihan fluks (FRR). Ia didapati bahawa tekanan kritikal harus rendah daripada 1.5 bar untuk mengelakkan kotoran di mana rintangan lapisan kek adalah mekanisma utama pengotoran. Selepas 30 min sinaran UV, membran matriks bercampur menunjukkan peningkatan yang drastik dalam nisbah pemulihan fluks, iaitu sebanyak 90.42 ± 4.90 % di mana ia mengesahkan sifat pembersihan sendiri

zarah nano TiO_2 dalam mendegredasikan emulsi minyak yang terjerap pada permukaan membran. Namun begitu, penyinaran UV dalam jangka masa yang lebih panjang dan intensiti yang lebih tinggi boleh mengurangkan prestasi membran kerana liang tersumbat disebabkan oleh pemecahan minyak dan pembesaran liang.

PVDF-TiO₂ NANOCOMPOSITE MEMBRANE WITH ANTI-FOULING PROPERTIES FOR OIL EMULSION REMOVAL

ABSTRACT

Polyvinylidene fluoride (PVDF) membrane is prone to be fouled by oil emulsions which could not be easily cleaned via surface washing. Besides, hydrophilic nature of titanium dioxide (TiO₂) changes the thermodynamic stability of the polymer solution during phase inversion and caused membrane with altered morphology. In this study, PVDF-TiO₂ mixed-matrix membranes with UV-cleaning properties were synthesized for crude oil emulsion removal at high salinity condition. The effect of membrane synthesis parameter, namely polymer concentrations, type of solvents, TiO₂ type and concentrations, and polyethylene glycol (PEG) concentrations were investigated. The physicochemical properties of the membrane were characterized and related to its performance and antifouling properties. Membrane pore size and porosity were the dominating effects of membrane fouling by oil emulsions. In term of antifouling, the optimum membrane synthesis parameter was obtained by 18 wt.% PVDF with N, N-dimethylacetamide (DMAc) as solvent added with 3 wt.% of P25 TiO₂. The obtained pure water permeation flux was 160.19 ± 11.54 L/m².hr, rejection of 96.27 ± 0.28 % with flux recovery ratio (FRR) of 23.40 ± 1.10 %. It was found that the critical pressure to avoid irreversible fouling should be lower than 1.5 bar whereby cake layer resistance is the main fouling mechanism. Upon 30 min of UV irradiation, the mixed-matrix membrane exhibited drastic FRR improvement of 90.42 ± 4.90 %, which confirms the photocatalytic property of TiO₂ nanoparticles in degrading the adsorbed

oil emulsions on the membrane surface. Nonetheless, further increased of UV irradiation duration and intensity could deteriorate the membrane performance due to pore blockage caused by the oil fragmentation and pore enlargement.

CHAPTER ONE

INTRODUCTION

1.1 Oil-in-water Emulsion and Produced Water Treatment

The rapid growth in metallurgical, transportation, food processing, pharmaceutical, petrochemical industries as well as oil and gas refineries has generated a large volume of wastewater in the form of either oil-in-water or water-in-oil emulsions. Produced water is any fossil water that being injected into the reservoir and brought to the surface along with crude oil and natural gas. It contains various organic and inorganic compounds such as dissolved formation minerals, dissolved and dispersed oil compounds, production chemical compounds, production solids and dissolved gases (Hansen and Davies, 1994). Produced water serves as the largest byproduct or waste stream by volume associated with oil and gas production. Daily global production of produced water is around 250 million barrels which are three times than that of the produced oil (80 million) and this factor goes up with the maturity of the oil fields (Dal Ferro and Smith, 2007, Khatib and Verbeek, 2003). Oil which acts as the major pollutant in the produced water generated from oil field is in the range between 100 and 1000 mg/L or higher depending on the efficiency of demulsification and nature of the crude oil (Chakrabarty *et al.*, 2008b). Produced water can pollute surface and underground water and soil which poses serious environment threats.

Different countries established different oil discharge limit to prevent the severe pollution in water environment as shown in Figure 1.1. The different oil discharge standard for each country is depends on the geographical condition and the characteristics of the original wastewater. In Malaysia, the effluent discharge should

comply with the national primary regulatory of discharge standard as stipulated in the Environmental Quality Act (EQA), 1974. Malaysia only allowed the maximum of 10 ppm oil and grease discharged concentration which is much lower as compared to other countries. Thus, more exploration in produced water treatment is required to meet this stringent discharge standard and to deal with increasing global oil demand.

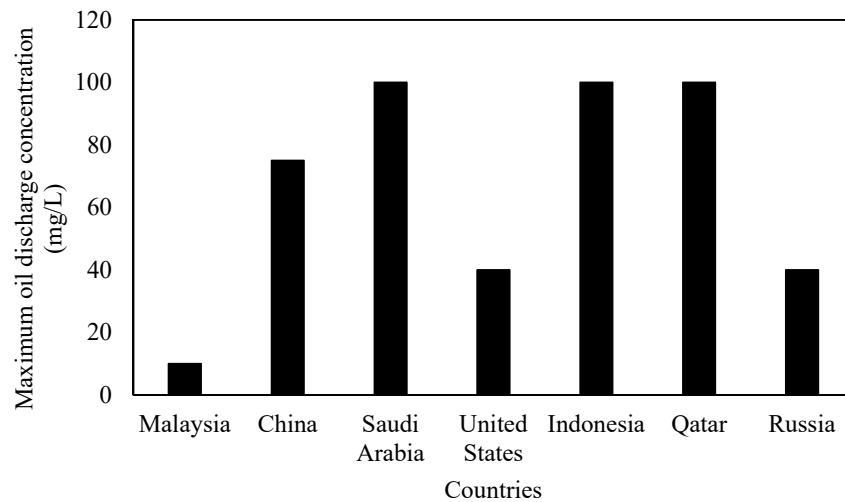


Figure 1.1: Oil discharge limit for different countries (Veil, 2006)

1.2 Limitations of Conventional Separation Method

Industrial oily wastewater is existed in three broad categories: free-floating oil, unstable oil/water emulsion and stable oil/water emulsion (Um *et al.*, 2001). Conventional separation technologies can readily separate the free-floating oil and unstable oil/water emulsions (El-Kayar *et al.*, 1993, Hosny, 1996). Conventional methods available for oily wastewater treatment including physical, chemical, and biological methods. Physical treatment includes adsorption (activated carbon, organoclay, copolymers, zeolites and resins) (Carvalho *et al.*, 2002, Janks and Cadena, 1992), sand filters (Adewumi *et al.*, 1992), cyclones (van den Broek *et al.*, 1998),

evaporation (Becker, 2000) and dissolved air precipitation (Thoma *et al.*, 1999); chemical treatment includes chemical precipitation (Zhou *et al.*, 2000), chemical oxidation (Oller *et al.*, 2011), electrochemical process (Ma and Wang, 2006), photocatalytic treatment (Li *et al.*, 2007), Fenton process (Yang and Zhang, 2005), room temperature ionic liquids (McFarlane *et al.*, 2005) and demulsifiers (Deng *et al.*, 2005); biological treatment (Li *et al.*, 2005, Wang *et al.*, 2012). However, these conventional methods have some drawbacks such as high operating cost, large space for installation and pollute the environment due to usage of toxic compounds and the production of secondary pollutants. In view of these drawbacks, membrane technology has been considered as an efficient method for the oily wastewater treatment. Besides, membrane technology able to separate much smaller oil droplets from stable oil emulsions. Membrane technology works without chemical addition, lower energy consumption and moderate operating cost, easy to operate and able to produce high permeate quality (Shams Ashaghi *et al.*, 2007, Arthur *et al.*, 2005, Mondal and Wickramasinghe, 2008).

The pressure-driven membrane process consists of microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). They are conceptually similar processes but the key difference is the surface pore size of the membrane. Among the membrane processes, UF is known as one of the most effective treatments for oily wastewater. In comparison with the traditional separation methods, UF has higher oil removal efficiency without the use of chemical additives and low energy cost (He and Jiang, 2008). MF membranes have been utilized for surfactant recovery in permeate. MF offers higher flux but possesses the risk of oil breakthrough. While RO and NF normally used to treat oily wastewater which composed of higher

salt content (Cheryan and Rajagopalan, 1998). However, membrane comes with some drawbacks including membrane fouling or concentration polarization due to its low surface energy that causes the decline in permeation flux and shorten the membrane lifetime.

1.3 Membrane Fouling

In the treatment of produced water using membranes, the permeate flux may decrease due to concentration polarization or fouling (Field, 2010). Concentration polarization is a natural phenomenon of semi-permeable membrane, at which rejected particles or solutes will accumulate in the mass transfer boundary layer adjacent to the membrane surface (Tashvigh *et al.*, 2015). In UF, concentration polarization is a common issue during filtration of low molecular weight macromolecules (Hughes *et al.*, 2006). During filtration, solvent passes through the membrane pores while the larger solutes are rejected on the membrane surface (Hu and Scott, 2008, Corbatón-Báguena *et al.*, 2015, Mueller *et al.*, 1997). The rejected solutes accumulate on the membrane surface cause a concentration gradient on the membrane surface. According to Baker (2000), the concentration of solutes accumulated on the membrane surface could reach 20 to 50 times than that in the bulk solution. Such a high amount of solutes accumulated on the membrane blocked the solvent to pass through the membrane, at the same time created an osmotic back pressure that reduced the effective transmembrane pressure (TMP) of the system (Field, 2010). Concentration polarization is considered to be a hydrodynamic phenomenon which could be alleviated by physical cleaning operating at higher velocity (Merin and Cheryan, 1980). In general, concentration polarization is a reversible phenomenon that will not affect the membrane intrinsic properties.

Membrane fouling is a second phenomenon leads to flux reduction, which the solutes from the feed solution either adsorb on the membrane surface (external fouling) or inside membrane porous structure (internal fouling) (Abbasi and Taheri, 2014). Internal or external fouling is based on the ratio of solute size to membrane pore size. In contrast to the reversible nature of concentration polarization, irreversible membrane fouling may cause loss of the membrane permeability.

A clear distinction must be made between concentration polarization and membrane fouling. The main difference between concentration polarization and membrane fouling is that concentration polarization is formed on the membrane surface, whereas membrane fouling is formed by solute-membrane interactions which are more closely bounded to the membrane surface. In fact, fouling characteristic can be defined based on its fouling reversibility.

There are two general types of membrane fouling exist for oily wastewater treatment known as reversible and irreversible fouling. Reversible fouling is a result of deposited colloid particles or solutes on the membrane surface and in the membrane pores. Pure water cross-flushing or backwashing may be utilized to reverse the flux declination in reversible fouling. On the other hands, irreversible fouling is a result of strong chemical or physical sorption of particles and solutes on the membrane surface and in the porous structure to form the gel layer. The only method to recover the flux caused by irreversible fouling is via chemical washing. However, aggressive cleaning methods may not be able to recover to its initial permeability due to the chemical instability of the membrane as well as pore blocking (Salahi *et al.*, 2010).