ZWITTERION EMBEDDED THIN FILM COMPOSITE FORWARD OSMOSIS MEMBRANE FOR OILY WASTEWATER TREATMENT

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DEDICATION

To my beloved mother and father

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ABSTRACT

The rising oil consumption in oil and gas industries has exacerbated the disposal of oil waste into the water stream. Hence, oily wastewater treatment is required to prevent threats to the human and environment. With some great advantages such as lower membrane fouling rate, lower energy requirement and higher water recovery rate compared to the conventional pressure-driven membrane processes, forward osmosis (FO) has been recognized as a potential candidate for oily wastewater treatment. In this study, zwitterionic polymer, poly[3-(N-2-methacryloylxyethyl-N,N-dimethyl)-ammonatopropanesulfonate] (PMAPS) was incorporated into thin film composite (TFC) membrane to render excellent anti-fouling properties to the membrane. PMAPS was blended with polyethersulfone (PES) polymer solution and cast into PES support layer. Interfacial polymerization technique was applied to form a thin polyamide layer a top of the PES support layer. The PMAPS incorporated TFC membranes were characterized for their morphology and surface hydrophilicity. The oily wastewater treatment performance of the PMAPS incorporated TFC membrane was evaluated through the FO process. The resultant 1% PMAPS-TFC membrane exhibited high water flux of 15.79±0.3 L/m^2.h and oil flux of 12.54±0.8 L/m^2.h when tested in FO mode for oil removal from oily wastewater using 1000 ppm emulsified oily solution as the feed solution and 2M sodium chloride as the draw solution. The oil rejection up to 99% was also obtained and most of the clean water was extracted from the feed solution. Most significantly, PMAPS incorporated TFC membrane outperformed neat TFC membrane with a lower fouling propensity for oily waste treatment. When treating 10000 ppm oil emulsion, PMAPS-TFC was able to achieve an average flux recovery rate of 97% while neat TFC was only able to achieve 70.8% of average flux recovery rate. Overall, the PMAPS incorporated TFC membrane has a great potential as it possesses superior hydrophilicity and strong anti-fouling behavior which helps to save the periodic cost of membrane replacement.

ABSTRAK

Peningkatan penggunaan minyak dalam industri minyak dan gas semakin memburukkan fenomena pembuangan sisa minyak ke aliran air. Oleh itu, rawatan air sisa berminyak amat diperlukan untuk mencegah ancaman terhadap manusia dan alam sekitar. Dengan beberapa kelebihan seperti kadar pengotoran membran yang rendah, keperluan tenaga yang lebih rendah dan kadar perolehan air yang lebih tinggi berbanding dengan proses membrane dipacu tekanan konvensional, osmosis hadapan (FO) telah diiktiraf sebagai cara yang berpotensi untuk rawatan air sisa berminyak. Dalam kajian ini, polimer zwitterion, poli [3- (N-2-metakriloilxietil-N, N-dimetil) -ammonatopropanasulfonat] (PMAPS) digabungkan dengan membran komposit filem nipis (TFC) dengan sifat anti-kotoran yang sangat baik. PMAPS diadun dengan larutan polimer polietersulfona (PES) dan dituang ke dalam lapisan sokongan PES. Teknik pempolimeran antara muka digunakan untuk membentuk lapisan poliamida nipis di atas lapisan sokongan PES. Membran TFC yang digabungkan dengan PMAPS telah dicirikan dari segi morfologi dan sifat hidrofilik permukaannya. Prestasi rawatan air sisa berminyak daripada PMAPS yang digabungkan dengan membran TFC telah dinilai melalui proses FO. Membran 1% PMAPS-TFC yang dihasilkan menunjukkan fluks air yang tinggi, iaitu 15.79 ± 0.3 L / m^2.h dan fluks minyak 12.54 ± 0.8 L / m^2.h apabila diuji dalam mod FO untuk penyingkiran minyak dari air sisa berminyak menggunakan larutan emulsi berminyak 1000 ppm sebagai larutan suapan dan 2M natrium klorida sebagai larutan luaran. Penolakan minyak sebanyak 99% juga diperolehi dan kebanyakan air bersih telah diperahkan dari larutan suapan. Yang paling ketara, membran TFC yang digabungkan dengan PMAPS lebih unggul daripada membran TFC kawalan dengan kecenderungan kotoran yang lebih rendah untuk rawatan sisa berminyak. Apabila merawat emulsi minyak 10000 ppm, PMAPS-TFC dapat mencapai kadar perolehan fluks purata sebanyak 97% manakala TFC kawalan hanya dapat mencapai 70.8% daripada kadar perolehan fluks purata. Membran TFC yang digabungkan PMAPS amat berpotensi tinggi kerana ia mempunyai sifat hidrofilik dan anti-kotoran yang baik yang mana membantu menjimatkan kos berkala penggantian membran.

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LIST OF ABBREVIATIONS

1,3-PS	-	1,3-propanesulfonate
AFM	-	atomic force microscopy
AL-DS	-	active layer – draw solution
AL-FS	-	active layer – feed solution
A-PAM	-	anionic polyacrylamide
C	-	carbon
CA	-	cellulose acetate
CAB	-	cellulose acetate butyrate
CNTs	-	carbon nanotubes
CTA	-	cellulose triacetate
DAPPC	-	1,4-Bis(3-aminopropyl)piperazine propane carboxylate
DCE	-	1,2-dichloroethane
DEDA	-	N,N-diethylethylenediamine
DI	-	deionized
DMAEMA	-	N,N-Dimethylaminoethyl Methacrylate
DS	-	draw solution
EDL	-	electric double layer
EDS	-	energy-dispersive X-ray spectroscopy
FESEM	-	field emission scanning electron microscopy
FO	-	forward osmosis
FS	-	feed solution
FTIR	-	Fourier transform infrared spectroscopy
gMH	-	$gm^{-2}h^{-1}$
ICP	-	internal concentration polarization
IP	-	interfacial polymerization
IPC	-	isophthaloyl chloride
Layer-by-layer	-	LbL
LMH	-	$Lm^{-2}h^{-1}$
LMHB	-	$Lm^{-2}h^{-1}Bar^{-1}$
MAZ	-	mullite-alumina-zeolite

MD	-	membrane distillation
MMM	-	mixed matrix membrane
MPD	-	meta-phenyl diamine
MWCO	-	molecular weight cut off
MZ	-	mullite-zeolite
NF	-	nanofiltration
NIPAM	-	N-Isopropyl acrylamide
NMP	-	N-methyl-2-pyrrolidone
O	-	oxygen
OA	-	oxalic acid
OCA	-	optical contact angle
PA	-	polyamide
PAI	-	polyamide-imide
PC	-	polycarbonate
PDA	-	polydopamine
PES	-	polyethersulfone
PI	-	polyimide
PIP	-	piperazine
PISS	-	zinc silicate
PMAPS	-	Poly[3-(N-2-methacryloxyethyl-N,N-dimethyl)-ammonatopropanesulfonate
PPD	-	p-phenylenediamine
PRO	-	pressure retarded osmosis
PS	-	1,3-propane sultone
PSB	-	polysulfobetaine
PSF	-	polysulfone
PVDF	-	polyvinylidene fluoride
PVP40	-	polyvinylpyrrolidone40
RO	-	reverse osmosis
SDS	-	sodium dodecyl sulfate
SEM	-	scanning electron microscope
TFC	-	thin film composite
TFN	-	thin film nanocomposite
TMC	-	trimesoyl chloride

UF	-	ultrafiltration
Z-fSWNT	-	zwitterion-functionalized single-walled carbon nanotube

LIST OF SYMBOLS

ΔC_d	-	change in oil concentration in draw solution
ΔC_f	-	change in salt concentration in feed solution
ΔP	-	applied pressure difference
Δt	-	operation time
A	-	effective area of membrane
A_w	-	water permeability coefficient
c	-	concentration of salt
$C_{d,final}$	-	final oil concentration
$C_{d,initial}$	-	initial oil concentration
C_f	-	feed concentration
C_p	-	permeate concentration
J_o	-	flux determined at the beginning in the filtration
$J_{o,FO}$	-	oil flux for forward osmosis
J_r	-	flux recovery
J_s	-	reverse salt flux
J_t	-	flux determined at every hour in the filtration
J_v	-	pure water flux
J_w	-	water flux
n	-	number of ions
Ơ	-	reflection coefficient
R	-	universal gas constant
R_o	-	oil rejection rate
R_s	-	salt rejection
S	-	structural parameter
T	-	temperature
t	-	thicknesss
V	-	volume of permeate
$V_{d,final}$	-	final volume of draw solution
$V_{d,initial}$	-	initial volume of draw solution
V_p	-	volume of permeate passing across the membrane

wt %	-	weight percentage
X	-	pure water permeability coefficient
Y	-	salt permeability coefficient
$\Delta\pi$	-	effective osmotic pressure
ε	-	porosity
τ	-	tortuosity
φ	-	osmotic coefficient

CHAPTER 1

INTRODUCTION

1.1 Background of Research

Oily wastewater is one of the primary pollutants to the environment. The raising oil consumption in oil and gas industries has further exacerbated the disposal of oil waste into the water stream without further treatment (Yu *et al.*, 2013). Generally, the wastewater comprises of suspended solids, dispersed oils and dissolved solutes which are harmful to the environment and the water sources. There are few means where wastewater can endanger human such as affecting quality and purity of drinking water and other aquatic sources, threatening human health and aquatic lives, causing meteorological pollution, decreasing crop production as well as devastating natural landscape (Poulopoulos *et al.*, 2005). Therefore, finding promising approaches for oily wastewater treatment has become a crucial task for the water community.

Membrane technology is a viable approach for oily wastewater treatment as it is useful in completely removing suspended solids and biological degradable organic components from the oily wastewater. A few types of membrane technologies, such as ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), are readily available for oily wastewater treatment. However, UF is known to be ineffective in reducing waste with high oily concentration to a disposable level. Hereby, a secondary treatment using NF and RO is required to completely remove the remaining oil (Park and Barnett, 2001; Kasemset *et al.*, 2013). High pressure and high energy are required to work on all these processes. Meanwhile, frequent membrane cleaning as well as larger membrane area are also needed to ensure continuous production (Hickenbottom *et al.*, 2013; Duong *et al.*, 2014). Lately, by applying same principle as other membrane technologies but less energy required, forward osmosis (FO) has won itself an important place in wastewater treatment. The osmotic pressure gradient is utilized as the driving force in FO to separate pure water from feed solution. In addition, compared to pressure-driven membrane processes, FO is also known for its other advantages such as lesser energy required, lower membrane fouling tendency, easier fouling removal (Mi and Elimelech, 2010) and higher water recovery rate (Martinetti *et al.*, 2009) (Song *et al.*, 2015). Owing to these advantages, FO has been acknowledged as a potential candidate for oil removal (Zhang *et al.*, 2014). However, despite the lower membrane fouling compared to other pressure driven processes, the adverse effects of fouling cannot be neglected hence has to be treated carefully to ensure the durability of membrane (Lau *et al.*, 2015).

Conventional asymmetric FO membrane usually has very large pores ranging from 0.5 μm to 5.0 μm which is hard to separate very tiny particles (Liang *et al.*, 2017). So, thin film composite (TFC) is developed to enhance the membrane performance. Generally, fabrication of TFC involves the coating of an ultra thin film layer atop its substrate layer. In this study, the active layer atop substrate layer which is polyamide (PA) layer contains very fine pores to allow the separation of ultrafine particles. More improvement is necessary to improve membrane performance and also application range for membrane separation. One way for this is the incorporation of foreign materials onto membrane. Recently, various types of nanomaterials are used to fabricate the membrane to further enhance the membrane performance. The common nanomaterials used are metal or metal oxide, zeolite, silica, carbon nanotubes (CNTs) and graphene oxide (Tiraferri *et al.*, 2011b). The incorporation of nanomaterials could enhance membrane efficiency in several means. It can improve 'additional porosity' which provides pathway for low-resistant solvent transport. It can also improve additional hydrophilicity and alter the membrane structure (Van Goethem *et al.*, 2018). However, extra precaution needs to be taken as incompatible nanomaterials could severely disrupt the crosslink network. It can induce unwanted outcomes such as hindering the polymer end groups to react with other monomers, destroy the layer's stability and create larger defects (Chan *et al.*, 2016). Apart from nanomaterials, some researchers have discovered that incorporation of zwitterions into the membrane active layer creates positive insight. Briefly, a zwitterion is a compound having positive and negative charged groups in a same monomer group, while maintaining the overall charge neutrality. The strong dipole moments induced thus creates good interaction between PA layer and the substrate layer. Zwitterion can form stronger and more stable electrostatic and hydrogen bonds with water compared to most of the hydrophilic materials. The inter and intra-interactions between group of opposite charges thus create a 'free water' hydration layer on the surface of zwitterion. Therefore, it could reduce unwanted fouling as the foulants get adsorbed on the hydration layer instead of the membranes surface and can be easily removed by rinsing with water (Ohya *et al.*, 1997; Li *et al.*, 2014b) According to Chan *et al.* (2013), the zwitterion-functionalized single-walled CNTs (Z-SWNT) shows significant improvements in salt rejection and water permeation flux. Additionally, the surface fouling in the TFC membrane is reported to be lower as well.

Based on the desired anti-fouling properties possessed by zwitterion, the current study was conducted to investigate the effects of incorporation of zwitterion in the polymer substrate of TFC for oily wastewater treatment. Poly[3-(N-2-methacryloxyethyl-N,N-dimethyl)-ammonatopropanesulfonate (PMAPS) was chosen for this study as it exhibited oil detachment behaviour in both water and aqueous NaCl solution (Kobayashi *et al.*, 2013). The PMAPS incorporated TFC yielded good anti-fouling behavior prior to the oil detachment behavior of PMAPS while maintaining the water flux. The overall performance of zwitterion incorporated TFC membrane for oily wastewater treatment was evaluated based on the oil rejection rate, water flux and anti-fouling properties.

1.2 Problem Statement

Oily wastewater possesses threats to environments and human beings. The oil droplets retained in the wastewater is not practical to be separated from wastewater source without proper methods and technologies. Even with the existing technologies, there are still some shortcomings such as high costing, long duration and fouling issue when dealing with oil separation. Previously, UF, NF and RO are some promising membrane technologies used for oily wastewater treatment. However, when the oil feed concentration is too high, UF is not able to scale down the oil concentration of oily wastewater to a disposable level. It requires a secondary treatment using NF and RO to further remove the residual oil (Park and Barnett, 2001; Kasemset *et al.*, 2013). All these processes require high pressure and high energy to work on. To ensure continuous productivity, higher frequency of membrane cleaning as well as larger membrane area are also possibly required (Hickenbottom *et al.*, 2013; Duong *et al.*, 2014). Hence, FO as one of the emerging membrane technologies, that is favorable as the pressure required is relatively low compared to other processes. Instead of high pressure, FO utilizes the concentration gradient between feed solution and draw solution to allow water permeation across semi-permeable membrane. Thus, the energy consumption is desirably low as well.

Despite the low energy consumption, the oil droplets entrapped within the TFC FO membranes during separation process could potentially cause membrane contamination. Thus, even though it is able to separate oil from water, TFC FO membranes still suffer from fouling issue which unfavorably deteriorates the performance of the FO membranes. Apart from that, the phenomenon causes high maintenance cost and the membrane needs to be replaced periodically. The introduction of zwitterionic polymer has been evidenced as a promising approach to improve the surface hydrophilicity, as well as the anti-fouling properties of the modified FO membranes. However, current approaches mainly focused on the grafting or coating of zwitterions on the PA layer of the FO membrane (Zhang *et al.*, 2018). One significant drawback of this approach is the stability of the zwitterion layers as they might detach from the membrane surface during the filtration process (Mahdavi and Rahimi, 2018). A more reliable modification route is desired to ensure the integrity of the zwitterion modified membranes. In this study, PMAPS zwitterionic polymer was incorporated into the substrate layer through physical mixing prior to the phase inversion technique. Through this facile approach, the PMAPS can be feasibly introduced in a single-step procedure and can be effectively used to alter the structural properties of the TFC substrate. The PMAPS incorporation was expected to reduce the fouling rate and improve membrane reusability based on its oil detachment behaviour.

1.3 Objective of Study

Based on the preceding issues, this study was set out with the following objectives:

i. To fabricate and characterize PMAPS blended polyethersulfone (PES) substrate and TFC membranes.
ii. To evaluate the oily wastewater separation of PMAPS incorporated TFC membranes in terms of flux and oil rejection performance using FO system.
iii. To evaluate the separation and anti-fouling performances of the resultant PMAPS blended TFC for oily wastewater using several oil feed concentrations.

1.4 Scope of Study

In order to achieve the objectives of this study, the following scopes of study had been determined.

i. Formulating polymer dope solution containing PES, N-methyl-2-pyrrolidone (NMP), polyvinylpyrrolidone40 (PVP40) with weight percentage of 18%, 81% and 1% respectively.
ii. Blending PMAPS into the dope solution with dope weight ratio of 1%, and 5%.
iii. Casting of PES flat sheet substrate through phase inversion technique.
iv. Performing interfacial polymerization (IP) atop substrate layers using organic phase (trimesoyl chloride (TMC)/ Cyclohexane) and aqueous phase (meta-phenyl diamine (MPD) /H_2O) to produce the PA layer.
v. Characterizing the TFC membranes using Fourier Transform Infrared Spectroscopy (FTIR), Field Emission Scanning Electron Microscopy (FESEM), Atomic Force Microscopy (AFM) and Optical Contact Angle (OCA), mercury porosimeter, and zeta potential measurement.
vi. Evaluating the oily wastewater removal performance of the TFC in terms of water permeate flux, oil rejection rate, and anti-fouling behavior.

vii. Evaluating the performance of TFC in treating oily wastewater as feed solution with concentration of 1000 ppm, 5000 ppm and10000 ppm and 2M NaCl solution as draw solution using active layer facing draw solution orientation.

viii. Performing anti-fouling test by comparing oil rejection rate and water flux over periods of time, repeated for few cycles.

1.5 Significance of Study

Although TFC is deemed commonly used in membrane separation, however the incorporation of zwitterion is still new to be explored. The findings aimed to pioneer the advancement and knowledge of zwitterion incorporation in oily wastewater separation. Especially in oil and gas industries, the findings provided a new alternative to the oily wastewater treatment in a much efficient way, by having high oil rejection rate and superb anti-fouling behavior at the same time maintaining decent water flux. Thus, it could be of great interest and importance of this research to find out how would the incorporation of PMAPS into the TFC membrane affects the hydrophilicity, oleophobicity, anti-fouling behaviour and water permeation flux of the TFC formed.

1.6 Limitation of Study

i. This study represented the first attempt to incorporate PMAPS-TFC membrane. Hence the optimal weight ratio of PMAPS will be obtained through trials and errors approach.

ii. The parameters between each batch of experiments were varied, but the parameters of IP were remained constant. Since the main concern of the study was not on the manipulation of parameters such as duration, stirring speed and temperature, hence the minor manipulation of these parameters were ignored.

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