EFFECT OF AIR GAP ON POLYETHERSULFONE / POLYVINYL ALCOHOL – ZnO HOLLOW FIBER MEMBRANE FOR FOULING MITIGATION

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UNIVERSITI SAINS MALAYSIA

2017

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by

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Thesis submitted in fulfilment of the
requirement for the degree of
Master of Science

July 2017

ACKNOWLEDGEMENTS

In the name of Allah, the Most Beneficent and the Most Merciful. Prima facie, I am grateful for the good health and well-being that were necessary to complete this dissertation. None of this would be materialized without His uttermost grace bestowed upon me throughout my 25 years of life. Alhamdulillah. Secondly, I would like to thank my research supervisor, Prof Dr Abdul Latif Ahmad for his indebted guidance. His vast experience has certainly helped me, and without his financial support I may have lost my way in finishing my study. Praise to the USM Engineering Campus, particularly School of Chemical Engineering’s staffs and technicians for accommodating me throughout my MSc candidature. Lots of memories have been created in the past 4 years of my BSc degree, and I’m grateful to be given another chance to spend another memorable year as a graduate student here in USM. Shout out to Dr JK Lim, Dr SC Low, Dr BS Ooi & Dr Fazliani for their continuous support and advice. Not to forget, Dr Abdullah for his dedication in disseminating his experience & knowledge before leaving to Iraq as a PhD holder. My fellow colleagues, thanks for being a part of my extended family. Too many names to be mentioned, but I wish you guys all the best for your dissertation especially to Wei Ming, Farid & Rasyid. Another name worth to be mentioned; Dina, thanks for your apprehension towards my passion & your continuous support through thick and thin. You have been the de facto backbone throughout my circadian habit in pursuing knowledge, my motivator when I’m in vain, and the companion in my life. I thank you for your tireless support, and wishing you good luck for your own MSc study. Last but not least, special thanks to my beloved family as for always supporting me throughout my years of studies. Every alphabet written is the product of your teaching as my first teacher and mentor. None would be materialize if not for your tireless effort teaching me ABC & 123 many years ago. Thanks again everyone!

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LIST OF SYMBOLS

Symbol	**Description**	**Unit**
θ_0	Apparent contact angle	°
θ	Intrinsic contact angle	°
r	Roughness factor	null
γ_s	Solid surface free energy	mJ/m^2
γ_1	Liquid surface free energy (liquid surface tension)	mJ/m^2
γ_{s1}	Solid/liquid interfacial free energy	mJ/m^2
f_s	Fraction of liquid in contact with the solid	null
T_g	Glass transition temperature	°C
J	Permeate flux	$kg\ m^{-2}\ h^{-1}$
Δm	Change in mass of permeate	kg
C_o	Average outer circumference of the membrane	m
L_e	Effective length of the membrane strands	m
Δt	Change in permeation time	h
R	Humid acid rejection	%
C_p	Humid acid concentration of the permeate	mg/L
C_f	Humid acid concentration of the feed	mg/L
w	Weightage	null
f	Responding variable’s normalized value	null
S	Scan size	μm^2
R_a	Mean roughness	µm
R_{p-v}	Difference between maximum peak height & maximum valley depth	µm

R_q	Root mean squared roughness	µm
R_z	Mean height difference between the five highest peaks and lowest valleys	µm
D_i	Membrane's inner diameter	mm
D_o	Membrane's outer diameter	mm
V_b	Bore fluid volumetric flow rate	cm^3/s
V_d	Dope solution volumetric flow rate	cm^3/s
v_t	Hollow fiber take up speed	cm/s
ΔG_{mix}	Free energy of mixing	J/mol
R	Gas constant	$J\ K^{-1}\ mol^{-1}$
T	Absolute temperature	K
n	Number of moles	mol
$\emptyset$	Volume fraction	null
χ	Interaction parameter	null
ΔH_{mix}	Mixing enthalpy	J/mol

Subscripts

i	Responding variable
n	Order of membrane flux registered
1,2	Component/species to be evaluated

LIST OF ABBREVIATIONS

PES	Polyethersulfone
PSf	Polysulfone
PVDF	Polyvinylidene fluoride
MM	Mixed matrix
PVA	Polyvinyl alcohol
LiCl	Lithium chloride
PEG	Polyethylene glycol
PVP	Polyvinyl pyrrolidone
DMAc	N,N-dimethylacetamide
DMSO	Dimethyl sulfoxide
-OH	Hydroxyl
HF	Hollow fiber
ZnO	Zinc oxide
MF	Microfiltration
UF	Ultrafiltration
NF	Nanofiltration
RO	Reverse osmosis
TiO_2	Titanium dioxide
PVAc	Polyvinyl acetate
DMF	Dimethyl formamide
PVA-g-4VP	Polyvinyl alcohol graft 4-vinylpyridine
GA	Glutaraldehyde
4VP	4-vinylpyridine
TFC	Thin film composite
HPβCD	Hydroxypropyl-β-cyclodextrin
Zr	Zicronium
Ag	Silver
MW	Molecular weight
TFN	Thin film nanocomposite
PVC	Polyvinyl chloride
SEM	Scanning electron microscopy

AFM	Atomic force spectroscopy
DMA	Dynamic mechanical analysis
FTIR	Fourier transform infrared spectroscopy
EDX	Energy dispersive x-ray spectroscopy
ATR	Attenuated total reflection
PWF	Pure water flux
HAF	Humid acid flux
ICPMS	Inductively coupled plasma mass spectrometry
MD	Molecular dynamics

KESAN JURANG UDARA TERHADAP MEMBRAN GENTIAN BERONGGA POLIETERSULFONA / POLIVINIL ALKOHOL - ZnO UNTUK PENGURANGAN KOTORAN

ABSTRAK

Proses pemisahan membran untuk aplikasi air sentiasa dicabar oleh kecenderungannya untuk kotor. Kotoran, terutamanya pada skala industri adalah satu fenomena yang perlu ditangani yang kerap berlaku, meningkatkan kos, dan menurunkan prestasi. Pembersihan berkala, walaupun sedikit sebanyak berkesan untuk mengurangkan kesan dari kotoran, adalah merupakan ancaman kepada integriti mekanikal dan kimia membran. Ia juga didapati tidak berkesan dalam melawan pembentukan selaput bio; produk sampingan kotoran bio. Oleh itu, menerusi kajian ini, rumusan 'dope' baru telah disintesis sebagai usaha untuk menghasilkan membran gentian berongga (HF) yang anti-kotoran dengan menggunakan campuran PES/PVA. Membran tersebut telah diuji dengan asid humik sebagai model kotoran. Campuran ini dibantu oleh LiCl sebagai pembentuk liang membran dan untuk meningkatkan kebolehlarutan PVA menerusi pembentukan 'transition state' bersama dengan sistem pelarut N,N-dimetilasetamida (DMAc). Dengan menggunakan rumusan ini, membran HF telah dihasilkan menggunakan teknik 'dry jet-wet spinning' pada jarak jurang udara yang berbeza untuk mengkaji kesannya di bawah regangan graviti. Empat jarak jurang udara yang berbeza (5, 10, 15 & 20 sm, masing-masing bersamaan dengan sampel A.1, A.2, A.3 & A.4) telah dikaji dan dicirikan melalui pelbagai cara. Morfologi dan topografi yang unik telah diperolehi menerusi penggunaan rumusan baru ini, disamping dipengaruhi oleh ruang udara/regangan graviti. Selepas 30 minit pemadatan hidraulik dan 1 jam penyerapan air ternyahion, fluks air maksimum telah didapati pada nilai 42.32 ± 0.12 kg/m^2.j bagi sampel A.3 dengan jarak jurang udara sebanyak 15 sm. Corak variasi yang sama juga didapati selepas 1 jam penyerapan

kotoran, dengan fluks asid humik maksimum didapati pada nilai 42.86 ± 0.09 kg/m^2.j bagi sampel membran A.3 yang sama. Namun begitu, penolakan didapati tertinggi bagi sampel A.1, dihasilkan pada jarak jurang udara sebanyak 5 sm dengan nilai penolakan asid humik sebanyak 94.63 ± 2.13 %. Selepas mengambil kira hubungan penyerapan-penolakan dan faktor-faktor lain seperti kekasaran permukaan, kekuatan mekanikal & kehidrofilikan, 10 sm telah dipilih sebagai jarak jurang udara yang sesuai untuk pembentukan membran gentian berongga PES/PVA dan derivatif dari rumusan yang sama pada masa hadapan. Kajian berikutnya dilakukan dengan mencirikan dan membandingkan prestasi membran PES-PVA (sampel B.3) dengan membran PES kosong (sampel B.1), PES dicampur dengan partikel nano zink oksida (ZnO) (sampel B.2), dan PES dicampur dengan PVA-ZnO (sampel B.4). Penambahan PVA di dalam sampel B.3 & B.4 menyekat pembentukan liang makro dan meningkatkan sifat anti-kotoran membran dengan rekod terendah nilai fluks asid humik (HAF) relatif tidak kurang daripada 0.95, berbanding dengan membran HF tanpa PVA (sampel B.1 & B.2) yang mempunyai nilai HAF relatif sekitar 0.75-0.85 selepas berakhirnya tempoh fluks selama 2 jam. Walau bagaimanapun, penambahan PVA mengurangkan fluks air sampel B.3 kepada 33.04 ± 0.09 kg/m^2.j berbanding membran PES kosong (sampel B.1) pada nilai 91.42 ± 0.05 kg/m^2.j. Penambahan ZnO pula dapat meningkatkan fluks air sampel B.2 kepada 123.20 ± 0.14 kg/m^2.j berbanding membran PES kosong, tetapi membuatkan HF tersebut lebih terdedah kepada kotoran. Penambahan PVA-ZnO di dalam sampel B.4 tidak meningkatkan prestasi fluks, tetapi meningkatkan penolakan asid humik dari 91.27 ± 2.28 % bagi PES kosong (sampel B.1) kepada 96.03 ± 1.07 %. Dengan mengoptimumkan rumusan membran tersebut (terutamanya untuk nisbah PVA/ZnO), ia dijangka bahawa membran tersebut mampu untuk meningkatkan sifat anti-kotoran dan penolakan tanpa perlu mengorbankan prestasi fluksnya.

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ABSTRACT

Membrane separation process for water application has always been challenges by its tendency to foul. Fouling, especially at industrial scale is a ubiquitous, cost deterring, and performance degrading phenomenon which needs to be nullified. Periodic cleaning, while being effective to mitigate fouling consequences to some extent, impose a threat to the membrane's mechanical and chemical integrity. It has also been found to be ineffective in battling biofilm formation; a side product of biofouling. Hence, in the current work, new dope formulation was synthesized as an effort to fabricate an antifouling hollow fiber (HF) membrane using PES/PVA blend. The membrane was tested against humic acid as model foulant. The blend was mediated by LiCl as membrane pore former and to improve the solubility of PVA through the formation of transition state with N,N-dimethylacetamide (DMAc) solvent system. Using the formulation, HF membranes were spun (dry jet-wet spinning) at different air gap distances to study the effect under gravitational stretching. Four different air gap distances (5, 10, 15 & 20 cm, corresponds to sample A.1, A.2, A.3 & A.4 respectively) were investigated and characterized through various means. Peculiar morphology and topography was found through the use of this new formulation, on top of being idiosyncratically affected by the air gap/gravitational stretching. After 30 minutes of hydraulic compaction and 1 hour of deionized water permeation, maximum water flux was noted at 42.32 ± 0.12 kg/m^2.h for sample A.3 with air gap distance of 15 cm. Similar trend was noted after another 1 hour of foulant permeation, with maximum humic acid flux was found at 42.86 ± 0.09 kg/m^2.h for the same membrane sample A.3. Nevertheless, rejection was found to be highest for sample A.1, spun at 5 cm air gap distance with 94.63 ± 2.13 % humic acid rejection. After considering the permeation-rejection relationship and other factors such as surface roughness, mechanical strength & hydrophilicity, 10 cm was noted to be the suitable air gap distance for the fabricated PES/PVA hollow fiber membrane and its future derivative with similar formulation. Subsequent study was done in characterizing and comparing the performance of the PES-PVA membrane (sample B.3) with neat PES (sample B.1), PES blended with zinc oxide (ZnO) nanoparticle (sample B.2), and PES blended with PVA-ZnO (sample B.4). The addition of PVA in sample B.3 & B.4 suppressed the macrovoid formation and improved the antifouling properties of the membrane with the lowest recorded relative humic acid flux (HAF) of not less than 0.95, as compared to HF membranes without PVA (sample B.1 & B.2) which has relative HAF of around 0.75 – 0.85 by the end of the 2 hours flux duration. Nevertheless, incorporation of PVA reduced the water flux of sample B.3 down to 33.04 ± 0.09 kg/m^2.h as compared to neat PES membrane (sample B.1) at 91.42 ± 0.05 kg/m^2.h. ZnO on the other hand was able to improve the water flux of sample B.2 to 123.20 ± 0.14 kg/m^2.h as compared to the neat membrane, but made the HF much more susceptible to fouling. PVA-ZnO incorporation in sample B.4 didn’t improved the flux performance, but improved the humic acid rejection from 91.27 ± 2.28 % in neat PES (sample B.1) to 96.03 ± 1.07 %. With further optimization of the formulation (especially PVA/ZnO ratio), it is expected that the fabricated membranes would have improved anti-fouling properties and rejection without severing its flux performance.

CHAPTER ONE

INTRODUCTION

1.1 Membrane Fouling and Its Consequences

The research of synthetic membrane in water based separation processes have flourished rapidly over the past 55 years ever since the breakthrough by Sidney Loeb & Srinivasa Sourirajan in 1962 (Koltuniewicz, 2005, Korbutowicz and Nowak, 2011, Noble and Stern, 1995). This has further been escalated by the increase in world population, freshwater scarcity, and stringent water quality regulations, which further pushed the frontiers of membrane technology in the 1990s (Fane et al., 2011). Since then, membrane technology has found its way to be assimilated industrial-wide due to its additional advantages such as high stability & efficiency, low energy requirements and ease of operation (Zhao et al., 2015). The attraction of membrane separation also lies in its economics whereby it surpasses the conventional method by being low in maintenance cost on top of being cost efficient in terms of permeate production (Fane et al., 2011).

While the market would continue to rise, predicted to reach USD 11.95 billion by 2021 (MarketsandMarkets, 2017), membrane technology is still far from perfect. Despite the commercial success of polymeric membrane particularly in wastewater separation processes, major research still needs to be done in improving the long term performance of the membrane (Pearce, 2014). Major disadvantages come in terms of its low durability, particularly by concentration polarization, chemical damage, and fouling (Strathmann, 2011). Fouling for example, has been noted to pose a serious drawback for industrial membrane utilization. Deposition of foulant cake on the membrane surface reduced the flux performance, rapidly increases the rate of maintenance for periodical cleaning, and surging the frequency for membrane replacement. This significantly translated into the increase in expense, as membrane & membrane housings took between 17 to 40 % while cleaning system took between 10 to 18 % of total cost for large ultrafiltration/microfiltration plants (Perry, 1997). Hence, the consequences of membrane fouling is pretty much both performance and cost deterring; Huisman et.al. (2004) have reported a real industrial case whereby 10,000 Euro per year was allocated towards membrane replacement costs due to frequent membrane fiber damage and rapid fouling.

As membranes for water treatments are subjected to various kind of solutions; fouling is practically inevitable. But against all hopes and dreams, understanding the origin and type of fouling itself may shed light on the race to minimize the effect of membrane fouling. In response, various industrial membrane autopsy studies have been conducted throughout the globe in order to further elucidate the issues (Huisman and Williams, 2004, Gijsbertsen-Abrahamse et al., 2006, Siemens Water Technologies, 2011, Chesters et al., 2011). Membrane fouling phenomenon, as a whole, is very complex. While reversible fouling is easy to be removed by physical means, chemical cleaning is needed to overcome the irreversible fouling (Arnal et al., 2011). Hence, chemically resistant polymers such as polyethersulfone (PES), polysulfone (PSf), and polyvinylidene fluoride (PVDF) were the material of choice for membrane fabrication and commercialization purposes. Notwithstanding, these membranes are unfortunately hydrophobic; making it prone to fouling (Yuan et al., 2014, Zhang et al., 2014a, Zhao et al., 2015). To make things more complicated, the formation of biofilms during membrane fouling have been noted to limit the efficiency of chemical cleaning by shielding the embedded microorganisms (Anand et al., 2014). Hence, to synthesize membranes with anti-fouling capability, yet are physically viable for harsh conditions are one of the main research interest in membrane technology. To date, the search for antifouling membrane has become one of the most researched area in the field with more than 60 % of related Scopus indexed studies published in the past 5 years (2013-2017) (Scopus, 2017).

Increase in hydrophilicity has been noted as one of the methodology in mitigating fouling, which could be accomplished through several means. Among all of the hydrophilic modification proposed by fellow researchers, blending is the simplest yet effective to be done. Modification is done during the dope preparation phase through physical mixing of membrane solution with hydrophilic components which can be polymers, nanoparticles or mixture of both (Leo et al., 2012, Yuan et al., 2014, Zhang et al., 2014a, Zhao et al., 2015, Balta et al., 2012). With the current extent of nanotechnology, nanoparticles incorporation into membrane matrix dubbed as mixed matrix (MM) membrane has been the trend in membrane antifouling research. Nevertheless, it is important to note that the nanoparticle needs to be well dispersed as agglomerated nanoparticles reduced the surface area/weight ratio. Chances are, agglomerations are more prone to happen with the increase of incorporated nanoparticle percentage (Ng et al., 2011). The possibility for the membrane pores to be blocked are also increased with larger nanoparticle sizes, hence by further lowering the membrane’s permeability below than pristine membrane. The stability of the nanoparticle is also jeopardize by smaller nanoparticles due to the increase of surface energy. Hence, mixing of nanoparticles alone would not be highly beneficial towards the membrane’s overall performance. MM membrane works would need to incorporate a second polymer, which would act as nanoparticle stabilizer, hydrophilic additive, and pore former into the dope solution. This work is intended to tackle both antifouling and nanoparticle dispersion through a newly formulated dope solution using a mix of PES and polyvinyl alcohol (PVA).

1.2 Problem Statements

Typical membrane autopsy requires the elucidation of the common problems in membrane processes, which is fouling/scaling, or chemical/mechanical damage (American Water Chemicals, 2015). Among them, fouling has been noted to be the usual culprit behind membrane performance degradation. Siemens Water Technologies (2011) for example has conducted a thorough autopsy on two 7 years old membranes which has been suggested to undergo significant fouling. By comparing the weight of the received membranes with the weight of a new membrane module, both of the membranes were noted to gain 1.8 kg and 3.2 kg respectively of presumably foulant/water mixture and decrease in rejection, suggesting the effect of fouling on membrane performance degradation. While process parameter optimization and pretreatment could reduce membrane breakdown and improve membrane lifetime, preventive measures through the use of antifouling membranes would be a better solution for a newly commissioned separation system.

Polyvinyl alcohol (PVA), a highly hydrophilic polymer has been noted by fellow researchers as a candidate of polymeric modifiers to improve the hydrophilicity and antifouling properties of membranes. Yuan et al. (2014), Zhang et al. (2014), and Li et al. (2010) have studied the effect of blending PVA with PES, PVDF-PES, and PVDF respectively, with improved antifouling performance in all cases as compared to pristine membranes. However, blending of PVA was noted to be sporadic as compared to other hydrophilic polymers such as polyethylene glycol (PEG) (Li et al., 2008, Amirilargani and Mohammadi, 2009, Khorsand-Ghayeni et al., 2016, Idris et al., 2007, Baramurali and Preetha, 2014) and polyvinyl pyrrolidone (PVP) (Pellegrin et al., 2013, Vatsha et al., 2014, Hanafi et al., 2016, Hanafi et al., 2014, Pentair, 2016). In fact, majority of PVA membrane works were concentrating on crosslinked thin film composite (Ahmad et al., 2012, Hu et al., 2016, Du et al., 2009) rather than blending. While no visible reasons have been noted, it may possibly due to the insolubility of fully hydrolysed PVA in most organic solvents used for membrane fabrication. The lack of variation on PVA blended membranes suggested a possible gap in knowledge, particularly as all of the referenced PVA works above utilized dimethyl sulfoxide (DMSO) as the main solvent. Hence, in the current work, DMAc-LiCl solvent system was utilized for the fabrication of PES-PVA blend membranes, which has not yet been studied before.

On the other hand, several types of membrane housings or modules are available nowadays, namely flat sheet, spiral wound, tubular, and hollow fiber (Ghosh, 2009). Hollow fiber for example, came with several advantages as compared to other type of housings. Nevertheless, it suffers from its manufacturing complexity and being sensitive to fouling due to lower free space between the fibers (Moch, 2004, Kirk-Othmer, 1998, Ulbricht, 2011). Based on the author’s knowledge, no PES-PVA HF membranes have been found in the literatures. The possibility for a newly formulated PES-PVA blend membrane to be spun into self-supporting HF membrane would hence need to be tested, on top of determining the suitable spinning parameters for the formulation. One of the most important parameter not available in flat sheet fabrication would be the air gap distances, which will be tackled in the current work. Next, the comparison between neat PES, PES-PVA, PES-ZnO, and PES-PVA-ZnO HF membranes would need to be conducted to elucidate the effect of each additives on the membrane’s morphology and flux/rejection/antifouling performance, while enlighten the next step in optimizing the formulation.