

POLYVINYLIDENE FLUORIDE NANOFIBER-SUPPORTED POLYVINYL
ALCOHOL THIN FILM NANOFIBROUS
COMPOSITE MEMBRANE FOR FORWARD OSMOSIS PROCESS

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A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Philosophy

Faculty of Engineering
Universiti Teknologi Malaysia

NOVEMBER 2020

DEDICATION

This thesis is dedicated to my parents (Arsat Uyo and Nawyah Rambli), my beloved siblings (Mohd. Junaidi, Mohd. Jamalludin, Mohd. Iskandar, Mohd. Ismail and Nurlidza), family and friends 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.

ACKNOWLEDGEMENT

In the name of ALLAH, The Most Gracious and Most Merciful, praises be to ALLAH S.W.T and Salam to our Prophet Muhammad S.A.W for giving me the strength and blessing upon the completion of this study. In particular, I would like to express my sincere appreciation to my main supervisor, Associate Professor Dr. Juhana Jaafar, for her valuable advices and guidance throughout the time. I am also very thankful to my co-supervisor, Associate Professor Dr. Lau Woei Jye, for his encouragement and motivation. Without their continuous support, this thesis would not have been the same as presented here. Without their continued support and interest, this thesis would not have been the same as presented here.

My highest gratitude also goes to my fellow postgraduate friends at Advanced Membrane Technology Research Centre (AMTEC) UTM, for their friendship, motivations, and knowledge sharing. I am also indebted to my friends, Noor Syahida Mat Anan, Nur Atiqah Zularifin, Dr. Roziana Kamaludin and Dr. Wong Kar Chun for their assistance at various occasions. Their views and tips are useful indeed. Also, I would like to extend my gratitude to AMTEC and School of Chemical and Energy Engineering staffs for their helps and guidance throughout my master study.

Special thanks to my beloved family members especially my parents for their endless love, prayers, support and encouragement. My sincere appreciation also extends to those involved either directly or indirectly throughout the completion of this study.

ABSTRACT

Development of alternative water sources through seawater desalination by applying osmotic pressure-driven forward osmosis (FO) technologies has become one of the most reliable approaches to overcome the global water scarcity. In this study, as to achieve lower internal concentration polarization (ICP), nanofiber membrane with highly porous, thin and has low tortuosity was used as the substrate for FO membrane. Additionally, to minimize the penetration issue arising from conventional method of fabricating selective layer in which the casting solutions penetrated into the scaffold structure of nanofibrous substrates, this current work utilized the dual-layered nanofibrous mats and cross-link technique to fabricate polyvinyl alcohol (PVA) selective layer. PVA was chosen because it is highly hydrophilic and possesses good film-forming properties. The main objective of this research is to fabricate polyvinylidene fluoride (PVDF) nanofiber-supported PVA thin film nanofibrous composite (TFNC) membrane for FO process. Meanwhile, the sub-objectives are to investigate the effects of PVA loadings and to evaluate the performances of the resultant composite membranes in terms of intrinsic separation properties, FO testing and ICP comparison with asymmetric structure-supported composite membrane prepared via phase inversion technique. The experiment began with the fabrication of PVDF nanofibrous substrate via electrospinning. Subsequently, the selective layer of PVA nanofibers was prepared via electrospinning at different PVA loadings (2, 4, 6, 8, 9 and 10% w/v), prior to PVA cross-linking process. The characterizations of the substrate and PVA/PVDF composite membranes were done using scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) spectroscopy, atomic force microscopy (AFM), Fourier transform infrared (FTIR) spectroscopy, contact angle measurement and mercury intrusion porosimetry (MIP). Finally, the resulting TFNC membranes were evaluated in terms of intrinsic separation properties and FO performances, followed by the ICP evaluation comparison between the chosen nanofiber-supported TFNC membranes and asymmetric structure-supported TFC membranes. It was found that the best loading of PVA was 8% w/v (denoted as PVA 8/PVDF) as it possessed the highest water permeability (1.33 L/m².h.bar) with 43.35% salt rejection and a ratio of 6.20 kPa between water and salt permeabilities. Also, PVA 8/PVDF composite membranes showed considerable performances in FO process with water flux of 4.83 LMH, reverse solute flux of 0.0242 gMH and significantly low specific reverse solute flux of 0.005 g/L. Besides, ICP effect in nanofiber-supported TFNC membrane was reduced by 30% as compared with asymmetric structure-supported TFC membrane. Therefore, this study may lead to a new strategy of developing dual-layered TFNC membrane via PVA cross-linking technique which could provide a good solution to solve the penetration issue, apart from mitigating the ICP bottleneck.

ABSTRAK

Pembangunan sumber air alternatif melalui penyahgaraman air laut dengan menggunakan teknologi osmosis hadapan (FO) menerusi dorongan tekanan osmotik telah menjadi salah satu pendekatan yang paling boleh dipercayai untuk menangani masalah kekurangan air global. Dalam kajian ini, untuk mencapai polarisasi kepekatan dalaman (ICP) yang lebih rendah, membran gentian nano yang sangat berpori, nipis dan mempunyai pintalan yang rendah telah digunakan sebagai substrat untuk membran FO. Selain itu, untuk meminimumkan isu penembusan yang timbul dari kaedah konvensional penghasilan lapisan selektif di mana larutan bahan acuan menembusi ke dalam struktur substrat gentian nano, kajian ini menggunakan teknik gentian nano dwi-lapisan dan pautan silang untuk membentuk lapisan selektif polivinil alcohol (PVA). PVA dipilih kerana sifat hidrofiliknya yang tinggi dan mempunyai sifat pembentuk filem yang baik. Objektif utama kajian ini adalah untuk menghasilkan membran PVA filem nipis komposit gentian nano (TFNC) yang menggunakan gentian nano poliviniliden florida (PVDF) sebagai membran sokongan untuk proses FO. Manakala sub-objektif kajian ini adalah untuk mengenal pasti kesan penambahan PVA dan juga untuk menilai prestasi membran komposit yang telah dihasilkan dari segi sifat pemisahan intrinsik, ujian FO dan perbandingan ICP dengan membran komposit yang menggunakan membran sokongan dengan struktur asimetrik yang dibuat melalui proses inversi fasa. Eksperimen bermula dengan penghasilan substrat gentian nano PVDF melalui proses pemintalan elektro. Seterusnya, lapisan selektif gentian nano PVA dihasilkan melalui proses pemintalan elektro pada kuantiti PVA yang berlainan (2, 4, 6, 8, 9 and 10% w/v), sebelum diteruskan dengan proses pautan silang PVA. Pencirian substrat dan membran komposit PVA/PVDF dilakukan dengan menggunakan mikroskop imbasan elektron (SEM), spektroskopi sinaran sinar-X (EDX), mikroskop daya atom (AFM), spektroskopi transformasi infra merah Fourier (FTIR), ukuran sudut sentuh dan porosimetri pencerobohan merkuri (MIP). Akhir sekali, prestasi membran TFNC yang dihasilkan telah diuji dari segi sifat pemisahan intrinsik dan prestasi FO, diikuti dengan perbandingan ICP antara membran TFNC yang menggunakan gentian nano sebagai membran sokongan dan membran TFC yang menggunakan membran sokongan dengan struktur asimetrik. Hasil kajian mendapati bahawa kuantiti terbaik PVA ialah 8% w/v (dinamakan sebagai PVA 8/PVDF) yang mempunyai kebolehtelapan air tertinggi (1.33 L/m².j.bar) dengan penyingkiran garam sebanyak 43.35% dan nisbah kebolehtelapan air dan garam sebanyak 6.20 kPA. Didapati juga, membran komposit PVA 8/PVDF telah menunjukkan prestasi memberansangkan dalam proses FO dengan fluks air 4.83 LMH, fluks bahan larut balikan 0.0242 gMH, dan fluks spesifik bahan larut balikan yang rendah iaitu 0.005 g/L. Selain itu, kesan ICP dalam membran TFNC yang menggunakan gentian nano sebagai membran sokongan adalah kurang sebanyak 30% berbanding dengan membran TFC yang menggunakan membran sokongan dengan struktur asimetrik. Kesimpulannya, kajian ini membawa kepada strategi baru dalam penghasilan membran TFNC dwi-lapisan menerusi teknik pautan silang PVA, yang menyumbang kepada penyelesaian isu penembusan selain daripada mengurangkan kesan ICP.

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LIST OF ABBREVIATIONS

FO	-	Forward Osmosis
ICP	-	Internal concentration polarization
ENMs	-	Electrospun nanofibrous membranes
PVA	-	Polyvinyl alcohol
PVDF	-	Polyvinylidene fluoride
TFNC	-	Thin film nanofibrous composite
GA	-	Glutaraldehyde
IP	-	Interfacial polymerization
TFC	-	Thin film composite
NMP	-	N-methyl-2-pyrrolidone
SEM	-	Scanning electron microscopy
EDX	-	Energy-dispersive X-ray spectroscopy
AFM	-	Atomic force microscopy
FTIR	-	Fourier transform infrared spectroscopy
MIP	-	Mercury intrusion porosimetry
HCl	-	Hydrochloric acid
RO	-	Reverse Osmosis
SD	-	Solar distillation
MED	-	Multi-effect distillation
MSF	-	Multi-stage flash distillation
MVC	-	Mechanical vapour compression
TVC	-	Thermal vapour compression
ED	-	Electrodialysis
MD	-	Membrane distillation
TDS	-	Total dissolved solids
PRO	-	Pressure retarded osmosis
CNTs	-	Carbon nanotubes
PA	-	Polyamide
TFN	-	Thin film nanocomposite
MMMs	-	Mixed matrix membranes

UV	-	Ultraviolet
PS; PSf	-	Polysulfone
SiO ₂	-	Silica
PVP	-	Polyvinylpyrrolidone
NH ₂ -TNTs	-	Amino-functionalized titanate nanotubes
MWCNT-TNT	-	Multiwalled carbon nanotubes-titania nanotube
HNTs	-	Halloysite nanotubes
g-C ₃ H ₄	-	Graphitic carbon nitride
PES	-	Polyethersulfone
PEI	-	Polyetherimide
PEG	-	Polyethylene glycol
Na-CQDs	-	NA ⁺ -functionalized carbon quantum dots
f-nTiO ₂	-	Functionalized surface-modified nanoporous titanium oxide
f-TNT	-	Functionalized titanate nanotube
f-CNTs	-	Functionalized carbon nanotubes
PP	-	Polypropylene
TiO ₂ NTs	-	Titanium dioxide nanotubes
GO	-	Graphene oxide
AL-DS	-	Membrane active layer facing draw solution
AL-FS	-	Membrane active layer facing feed solution
CP	-	Concentration polarization
ECP	-	External concentration polarization
TCD	-	Tip-to-collector distance
MA	-	Maleic acid
NaCl	-	Sodium chloride
MgSO ₄	-	Magnesium sulfate
Na ₂ SO ₄	-	Sodium sulfate
DI	-	Deionized
ATR	-	Attenuated total reflection

LIST OF SYMBOLS

J	-	Pure water flux
ΔV	-	Permeate volume
A_m	-	Effective membrane area
Δt	-	Permeate time; time interval
A	-	Water permeability
ΔP	-	Feed pressure; pressure difference
R	-	Salt rejection
C_p	-	Salt concentrations in the permeate solution
C_f	-	Salt concentrations in the feed solution
B	-	Salt permeability coefficient
$\Delta\pi; \pi$	-	Osmotic pressure difference
C	-	NaCl concentration
J_v	-	Permeate flux
J_s	-	Reverse solute flux
C_0	-	Initial solute concentration of the feed solution
C_t	-	Final solute concentration of the feed solution
V_0	-	Initial volume of the feed solution
V_t	-	Final volume of the feed solution
S	-	Structural parameter
D	-	Solute diffusion coefficient in water
π_{draw}	-	Osmotic pressures of the draw solution
π_{feed}	-	Osmotic pressures of the feed solution
B/A	-	Membrane selectivity
J_s/J_v	-	Specific reverse solute flux
R_a	-	Mean roughness
R_q/RMS	-	Root mean square of the Z data
R_z/Rmax	-	Mean difference between highest peaks and lowest valleys
M	-	Molarity

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Over the past decade, rapid population growth as well as ongoing economic evolution led in substantial rise in demand and access to clean water (Gude, Nirmalakhandan, & Deng, 2010; Liao, Loh, Tian, Wang, & Fane, 2018). Among the different approaches adopted to supply an affordable as well as safe drinking water, membrane-based water treatment technologies have drawn intensive interests from academia and industries owing to its merits in generating high quality water and, in most instances, with lower energy (Liao et al., 2018). Forward osmosis (FO), of which is an excellent option to solve the global issue of water shortage, has been commonly used in latest years for water purification as well as seawater desalination owing to the benefits of high rejection efficiencies as well as self-supplied driving forces from osmotic pressure between draw solution and feed solution (M. Huang et al., 2019). In contrast to the existing pressure-driven processes, FO process in the absence of external hydraulic pressure has important qualities which include broad range of feed solutions, effective water recovery, high rejection for small compounds, low operating cost and energy-saving (Ghanbari et al., 2016; Shi et al., 2019).

Undoubtedly, both high in rejection and flux are the crucial aims in fabricating filtration membranes. As to improve the water filtration competency, the composite filtration membranes with multilayer composite structures have gain a lot of attention in water treatment because of their precedence of high rejection and good permeability, in addition to their pressure resistance (Shen et al., 2016; X. F. Wang et al., 2010). The FO composite membranes typically consists of a porous substrate with low resistant which contribute in terms of mechanical support for the membrane throughout the process of fabrication, handling and operation, and a thin coating

layer on top which acts as a filter (Liao et al., 2018; Shen et al., 2016; X. F. Wang et al., 2010). Both substrate and the top layer can be customized independently to achieve the optimal and advantageous characteristics for targeted applications. Previously, the performance of conventional flat sheet FO membranes is hindered by internal concentration polarization (ICP) problem. ICP occurs within the membrane substrate and it exhibits a more severe impact on the reduction of water flux in the FO process. In this regard, the development of nanofiber-supported FO membranes which relies on reducing the ICP bottleneck in the membrane substrate is highlighted in this current study.

Electrospun nanofibrous membranes (ENMs) fabricated through a process known as electrospinning are very suitable to be used as porous substrate for composite membranes owing to their distinctive properties of interconnected pore structures, high surface-to-volume ratio, excellent water permeability and good mechanical properties that provides a great contribution towards water treatment (Beachley & Wen, 2009; Z.-M. Huang, Zhang, Kotaki, & Ramakrishna, 2003; Nasreen, Sundarrajan, Nizar, Balamurugan, & Ramakrishna, 2013; Shen et al., 2016). However, in conventional method to fabricate surface coated composite membranes, a desirable top coating layer is difficult to obtain. This is because the cast solution penetrated into the matrix as a consequence of highly porous and interconnected structure of ENMs substrate. In this regard, a method of developing cross-linked polyvinyl alcohol (PVA) top coating on nanofibrous substrate was introduced. The resultant composite membranes with PVA top coating showed excellent performances in oil/water emulsion separation (X. F. Wang et al., 2010; You et al., 2012) as well as bovine serum albumin (BSA) filtration (Shen et al., 2016). However, the utilization of such composite membranes has never been tested in FO technology. Hence in this study, inspired from the facile technique introduced by X. F. Wang et al. (2010), cross-linked PVA top coating which acts as the selective layer has been fabricated on polyvinylidene fluoride (PVDF) nanofibrous substrate, resulting in thin film nanofibrous composite (TFNC) membranes to be used in FO process.

In this current study, PVA polymer is chosen because it is biologically compatible and highly hydrophilic, as well as chemical and thermally stable (Tang et al., 2009; X. Wang, Fang, Yoon, Hsiao, & Chu, 2006). In addition, PVA has good film-forming properties, highly soluble in water and environmental friendly. Apart from that, PVA is also a polyhydroxy (i.e. –OH groups which are good sites for further reactions) (Park, Gonzales, Abdel-Wahab, Phuntsho, & Shon, 2018). As to provide PVA the stability in aqueous phase, its water solubility can be reduced by cross-linking this polymer with another material, for instance, the used of glutaraldehyde (GA) in this work. On the other hand, PVDF is chosen as a membrane material for the substrate because PVDF is advantageous over other polymers due to its high mechanical strength, thermal stability and excellent chemical resistance (Obaid, Ghouri, et al., 2016; Shibuya et al., 2018), in which these properties make it suitable for water treatment.

As this dual-layered cross-linked PVA on electrospun PVDF nanofibers is not yet widely explored by researchers in FO technologies, hence this current study aims to investigate the effect of fabricating cross-linked PVA thin layer on PVDF nanofibers at different PVA loadings by means of few characterization methods, followed by the membrane performance evaluation in terms of intrinsic separation properties, FO performance, and also the ICP evaluation comparison with asymmetric structure-supported composite membrane. Therefore, this study is believed could serve as a useful approach to overcome the drawback of the existing issues related to the penetration of cast solution into the substrate and ICP bottleneck. Thus, the potential used of dual-layered nanofibrous composite membranes to be newly exploited in FO application can be explored.

1.2 Problem Statement

FO has been well recognized as a favourable future osmotically-driven membrane process to replace the conventional technologies. The effective FO membrane should possess high water permeability, more selectivity, high stability,

reduced ICP and high mechanical strength (Syed Ibrahim, Isloor, & Yuliwati, 2019). Among a variety of advanced progress in the development of FO membranes, the fabrication of a selective layer on electrospun nanofibrous substrate by interfacial polymerization (IP) or cross-linked PVA coating which resulting in TFNC membranes has been regarded to have the high potential of producing clean water in the years ahead.

Despite the high potential of FO technology, the application of FO process is limited due to ICP in the membrane substrate. ICP can be described as the development of CP layer inside the porous substrate due to the incompetence of the solute to penetrate easily into the dense membrane selective layer (Akther et al., 2015). For composite FO membranes, a small structural parameter (S) value is desired for the support layer in order to reduce the ICP during FO process. In detail, a smaller S value might be achieved by constructing a thinner structure of support layer, lower tortuosity as well as higher in porosity with extensively interconnected pores to enable an easier diffusion of solute from the draw solution to the active layer (Liu, Li, Zhou, Xie, & Lee, 2016). In this regard, attributed to its key features, ENMs has been recognized as a strong candidate to minimize the ICP problem in conventional FO membranes. The scaffold-like nanofiber structure of ENMs fulfills the characteristics needed to achieve smaller S value, which possess remarkable benefits over conventional sponge-like support layers. This distinctive structure of nanofiber support layer guarantees direct paths for salt and water diffusion (Song, Liu, & Sun, 2011), which could provide a good alternative to minimize the ICP problem. Therefore in the present work, nanofiber-supported TFNC membranes were fabricated using electrospun PVDF nanofiber membrane as the support layer. The resultant nanofiber-supported TFNC membrane was later tested and compared with asymmetric structure-supported thin film composite (TFC) membrane in terms of ICP evaluation.

The second problem was the penetrations issue that arising from the conventional IP process to fabricate selective layer on ENMs substrate. In detail, the cast solution used in IP process penetrated into the randomly oriented ENMs structure. Hence in this study, cross-linked PVA technique was utilized to replace the

conventional IP process. The highlight of this technique included electrospinning of PVA nanofibrous layer on electrospun PVDF nanofibrous support, followed by remelting the PVA nanofibrous layer by means of water vapor exposure prior to chemical cross-linking to form a layer of PVA coating. The aforementioned technique was applied in this current study to fabricate TFNC membranes at different PVA loadings, in which the composite membranes were later tested for FO process. This technique could overcome the penetration issue as there was no cast solution involved in the process. In addition, as the PVDF nanofibrous substrate was hydrophobic in nature, introducing the hydrophilic surface of PVA coating layer onto the substrate could enhanced the water permeability of the resultant membrane in FO process.

1.3 Research Objectives

Based on the aforementioned problem statements, the aim of this research is to fabricate nanofiber-supported TFNC FO membrane for seawater desalination. In order to achieve this objective, the following sub-objectives are identified:

- i. To investigate the effects of different loadings of PVA on the physical properties of PVA/PVDF TFNC membrane
- ii. To evaluate the intrinsic separation properties and FO performance of nanofiber-supported TFNC FO membranes
- iii. To compare the ICP evaluation between nanofiber-supported TFNC FO membranes and asymmetric structure-supported TFC FO membranes

1.4 Scope of Study

In order to achieve the objectives stated above, the following scopes of study are identified:

- i. Fabricating PVDF nanofibrous substrate via electrospinning process using 5 mL dope solution consisting of 18 wt% PVDF in N-methyl-2-pyrrolidone (NMP), at a rate of 1.0 mL/h, voltage of 10.0 kV and a distance of 15 cm (the most optimum processing parameter for synthesizing good electrospun PVDF nanofibers by Alhassan, Burezq, Nair, and Shehata (2018)).
- ii. Characterizing the fabricated PVDF nanofibrous substrate using scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) spectroscopy, atomic force microscopy (AFM), Fourier transform infrared (FTIR) spectroscopy, contact angle measurement and mercury intrusion porosimetry (MIP).
- iii. Fabricating PVA nanofibers onto PVDF nanofibrous substrate at different PVA loadings (2, 4, 6, 8, 9 and 10% w/v) for maximum volume of 2 mL dope solution at a rate of 1.0 mL/h, voltage of 20.0 kV and a distance of 18 cm.
- iv. Conducting the cross-linking process using GA as the cross-linker in the presence of hydrochloric acid (HCl) as the catalyst, to produce cross-linked PVA coating layer on electrospun PVDF support membrane.
- v. Characterizing the fabricated PVA/PVDF composite membranes at different PVA loadings using SEM, EDX, AFM, FTIR, contact angle measurement and MIP.
- vi. Evaluating the resulting TFNC membranes in terms of intrinsic separation properties (water permeability, salt rejection, B/A ratio) via dead-end reverse

osmosis (RO) cell unit; and FO performances (water flux, reverse solute flux and specific reverse solute flux) via cross flow FO system.

- vii. Evaluating the ICP performance of the chosen nanofiber-supported TFNC FO membranes as a comparison with asymmetric structure-supported TFC FO membranes.

1.5 Significance of Study

Along with the globally recognized progress of desalinating seawater to fulfil the growing water demands, FO membranes have showed their versatility thus owns great potential in the field of seawater desalination itself. Additionally, the surge in nanofiber-related research for desalination by FO technology in the last decades pointed out the significance of this study which highlighted the potential used of dual-layered nanofibrous composite membranes to be newly exploited in FO application. In the current research, the cross-linked PVA coating layer on PVDF nanofibrous substrate was introduced as to overcome the existing issue in conventional surface modification methods of ENMs, which related to the penetration of the cast solution into the ENMs scaffolds. Though further modifications are still needed for PVDF nanofibrous substrate, the capability of cross-linked PVA top coating on ENMs support layer to be used as FO membrane could serve as a viable alternative to manufacture high performance dual-layered nanofibrous composite membranes in the future technology of FO for desalination. Besides, as an addition to water application, the potential of dual-layered nanofibrous composite membranes in the other four main areas of interest which are biotechnology, food, environment and energy should be considered and explored.

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LIST OF PUBLICATIONS

Indexed Journal

1. **Arsat, N.**, Jaafar, J., Lau, W. J., Othman, M. H. D., Rahman, M. A., Yusof, N., Salleh, W. N. W., & Ismail, A. F. (2020). Physical Studies of Forward Osmosis Membranes Prepared by Cross-linking Polyvinyl Alcohol on Electrospun Nanofibers. *Journal of Membrane Science & Research* 6 (4), 359-366. <https://doi.org/10.22079/JMSR.2020.117738.1310>. **(Indexed by SCOPUS)**