IMPREGNATION OF MWCNT/ZnO DUAL NANOFILLER MIXED MATRIX MEMBRANE

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IMPREGNATION OF MWCNT/ZnO DUAL NANOFILLER MIXED MATRIX MEMBRANE

by

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TABLE OF CONTENTS

Page

ACKNOWLEDGEMENT ii

TABLE OF CONTENTS iii

LIST OF TABLES vii

LIST OF FIGURES viii

LIST OF ABBREVIATIONS x

LIST OF SYMBOLS xiii

ABSTRAK xv

ABSTRACT xvii

CHAPTER ONE: INTRODUCTION 1

1.1. Removal of humic acid from water source 1

1.2. Problem statement 2

1.3. Research objectives 5

1.4. Scope of Study 6

CHAPTER TWO: LITERATURE REVIEW 8

2.1. Humic substances 8

2.2. Membrane technology 10

2.3. Limitations of PES ultrafiltration membranes in humic acid removal 12

2.4. PES membrane modification methods 15

2.5. Modification of PES membrane by blending/composite 19

2.5.1. Hydrophilic polymer 20

2.5.2. Amphiphilic polymer 27

2.5.3. Inorganic and nanomaterial additives 35

2.5.3.(a) Single filler membrane 35

2.5.3.(b) Dual filler membrane 51

CHAPTER THREE: MATERIALS AND METHODOLOGY 54

3.1. Materials and chemicals 54

3.2. Flowchart of experimental activities 56

3.3. Purification and oxidation of multiwalled carbon nanotube 57

3.4. Characterization of multiwalled carbon nanotube 57

3.4.1. Qualitative verification via colloidal dispersion 57

3.4.2. Elemental analysis via SEM-EDS 58

3.4.3. Functional group analysis 58

3.4.4. Carbon structure analysis 59

3.4.5. Carbon nanotube morphology 59

3.5. Membrane preparation 59

3.6. Membranes characterization 61

3.6.1. Membrane cross section and surface morphology 62

3.6.2. Membrane surface roughness analysis 63

3.6.3. Rheological properties of membrane dope solution 63

3.6.4. Membrane surface element analysis 63

3.6.5. Membrane surface functional group analysis 64

3.6.6. Porosity and Pore Size Determination 64

3.6.7. Membrane hydrophilicity and wettability analysis 65

3.6.8. Thermal stability analysis 66

3.7. Performance evaluation of the fabricated membrane 66

3.7.1. Preparation of humic acid feed solution 66

3.7.2. Humic acid concentration measurement 67

3.7.3. Permeation system 67

3.8. Membrane fouling evaluation 69

3.9. Membrane antibacterial properties evaluation 71

3.9.1. Bacterial culture and concentration measurement 71

3.9.2. Membrane antibacterial test 72

CHAPTER FOUR: RESULT AND DISCUSSION 73

4.1. Characterization of functionalized multiwalled carbon nanotube (FCNT) 73

4.1.1. Colloidal dispersion for functionalization validation 73

4.1.2. Element analysis by EDS 74

4.1.3. Functional group analysis by FTIR 75

4.1.4. Carbon structure analysis 76

4.1.5. Carbon nanotube morphology 78

4.2. Preliminary study of dual nanofiller membrane with raw CNT and ZnO 79

4.2.1. Characterization of prepared membrane 80

4.2.2. Performance and antifouling evaluation of prepared membrane 89

4.3. Study of dual nanofiller membrane with FCNT and ZnO 94

4.3.1. Characterization of prepared membrane 95

4.3.2. Performance evaluation of the fabricated membrane 112

4.3.3. Antifouling evaluation of the ZnO/FCNT membrane 114

4.3.4. Antibacterial properties evaluation 120

4.3.5. Summary on dual nanofiller membrane with FCNT and ZnO 125

CHAPTER FIVE: CONCLUSION AND RECOMMENDATIONS 127

5.1. Conclusion 127

5.2. Recommendations 130

REFERENCES 132

LIST OF PUBLICATIONS

LIST OF TABLES

Page

Table 2.1: Summary for single filler membrane 46

Table 3.1: Materials and chemicals used in the research 54

Table 3.2: Composition of the fabricated membrane using raw MWCNT 60

Table 3.3: Composition of the fabricated membrane using functionalized MWCNT 61

Table 4.1: EDS chemical composition for raw CNT and FCNT 75

Table 4.2: The membrane thickness, porosity and mean pore size of the fabricated membrane 85

Table 4.3: Surface roughness parameters obtained from AFM images 86

Table 4.4: Initial pure water flux, HA permeate flux and final pure water flux of the membranes 90

Table 4.5: Relative flux reduction (RFR) and flux recovery ratio (FRR) of the membranes 92

Table 4.6: Surface roughness parameter of FZ series membrane 101

Table 4.7: Elemental analysis for membrane prepared with different ratio of ZnO and FCNT 104

Table 4.8: Mean pore size and porosity of FZ series membrane 107

Table 4.9: Pure water flux (PWF), permeate flux (HAF) and HA rejection for FZ0, FZ1, FZ2, FZ3, FZ4 and FZ5 112

Table 4.10: Membrane flux, RFR and FRR of FZ0, FZ1, FZ2, FZ3, FZ4 and FZ5 116

LIST OF FIGURES

		Page
Figure 2-1:	Typical humic acid (HA) structure (Stevenson, 1994)	10
Figure 2-2:	Structure of PES monomer (Alenazi et al., 2017)	12
Figure 2-3:	Pore “open” and pore “closed” state of membrane at different pH (Zhao et al., 2011b)	34
Figure 3-1:	Overall research methodology flowchart	56
Figure 3-2:	Schematic diagram of dead-end filtration unit	68
Figure 4-1:	Colloidal dispersion of raw CNT (A) and functionalized CNT (FCNT) (B) in ethanol after 24 hr.	74
Figure 4-2:	FTIR spectra showing functional group for raw CNT and FCNT	76
Figure 4-3:	Raman spectra of the raw CNT a nd FCNT	77
Figure 4-4:	TEM image of raw CNT (A) and FCNT (B)	79
Figure 4-5:	SEM image of membrane cross-sections: a) RZ0, b) RZ1, c) RZ2, d) RZ3, e) RZ4, f) RZ5	81
Figure 4-6:	Viscosity of casting dope solution for RZ series membrane	82
Figure 4-7:	SEM image of membrane surface: a) RZ0, b) RZ1, c) RZ2, d) RZ3, e) RZ4, f) RZ5	83
Figure 4-8:	Contact angle of the fabricated membrane	88
Figure 4-9:	SEM image of membrane surface: a) FZ0, b) FZ1, c) FZ2, d) FZ3, e) FZ4, f) FZ5	96
Figure 4-10:	Magnified SEM image of FZ3 under magnification of 40,000X	97

Figure 4-11: Digital photographs of PES/MWCNT or PES/MWCNT/ZnO dual nanofiller membrane (a) top side and (b) back side 98

Figure 4-12: SEM image of membrane cross-sections: a) FZ0, b) FZ1, c) FZ2, d) FZ3, e) FZ4, f) FZ5 99

Figure 4-13: Viscosity of casting dope solution for FZ series membrane 100

Figure 4-14: Three-dimensional (3D) surface AFM images of the fabricated membrane a) FZ0, b) FZ1, c) FZ2, d) FZ3, e) FZ4, f) FZ5 102

Figure 4-15: FTIR spectra of FZ0, FZ1, FZ3 and FZ5 membrane 106

Figure 4-16: Contact angle of FZ0, FZ1, FZ2, FZ3, FZ4 and FZ5 109

Figure 4-17: TGA curve under nitrogen atmosphere for FZ0, FZ1, FZ2, FZ3, FZ4 and FZ5 110

Figure 4-18: Decomposition temperature of the fabricated membrane 111

Figure 4-19: Normalized flux of different membrane against filtration time 115

Figure 4-20: Filtration resistance (R_m, R_f, R_r, R_{ir}) of FZ0, FZ1, FZ2, FZ3, FZ4 and FZ5 118

Figure 4-21: Bacteria extracted from the membrane with dilution of 10^5 for : a) FZ0, b) FZ1, c) FZ2, d) FZ3, e) FZ4, f) FZ5 122

Figure 4-22: CFU count at the end of the experiment 123

LIST OF ABBREVIATIONS

AA	Acrylic acid
AFM	Atomic force microscopy
BSA	Bovine serum albumin
CA	Cellulose acetate
CAP	Cellulose phthalate
CFU	Colony forming unit
CNT	Carbon nanotube
DBP	Disinfectant by products
DI	Deionized
DMAc	Dimethylacetamide
E.coli	*Escherichia coli*
EDS	Energy dispersive X-ray spectroscopy
EPA	Environment Protection Agency
EPS	Extracellular polymeric substances
FA	Fulvic acid
FCNT	Functionalized carbon nanotube
FRR	Flux recovery ratio
FS	Flat sheet
FTIR	Fourier transform infrared spectroscopy
GO	Graphene oxide
HA	Humic acid
HF	Hollow fiber
HMO	Hydrous manganese oxide

HS	Humic substance
ID	Inner diameter
MBR	Membrane bioreactor
MCL	Minimum contaminant limit
MEA	Malt extract agar
MF	Microfiltration
MM	Mixed matrix
MMA-AA-VP	Poly (methyl methacrylate–acrylic acid–vinyl pyrrolidone)
MMM	Mixed matrix membrane
MW	Molecular weight
MWCNT	Multiwalled carbon nanotube
NF	Nanofiltration
NIPS	Non-solvent induced phase separation
NOM	Natural organic matter
NP	nanoparticles
OD	Outer diameter
PAN	Polyacrylonitrile
PANI	Polyaniline
PDMAEMA	Poly(N,N–dimethylamino-2-ethyl methacrylate)
PEG	Polyethylene glycol
PEO	Poly(ethylene oxide)
PES	Polyethersulfone
PES-b-PHEMA	Polyethersulfone-*block*-poly(2-hydroxyethyl methacrylate)
PP	Polypropylene
PPO	Poly(propylene oxide)

PS-b-PAA	Polystyrene-block poly(acrylic acid)
PS-b-PEG	Amphiphilic copolymer comb of PEG and polystyrene
PSf	Polysulfone
PVC	Polyvinyl chloride
PVDF	Polyninylvinylidene fluoride
PVP-b-PMMA-b-PVP	Poly(vinyl pyrrolidone)-b-poly(methyl methacrylate)-b-poly(vinyl pyrrolidone)
PWF	Pure water flux
RAFT	Reversible addition-fragmentation chain transfer
RFR	Relative flux reduction
rGO	Reduced graphene oxide
RO	Reverse osmosis
SA	Sodium alginate
SEM	Scanning electron microsope
SPC	Soybean phosphatidylcholine
SPES	Sulfonated polyethersulfone
TEM	Transmission electron microscope
TGA	Thermagravimetric analysis
THM	Trihalomethanes
TMP	Transmembrane pressure
UF	Ultrafiltration
UV	Ultraviolet
VIPS	Vapor induced phase separation

LIST OF SYMBOLS

A_m	Membrane effective area	cm^2
C_f	Feed HA concentration	mg/L
C_p	Permeate HA concentration	mg/L
d_p	Polymer density	g/cm^3
I_D	Intensity of D band	-
I_R	Intensity of G band	-
J_{HA}	Humic acid permeate flux	$L/m^2.h$
J_{WF}	Pure water flux	$L/m^2.h$
J_{WF2}	Final water flux	$L/m^2.h$
R	Ratio of intensities for D and G band	-
R_a	Mean roughness	nm
R_f	Total fouling resistance	m^{-1}
R_{ir}	Irreversible fouling resistance	m^{-1}
R_m	Membrane resistance	m^{-1}
R_q	Root mean square roughness	nm
R_r	Reversible fouling resistance	m^{-1}
R_t	Total fouling resistance	m^{-1}
R_z	Average difference in the height between the highest and the lowest point	nm
t	Filtration time	h
T_d	Decomposition temperature	-
V	Collected permeated volume	L
W_d	Dry membrane weight	g

W_w	Wet membrane weight	g
ΔP	Transmembrane pressure	Pa

GREEK LETTERS

μ	Viscosity	Pa.s
ε	Porosity	%

SUBSCIPT

d	Decomposition
f	Fouling
ir	Irreversible
m	Membrane
r	Reversible
t	Total

IMPREGNASI DWI PENGISI NANO MWCNT/ZnO MEMBRAN MATRIKS BERCAMPUR

ABSTRAK

Penapisan membran untuk penyingkiran asid humik merupakan cabaran dari segi penyumbatan membran yang berlaku melalui penyumbatan zarah asid humik dan bakteria yang terdapat dalam aliran suapan pada membran. Membran berpengisi tunggal mengalami masalah untuk mencapai sifat antisumbat dan antibakteria pada masa yang sama. Oleh itu, membran polietersulfona (PES) dwi pengisi dihasilkan melalui proses pemisahan fasa dengan mencampurkan zarah nano zink oksida (ZnO) dan tiub karbon nano dinding berlapis (MWCNT) pada pelbagai nisbah ke dalam larutan dop PES. Sebelum dicampurkan, MWCNT difungsikan (FCNT) dengan mengunakan asid nitric bagi menghasilkan kumpulan berfungsi hidrofilik hidroksil dan karboksilik pada permukan tiub. Oleh itu, kedua-dua pengisi nano tersebut digunakan untuk menghasilkan membran bersifat antisumbat dan antibakteria yang baik. Kesan sinergi kedua-dua pengisi nano akan dicirikan dari segi kelikatan larutan dop, morfologi, kekasaran permukaan, size liang membran dan keliangan membran, kehidrofilikan, kestabilan haba serta prestasi penapisan. Dapatan penyelidikan menunjukkan bahawa membran yang mengandungi dwi pengisi adalah lebih berliang berbanding dengan membran berpengisi tunggal dan membran PES yang tidak berpengisi. Di samping itu, peningkatan nisbah FCNT telah menyebabkan peningkatan kehidrofilikan membran. Penambahan kedua-dua pengisi nano didapati meningkatkan kelikatan larutan dop dan mengurangkan kekasaran permukaan membran. Fluks resapan meningkat dengan peningkatan nisbah FCNT. Apabila pengisi nano pada membran didominasi oleh FCNT (nisbah melebihi 0.5), penolakan asid humik (HA) tidak terjejas walaupun keluasan liang membran meningkat. Dapatan juga menunjukkan bahawa tanpa tindakbalas fotobermangkin, fungsi antibakteria disumbangkan oleh ZnO adalah dengan fungi antirekatan dan bukannya perencetan bakteria. Dari semua membran yang dihasilkan, FZ3 dengan nisbah FCNT dan ZnO yang sama dapat mencapai prestasi optima dengan fluks air tulen sebanyak 89.66 $L/m^2.h$ dan penolakan HA sebanyak 93.21%. Berpandukan pada perintang kotoran dan kurang pelekatan bakteria pada permukaan membran, FZ3 merupakan membran dwi pengisi bersifat antisumbat dan antibakteria yang terbaik.

IMPREGNATION OF MWCNT/ZnO DUAL NANOFILLER MIXED MATRIX MEMBRANE

ABSTRACT

Membrane filtration for humic acid removal faced challenges in term of fouling caused by solute itself and the bacteria found in the feed stream. There were a lot of studies showed great antifouling and antibacterial properties at the same time. Hence, dual nanofiller polyethersulfone (PES) membrane was synthesized via phase inversion method by blending different ratio zinc oxide (ZnO) and multiwalled carbon nanotube (MWCNT) into PES dope solution. Prior blending, MWCNT was functionalized using nitric acid to form hydrophilic hydroxyl and carboxylic group on the tube surface for dispersion. The combination of both MWCNT and ZnO was able to produce combined effect improved antifouling and antibacterial synergistic effect that does not require additional reaction or interaction between them. The synergistic effect of both nanofiller on the membrane properties was characterized in term of dope solution viscosity, morphology, surface roughness, membrane pore size and porosity, hydrophilicity, thermal stability and filtration performance. The results reveal that the membrane containing dual nanofiller was porous compared to single filler membrane and neat PES membrane. Furthermore, the increase of FCNT ratio caused the membrane hydrophilicity increased. The addition of both nanofiller was found to increase the dope solution viscosity and reduced the surface roughness of the membrane. As FCNT ratio in the membrane increased, higher permeate flux was recorded. When the nanofiller of the membrane was dominated by FCNT (i.e., ratio more than 0.5), the humic acid (HA) rejection was not affected much even though pore size of the membrane was increased. It was also been found that without photocatalytic reaction, the antibacterial properties contributed by ZnO was antiadhesion effect rather than inhibition of the bacteria. Out of all the fabricated membranes, FZ3 (dual nanofiller membrane produced with 1wt% of equal ratio functionalized MWCNT and ZnO mixture) was able to achieve optimum performance with pure water flux of 89.66 L/m^2.h and HA rejection of 93.21%. Judging from its lower fouling resistance and less bacterial adhesion onto the membrane surface, FZ3 was the most antifouling and antibacterial dual nanofiller membrane.

CHAPTER ONE

INTRODUCTION

This chapter begins with some brief introduction on membrane technology in water treatment. Then, it was followed with surface discussion about mixed matrix membrane (MMM) and their role in improving the antifouling and antibacterial properties of the membrane. Finally, the chapter is wrapped up with the problem statement, objectives and thesis organization of this research project.

1.1. Removal of humic acid from water source

Humic acid (HA) is an ancient soil-derived substance aged 50-100,000 years old that originated from vegetation in freshwater lakes or edge of marine environments as well as other water source (Laub, 2012). It been proven to be beneficial for plant growth and only caused colour problem. However, the present of it in conventional treatment processes especially chlorination can induce the formation of carcinogenic disinfectant by-product (Cowman and Singer, 1996). Therefore, humic substances were limited to value of 2.5 mg/L in drinking water according to standard STN 757111 (Barlokova and Ilavsky, 2012). Various method such as coagulation (Sudoh et al., 2015), electromagnetic treatment (Ghernaout et al., 2010), flotation (Zouboulis et al., 2003) and oxidation processes (Matilainen and Sillanpää, 2010) been employed to remove humic acid prior chlorination process. However, these methods are prone to electrode fouling, required higher operating cost and energy input (Teow et al., 2017b). This situation has led researchers to select membrane technology as the more favourable separation method for humic acid due to its relatively simple operation with lower cost and high efficiency. However, the major concern surrounding the usage of UF membrane for HA removal was the fouling of the membrane due to HA deposition and adsorption. Since, the HA removal is done prior to chlorination or the disinfection step, biofouling can also be another source of membrane fouling. Looking into this situation, extensive researches been carried out by researcher to improve the membrane resistance both toward HA and bacteria to make the application of UF membrane for HA feasible in future.

To improve the membrane properties, filler integration into membrane has been the preference and various researches. In this perspective, the selection of filler could be a key point to decide the membrane behaviour based on the intended separation performance. This was because different nanofiller inherited different properties and can interact differently with membrane base material. As stated Mari et al. (2017), the selection of fillers was the main challenges that decide the performance and separation characteristic of the membrane. Furthermore, integration of these filler into membrane often limited by their agglomeration due to their large surface area/particle size ratio. Agglomeration of filler could potentially degrade the membrane performance and separation efficiency (Ursino et al., 2018). Therefore, in recent researches, researches start to pay more attention on filler dispersion rather than filler selection since most filler has been well studied.

1.2. Problem statement

With increasing demand toward portable water, membrane technology emerges as versatile method to recover water from various sources. Polymeric UF membrane is commonly made of polymer such as polyethersulfone (PES), polyvinylidene fluoride (PVDF) and polysulfone (PSf). Out of these, PES is one of the most popular polymers used for UF water treatment membrane researches. The reason being is due to their excellent thermal and mechanical properties and lower swelling tendency compared to other hydrophilic polymers. However, this anti-swelling property that come with the hydrophobicity of PES can be a major cause that made PES prone for the fouling by hydrophobic solute such as humic acid (HA). Besides solute fouling, biofouling due to attachment of bacterial onto the membrane surface can also be another major concern for membrane separation especially in case of separation of HA, since UF is done prior disinfection/chlorination step which bacterial can potentially found in the feed water. Such fouling can greatly reduce the membrane performance and reduce the membrane flux along time. Thus, reduce the lifespan of the membrane and its reusability. Moreover, as fouling occur along the time, pumping cost can also increase too. Both of this indirectly increase the membrane unit operating cost. To mitigate the problem, extensive researches been done to reduce the fouling tendency of the membrane as well as improve the antibacterial properties of the membrane. One of the most used method is the blending of nanoparticles into polymeric membrane to form composite or mixed matrix membrane (MMM).

Out of the all polymeric material, PES is one of the most popular polymers for ultrafiltration membrane study. This is due to their low commercial prize, outstanding oxidative, thermal, hydrolytic stability and good mechanical property (Zhao et al., 2013a). These properties are granted due to the present of aromatic compound which able to restrain the chain mobility (Bowen et al., 2001, Mockel et al., 1999). Despite all these advantages, the major problem of the PES membrane is due to its high hydrophobicity (Rahimpour and Madaeni, 2010)

As far as the author aware, most of the mixed matrix PES membrane produced only focused on the study of antifouling properties by model solute such as HA and bovine serum albumin (BSA) (Saraswathi et al., 2018, Teow et al., 2017a, Lavanya et al., 2019). Yet, there are fewer study of UF membrane that focus on the antibacterial properties of the membrane. One of the method was utilize silver as the nanofiller in the MMM as Ag was a bactericide nanoparticles which also able to improve the membrane surface hydrophilicity (Sawada et al., 2012). However, concern raise on its toxicity when leaching occur (Fewtrell, 2014). Hence, researchers move on to utilization of ZnO nanoparticles for antibacterial study (Chung et al., 2017). Yet, ZnO mixed matrix membrane could suffer from flux reduction if used at higher ZnO loading due to pore plugging (Ahmad et al., 2015). MWCNT also another particle that able to inhibit bacterial growth (Lohan et al., 2016), but blending MWCNT into membrane required it to be functionalized first for better dispersion (Daramola et al., 2017). Unfortunately, MWCNT will lost it bactericide activity once being functionalized (Arias and Yang, 2009). MWCNT blending into the membrane could be challenging method as raw MWCNT tend to agglomerate and hence, blending of functionalized MWCNT was done to improve it dispersion. To date, there are various methods used to functionalize MWCNT. Depending on the reaction involved, the properties functionalized carbon nanotube can be different Great oxidized surface always involves aggressive reaction condition and this always associated with serious damage toward the tube structure or rupture of carbon nanotube wall. Thus, affecting the performance of functionalize MWCNT in the membrane. Hence, functionalized MWCNT should be carefully characterized prior blending into membrane.

Currently, most of the research being done to produce mixed matrix membrane was through blending only one type of nanoparticles into the membrane matrix. Only few papers focused to study the synergism and the membrane properties of mixed matrix membrane produced by blending two types of nanofillers. Looking into this situation, in this work, mixed matrix membrane was prepared by blending well dispersed oxidized MWCNT that can improve/maintain the membrane flux and hydrophilicity with the hydrophilic ZnO with antibacterial properties into PES membrane, producing PES membrane with both antifouling and antibacterial properties for separation of HA in long run. The combined properties contributed by both ZnO and functionalized MWCNT grant synergistic effect toward the membrane. The synergistic effect contribute by the intrinsic properties of both nanofiller membrane can be varies based on their mixture ratio as studied by Esfahani et al. (2015). The variation of this properties in turn can effectively affected the separation performance as well as the antifouling properties and antibacterial properties of the membrane. Therefore, in this study dual nanofiller membrane was done by blending different ratio of nanofiller into the membrane at the same time maintaining the overall nanofiller content in the membrane.

1.3. Research objectives

The objectives of this research are:-

1. To study the characteristics of functionalized carbon nanotubes for membrane fabrication.
2. To fabricate and characterize dual nanofiller mixed matrix membrane with different ratio of MWCNT and ZnO.
3. To investigate the performance, antifouling and antibacterial behaviour of the fabricated dual nanofiller mixed matrix membrane toward HA separation.

1.4. Scope of study

In this present work, raw MWCNT was oxidized by using mild nitric acid prior used for membrane fabrication. Meanwhile, the mixed matrix (MM) flat sheet (FS) membrane was prepared by via dry wet phase inversion method. In all the membrane, polyvinylpyrrolidone (PVP) was added in all the formulation to enhance the dispersion of ZnO as well as to aid the pore formation in the membrane structure. Different dope solution was prepared by blending 17 wt.% PES, 1.5 wt.% PVP and 1 wt.% of nanoparticles. The selection of such membrane was done with reference to Ahmad et al study. The nanoparticle consists of oxidized MWCNT and ZnO mixed different ratio (ranging from 0 to 1). The rest of the weight percent is made up of dimethylacetamide (DMAc) solvent.

The oxidized MWCNT was characterized using energy dispersive x-ray spectroscopy (EDS), Fourier transform infrared (FTIR) and Raman spectroscopy to determine the present of functional group on the nanotube surface. Then, the casted MM FS membrane was characterized in term of morphology, surface roughness, hydrophilicity, pore size and functional group using scanning electron microsope (SEM), atomic force microscopy (AFM), contact angle (CA), porometer, FTIR, EDS and Raman spectroscopy. The thermal and mechanical properties of the membrane also being determined using thermagravimetric analysis (TGA) and tensile analysis. For performance evaluation, the characterized dual nanofiller MM FS membrane was first compressed at pressure of 1.5 bar. Under normal situation, UF will be carried out at 1 bar transmembrane pressure. Hence, to stabilize the flux in UF filtration study, the membrane was subjected to slightly higher pressure to compress the membrane. Then, the pure water flux (J_{WF}) and humic acid permeate flux (J_{HA}) of the MM HF membranes were performed at pressure of 1 bar. The data been analysed and used to calculate the flux recovery ratio (FRR) and relative flux reduction (RFR) as well as the membrane fouling resistance.

CHAPTER TWO

LITERATURE REVIEW

2.1. Humic substances

Pedosphere or soil is one of Earth most important and abundant component that support life in many ways. It consists of naturally unconsolidated mineral and organic material. Within the organic material portion of soil, humic substances account for about 50% (Paul, 2007). According to Aiken et al. (1985) humic substance (HS) is "a general category of naturally occurring biogenic, heterogenous organic substances that can generally be characterized as being yellow to black in colour, of high molecular weight (MW) and refractory". Humic substances can be further divided into three fractions based on their solubility in water at different pH. These fractions included humins, fluvic acid (FA) and humic acid (HA). Humins are alkali insoluble fraction of humus while HA is dark coloured organic matter extracted from soil using various reagents. Meanwhile, FA is the coloured organic matter which remain removal of HA via acidification (Stevenson, 1994). The formation HS can be related to the geochemical carbon cycle especially via the oxidative weathering of sedimentary organic matter in Earth's surficial environment. (Chang and Berner, 1998).

Over the century, various HS application in agriculture, industry, environment and biomedicine field been summarized by Peña-Méndez et al. (2005). The unique structure of HA with various functional group present on it has granted its different function to which applicable in wide range of field (de Melo et al., 2016). Recently, the sodium salt of humic acid, sodium humate successfully drawn the attention of researchers in oncology field as photothermal agent (Miao et al., 2018). It been proven that combination of sodium humate with photothermal therapy able to enhance the drug uptake by the cell and further prevent the cancerous cell from recurrence (Hou et al., 2018). In term of agricultural industry, HA as a natural source has large potential in enhancing plant growth. In the past HA play important role as additives in fertilizer (Liu et al., 2012). Researches also revealed that present of HA highly improve the plant growth by enhance the nitric oxide and reactive oxygen species production and phosphorus release from the surrounding source (Cordeiro et al., 2017, Ullah et al., 2017).

However, their present in drinking water purification process possesses a major problem (Joo and Földényi, 2009). This is because the aromatic form of HS can easily form harmful carcinogenic disinfection by products (DBP) such as trihalomethanes (THM) and haloacetic acids during chlorination of drinking water is related to aromatic compound in water (Singer, 1999). This kind DBP is proven *in-vitro* that they are potentially in causing chromosomal mutation. Therefore, EPA has established the minimum contaminant limit (MCL) in drinking water for both THM and haloacetic acid to 0.080 and 0.060 mg/L, respectively (EPA, 2009).

HA is one of the major components of HS which composed of soil (humus), peat, upland streams, dystrophic lakes and ocean water (Stevenson, 1994). It been produced by the biodegradation of organic matter in the nature carbon cycle. Instead of simple single acid, HA comprise of mixture of weak aliphatic and aromatic organic acid which is insoluble in water under acidic condition but soluble in alkaline conditions (Robert E. Pettit, 2012). Hence, the major component of HA will be oxygen (O) and carbon (C) which range between 33-38% and 54-59% respectively. This C and O was mostly comprised of the acidic functional group which included the carboxylic group (-COOH), phenolic or alcoholic group (-OH) and carbonyl group (C=O) (DeLaune and Reddy, 2008). It's been proven that the solubility of HA in water is affected by both pH and ionic strength of the water. HA solubility increase as the pH of water increase (e.g. alkaline condition). However, increasing ionic strength will in turn reduce the solubility of HA (Kipton et al., 1992). The structure of HA is rather complex, and some said to be unknown. However, Stevenson (1994) suggested the most widely accepted HA structure which shown in Figure 2-1. The HA structure suggested consists of variety of functional group such as carbonyl or quinone group, phenol, catechol and sugar moieties with a motif of aromatic nuclei.

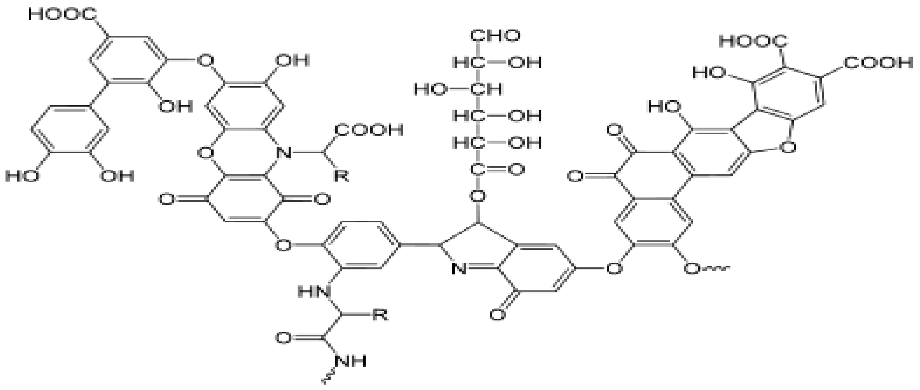

Figure 2-1: Typical humic acid (HA) structure (Stevenson, 1994)

2.2. Membrane technology

With increasing population and rapid development of industry, water pollution has become the main concern of current society. Looking at this situation, membrane technology was found to be useful in handling and treating this polluted water which provides many advantages compared to conventional method (Zularisam et al., 2006). Membrane can be considered as versatile water treatment method that can be used for various water sources such as brackish water, well water, surface water and seawater. Development of membrane also make it possible to recover drinking water from unexpected sources (Nicolaisen, 2002). In United State, membrane technology played various role in drinking water treatment process which include desalination, DBP removal, disinfection, clarification and removal of various other chemicals (Jacangelo et al., 1997).

Depending on the pore size of the membrane, pressure driven membrane can be categorized into microfiltration, ultrafiltration, nanofiltration and reverse osmosis (Nicolaisen, 2002). The pore size of the membrane along with the membrane porosity play important role to determine the selectivity of the membrane as well as the membrane flux. For separation of HA, ultrafiltration was the suitable membrane with sufficiently small pore size and the operating pressure was relatively lower compared to reverse osmosis and nanofiltration. Different material can be used to produce ultrafiltration membrane based on their specific application. As for commonly discussed polymeric material, the membrane base material included cellulose acetate (CA) (Lv et al., 2017, Liu et al., 2017), polysulfone (PSf) (Khajouei et al., 2019, Huang et al., 2017), polyethersulfone (PES) (Mohamad et al., 2017, Li et al., 2014b, Huang et al., 2012), polyacrylonitrile (PAN) (Lohokare et al., 2011, Nouzaki et al., 2002), polypropylene (PP) (Yang et al., 2010), polyvinyl chloride (PVC) (Liu et al., 2012, Rabiee et al., 2015), polyvinylidene fluoride (PVDF) (Sri Abirami Saraswathi et al., 2017, Dong et al., 2017) and etc. With the discover of carbon nanotube, researchers even step in to discover nanotube membrane fabricated using carbon nanotube as base material (Ang et al., 2017). The fabrication method involved is rather complicated and the membrane fabricated no longer categorized as polymeric membrane but called as advanced membrane (Das et al., 2014).

Out of the listed polymeric material, PES is one of the most popular polymers for ultrafiltration membrane study. This is due to their low commercial prize, outstanding oxidative, thermal, hydrolytic stability and good mechanical property (Zhao et al., 2013a). These properties are granted due to the present of aromatic compound which able to restrain the chain mobility (Bowen et al., 2001, Mockel et al., 1999). The widely accepted structure of PES was shown in Figure 2-2 Due to this high stability, PES has a relatively high glass transition temperature (230°C). Despite all these advantages, the major problem of the PES membrane is due to its high hydrophobicity (Rahimpour and Madaeni, 2010). Its high hydrophobicity makes it prone to fouling due to the interaction and adsorption of organic solute on the membrane material especially (Rahimpour and Madaeni, 2010, Ahmad et al., 2013).

Looking at this situation, lot of researches been carried out to increase the hydrophilicity of PES membrane in order to improve the fouling resistance of PES membrane (Wang et al., 2009, Gohari et al., 2014, Zinadini et al., 2017, Gzara et al., 2016, Mahlangu et al., 2017). When the membrane surface become more hydrophilic, water molecule will be adsorbed on the membrane surface and form a hydrophilic layer between the membrane surface and the organic molecules (i.e. HA). Moreover, foulants such as HA is hydrophobic in nature. Hence, a more hydrophilic surface will repel these hydrophobic foulant and will not has tendency to adsorb them (Mehrparvar et al., 2014).

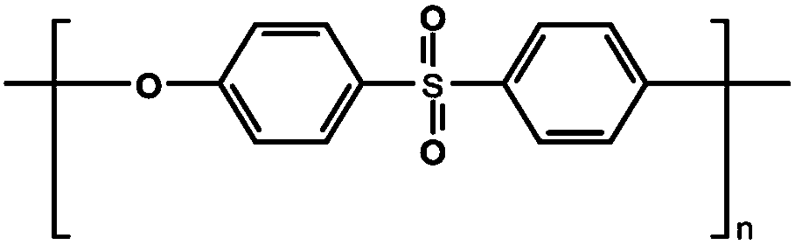

Figure 2-2: Structure of PES monomer (Alenazi et al., 2017)

2.3. Limitations of PES ultrafiltration membranes in humic acid removal

Ultrafiltration (UF) is a pressure driven process in which certain component is selectively forced through the membrane. The membrane can be configured to operate as dead-end filtration or cross flow filtration. In dead end filtration, the feed will flow perpendicular to the membrane whereas for cross flow filtration, the feed will flow parallelly with the membrane. Due to the parallel flow in cross flow filtration, it has a swept mechanism which help to reduce the deposition of foulant on the membrane. Hence, cross flow filtration is said to less sensitive to concentration polarization. As for dead end filtration, the particle or solute will build up on the membrane surface as the filtration process occur and form a layer of filtration cake. This cake layer will give extra filtration resistance to the membrane over time. Hence, after a certain amount of operation period, the membrane module must be shut down to remove this cake layer before the operation can be restored (Tansel et al., 2017). Even though, dead end filtration seem to be more energy consuming, however, Massé et al. (2011) proven that the specific energy consumption of dead end filtration is actually lower than that of cross flow.

With the increasing demand on quality life, ultrafiltration has drawn large attention in drinking water industry for its better ability to remove particles, turbidity, microorganisms and natural organic matter (NOM) compared to conventional filtration and clarification (Katsaufidou et al., 2005). Since the present of HA in drinking water is life threatening, lot effort been done to remove HA via membrane filtration. However, HA is hydrophobic in nature and this will cause membrane fouling to occur more often on hydrophobic membrane. The fouling occurs due to the adsorption of HA onto the hydrophobic membrane surface as recorded by several researchers (Ahmad et al., 2013). This kind of HA hydrophobic adsorption been investigated by Mozia et al. (2005) using 3 different polymeric membrane material (i.e. PSf, PAN and CA). Out of the 3 investigated materials, PSf and CA are very susceptible to fouling when tested using water containing phenol and HA. The fouling is reported due to the adsorption of HA. Meanwhile, PAN is less susceptible to HA fouling due to its hydrophilic surface properties. However, the hydrophilic membrane has high tendency to swell in water and loss its mechanical strength. Hence, modification on hydrophobic membrane material to find a compromise between the material hydrophobicity and hydrophilicity is considered as the best method to increase the membrane flux and reduce the membrane fouling (Zhao et al., 2013a).

Apart from the fouling caused by the solute itself, PES membrane filtration process also suffered from the fouling caused by biofilm formation which called as the biofouling. The contribution of biofouling can attribute up to 45% of the all membrane fouling (Komlenic, 2010). Biofouling can have severely affected membrane operation in term of reduction of permeate flux, increase energy consumption and operating cost, membrane degradation and premature membrane replacement. In most of the research, mitigation biofouling became the main focus especially for membrane with small pore size (i.e. nanofiltration (NF) and reverse osmosis (RO)) (Yu et al., 2012, Khan et al., 2011). However, biofouling may also occur on ultrafiltration process too (Saeki et al., 2017, Guo et al., 2012). In biofouling, it first involved the migration of the microorganisms to the membrane surface followed by the attachment of the microorganisms on the surface. Upon further cell growth proceed, the microorganisms will secrete extracellular polymeric substances (EPS) to enable the microorganisms to attach well on the membrane and further enhance colonization of microbe on the membrane surface (Nguyen et al., 2012). Biofouling actually is a more critical issue compared to solute fouling as microorganisms can grow from a tiny amount up to a well establish colony in relatively little time with the appropriate condition (Flemming et al., 1997). The condition can become more severe for HA filtration. As fouling of HA occur due to the deposition of HA solute on the membrane surface, the deposited organic HA can also become the carbon source for some microbes present in the feed water stream (Tikhonov et al., 2010).

It been shown by previous research that HA fouling and biofouling can be handled by membrane with more hydrophilic surface. Some researchers also proven that membrane with additive that is toxic toward the microorganisms can further aid to inhibit the bacteria growth on the membrane surface and further alleviate the biofouling problem. The effectiveness of the membrane in handling the both solute and biofouling problem lies highly on the polymer type, solvent type, additive/filler, membrane type as well as the operating condition. Nevertheless, the surface properties of the membrane play an important role to determine the effectiveness of the membrane in alleviating the fouling problem. In the following section, brief discussion was given on the method of modification available for membrane modification. Extensive discussion of the available modification additive that been investigated by researchers to handle the biofouling and solute fouling of membrane also being provided. Most of the discussion included was limited to PES membrane as PES was the polymer chosen to achieve the research objective. Yet, few researches discussed on the modification done on PVDF and PSf also being included due to the hydrophobic nature of PES, PVDF and PSf.

2.4. PES membrane modification methods

To enhance PES membrane hydrophilicity and antibacterial properties, several methods can be used to modify the membrane. These methods included surface modification such as surface coating (Cheng et al., 2012) and grafting (Sadeghi et al., 2013, Rahimpour, 2011), bulk modification (2013c) and blending (Li et al., 2014b).

Both surface costing and grafting were categorized under surface modification method. In the following section, brief discussion of these technique used in improve the membrane antibacterial properties, hydrophilicity and flux was being discussed.

To improve the membrane hydrophilicity and fouling resistance toward both solute and bacterial, a hydrophilic or antibacterial layer can be applied on the membrane surface by coating or grafting technology. This kind of modification do not involve alteration of the PES structure backbone, thus, preserve the great properties of PES such as its mechanical strength. Solely on coating technologies, different method been discovered by researcher such as physical adsorption (Malaisamy et al., 2011), coating with monolayer using Langmuir-Blodgett (Wei et al., 2011a), deposition from glow discharge plasma (Kull et al., 2005, Li et al., 2013) and simultaneous casting or spinning of two polymer solution (Dzinun et al., 2015, Setiawan et al., 2012). The coating of these hydrophilic layer on the membrane surface has proven to be able to improve the membrane antifouling properties. For example, Cheng et al. (2012) successfully coated PES UF membrane with polydopamine. The coated membrane displayed better antifouling properties toward bovine serum albumin (BSA) as well as flux improvement. Nevertheless, coating technologies still suffer from some drawback such as degradation of membrane coating on long run, lower pure water flux due to pore blockage by coating and utilization of non-environmental friendly chemical, hazardous condition as well as complex equipment (Cheng et al., 2012, Rana and Matsuura, 2010, Wei et al., 2011a).

Surface grafting technology also one of the most popular method employed to improve the membrane surface hydrophilicity for PES ultrafiltration membrane. With the continuous development of membrane grafting technology, different technique has been established in literature including chemical initiated, plasma-induced, ultraviolet (UV) or photo-induced, enzyme-catalysed as well as assisted by ink-jet printing (Bernstein et al., 2018, Nady, 2016, Gu et al., 2012, Emin et al., 2014). Basically, grafting technology involve the bonding of monomer covalently onto the polymer chains induced by or assisted by the method mentioned afore (R et al., 2015). In order to achieve membrane with high surface hydrophilicity and great antifouling properties, grafting with hydrophilic polymer or polymer containing hydrophilic and antibacterial nanoparticle was done. Sawada et al. (2012) grafted acrylamide layer containing silver (Ag) nanoparticle into the membrane. The grafted layer proved to improve the membrane hydrophilicity and flux as well as able to inhibit the growth of bacteria. Depending the method used to induce or initiated the grafting process, different surface properties can be produced. However, similar as coating process, it also being reported that membrane flux reduction was experienced for grafted membrane due to pore blocking by the grafted polymer (Li et al., 2015a, Yang et al., 2015). Moreover, chemical grafting process required harsh condition and involvement of non-environmental friendly chemical (Nady et al., 2011). On the other hand, irradiation induced graft may cause membrane to loss its mechanical strength too (Yang et al., 2015). These problems eventually led to the difficulty in producing graft membrane at large or industrial scale as it's economically infeasible and complex (Nady et al., 2011, Zhao et al., 2013a).

Bulk modification involved the attachment of certain functional group into the PES polymer structure backbone. These functional group included the sulfonic acid group (-SO_3H), hydroxyl group (-OH), carboxyl group (-COOH), amino group (-NH_2) and other functional group which are hydrophilic in nature. Unlike surface coating and grafting method, the bulk modification method involved the modification of the membrane material instead of modifying the fabricated membrane. Depending on the required functional group different chemical, method and condition was needed. However, such modification can be complex and come with their individual drawback too. For instance, Bruggen et al. (2009) stated that sulfonation using sulfuric acid and chlorosulfonic acid may cause polymer chain degradation while utilization of sulfur trioxide (SO_3) may initiate unnecessary side reaction. To avoid these problem, lot different research been done. Looking into these situations, researchers tend to move into blending methods. Blending is relatively simple and chemical reaction is avoided in most of the process. The integration of inorganic filler into the membrane via blending produced composite or mixed matrix membrane (MMM). In most of the research regarding membrane modification, blending is by far one of the easiest and most widely studied methods to produce hydrophilic membrane with the desired properties.

However, there are some drawback regarding blending method. One of the major drawbacks is agglomeration. Agglomeration phenomena can be caused due to instability in the casting solution and poor compatible of filler with polymer which eventually lead to uneven distribution of filler/particles in the membrane matrix. It can also happen due to the nature of nanofiller such as high surface energy and interaction between particles. Agglomeration possessed challenge toward blending method as it could further affect the membrane topology, microstructure and eventually reduce the separation and antifouling behaviour of the membrane (Drioli et al., 2010). To prevent that, dispersion of nanofiller has been improved through sonication and mechanical stirring (Atif and Inam, 2016). Moreover, in recent researches, researchers even start to focus more on nanofiller modification and in situ nanofiller formation to further improve the nanofiller distribution (Rong et al., 2006, Heinz et al., 2017). Besides agglomeration, leaching also another worth mention challenges for blending process.

Leaching occur due to the weak anchorage of filler in the membrane structure (Zhang 2016). It could be a big concern if the utilized nanofiller is health threatening (Fewtrell, 2014). It been reported that out leach of nanomaterials could render the enhancement effect granted by the nanofiller to the membrane. Looking into this situation, researches intend to create interaction between nanofiller and membrane polymer to enhance the anchorage of filler in membrane matrix. In the following section, in deep discussion on various blended filler was outlined.

2.5. Modification of PES membrane by blending/composite

Over the decade, lot researches been carried out to blend PES membrane with other non-solvent additive to achieve optimum membrane with high flux and rejection, great mechanical strength, excellent antifouling and antibacterial properties as well as low in production cost (Esfahani et al., 2015). However, such perfect membrane cannot be obtained as to make the membrane excel in one aspect it involved the compromise of other aspect. As soon as the trade-off was acceptable, such membrane can be considered well enough.

Despite bulk modification and surface modification, PES membrane can be modified and enhanced via blending method. Blending can also be considered as one of the surface modification methods as some of the blended material such as some of the blended filler (especially polymer) will segregate to the surface region and modified the surface region while the bulk properties remain the same (Chen and Gardella, 1994). Moreover, blending of nanofiller often involve migration of the blended filler to membrane surface which made the modification more obvious on membrane surface (Zhou et al., 2015). Out of all the PES enhancement methods, blending is the most widely used and simplest method to produce high efficiency FS and hollow fiber (HF) membrane, yet the leaching of blended filler or polymer was unavoidable (Basri et al., 2011, Mavukkandy et al., 2016). Moreover, blending also relatively convenient in term of operation and only mild preparation condition was needed (Richard et al., 2012).. These additives can be classified into hydrophilic polymers, amphiphilic polymers and nanoparticle or other composite material. Blending of PES with other material able to produce MMM that able to obtain both advantages of PES and the blended material. In the following section, these three additives were described individually.

2.5.1. Hydrophilic polymer

Hydrophilic polymer is one of the most widely used blending additive and it been proven by various researchers that the present of hydrophilic polymer with PES can successfully improve the filtration efficiency of PES membrane. Two of the most widely investigated hydrophilic polymers are polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG) Beside these two polymers, some researches also reported the blending of other rarely used hydrophilic polymer such as cellulose phthalate and soybean phosphatidylcholine (Rahimpour and Madaeni, 2007, Wang et al., 2005). Blending of hydrophilic polymer into hydrophobic PES membrane was a direct method to improve the membrane hydrophilicity. However, this solution was not feasible under long term operation. Due to their hydrophilic nature, these polymers they tend to dissolve and leach out from the membrane matrix. Under phase inversion process, this can be an advantage to improve the membrane porosity. Nevertheless, under long term filtration operation, the membrane may eventually become hydrophobic again once the hydrophilic polymer embedded in the membrane fully leached or degraded (Mavukkandy et al., 2016).

Out of all the studied hydrophilic polymer, PVP remain as one of the most popular blended polymers to modify PES membrane. Blending of hydrophilic aid in improve the membrane hydrophilicity but the effect won’t last long due to degradation and elution of PVP. Vatsha et al. (2014) studied the performance of PES membrane blended with different concentration of PVP with molecular weight of 40KDa. In this studied, it been reported that for membrane with 16 wt.% PES concentration, the membrane hydrophilicity and pore size increased with increase in PVP concentration. However, PVP acted as pore forming agent rather than permanent filler in the membrane. This further proven what been mentioned afore. In most of the researches PVP was used as pore forming agent rather than permanent hydrophilic improving agent.

Marchese et al. (2003) studied the blended PVP with different molecular weight on PES membrane. Two types of PVP with different molecular weight (40,000 Da and 360,000 Da) was selected. When the casted FS tested with BSA at its isoelectric point, it been shown that the fouling due to BSA pore blockage and cake formation occur more seriously in PES membrane compared to PES/PVP blended membrane. This is being explained due to the hydrophilic properties of PVP which can prevent the pore blockage by BSA and become site of nucleation for cake formation. Moreover, the presence of PVP to some extent prevent the cake formation from excessive compaction. Thus, improving the fouling resistance of PES membrane.

Effect of PVP with different molecular weight (MW) on PES microfiltration also being investigated in deep by Astakhov et al. (2012). In this study, blending of PVP again prove to improve the membrane hydrophilicity and its performance. High molecular weight was reported to be more resist to leaching. However, blending of high molecular weight PVP may lead to increase in viscosity of the dope solution. This eventually caused the casted membrane to have smaller pore size and reduce the membrane permeability greatly. Especially for PVP with molecular weight close to that of the PES, significant improvement on the mechanical properties and permeate flux.

Utilization of PVP as the main hydrophilic agent (Bi et al., 2013) to improving the membrane hydrophilicity can also face as huge problem when sodium hypochlorite (NaOCl) was utilized as the cleaning or sanitizing agent for the membrane especially in drinking water processing industry since it’s relatively cheap and widely available. It been reported by the strong oxidizing effect of NaOCl could fasten the oxidation and degradation of PVP and eventually reduce the life span of PES/PVP membrane (Kourde-Hanafi et al., 2017). Degradation of the may beneficial in term of membrane permeate flux due to pore enlargement, but the membrane selectivity was sacrificed greatly due to the larger pore size of the membrane (Pellegrin et al., 2015). In this context, PES/PVP blended membrane not only faced the leaching problem but also faced the degradation problem which both cause PVP to disappear quickly from the membrane matrix. Losing of the PVP content via oxidation process also prove to reduce the membrane mechanical and caused membrane embrittlement (Causserand et al., 2015). The membrane embrittlement was related to the chain scission phenomena at the ether-sulfone linkage upon exposure of PES/PVP with hypochlorite (Thominette 2006)

Shall the membrane washing process doesn’t involve utilization of NaOCl, PVP up to certain extend could also be a great agent to increase the membrane antifouling properties. Due to chemical inertness of PES and low toxicity of PVP, Borneman et al. (2001) produced PES/PVP membrane intended to remove polyphenols from apple juice. With the present of PVP, it again been proven that the

UF flux increase. Since the aim of the fabricated membrane was colour removal, the PES/PVP membrane showed a better colour reduction with polyphenol removal up 40% in a single UF process when PES/PVP ratio is 3.5. Despite all those advantages, it also being reported that the fouled membrane can be well regenerated using 0.1 M NaOH solution.

Wang et al. (2009) also modified PES membrane by blending it with PVP to enable application of PES membrane in biomedical field especially in haemodialysis field. In their study, PES membrane was blended with two type of hydrophilic polymer where PEG as pore forming agent along with small amount of PVP as additive. Additionally, PVP blended membrane have improved performance with higher water flux and lower bovine serum albumin (BSA) adsorption due to the increased PES membrane hydrophilicity. However, the hydrophilicity of only increase with increasing PVP content up to 6 wt%. Besides reduce membrane fouling due to BSA adsorption, the addition of hydrophilic PVP also retard the blood clotting time of the membrane. Thus, PVP was improve the PES membrane’s blood compatibility when used in haemodialysis process.

In order to handle the bacterial fouling problem on PES membrane, PVP alone cannot achieve such objective. Therefore, silver (Ag) was employed as nanofiller in the PES membrane by Basri et al. (2011). Since leaching of Ag from membrane raised concern of the public as Ag was toxic toward human (Fewtrell, 2014), PVP been used as dispersion agent of the membrane. The finding discovered that high MW PVP could aid the entrapment of Ag in the membrane and reduce the leaching of the Ag from the membrane.

Despite using PVP individually, Sun et al. (2010) modified PVP with silica to produce silica-PVP nanocomposite. The produced composite was blended into the membrane. Such composite proven to have a better surface dispersion then PVP alone. This was an essential factor to produce a lower fouling tendency as agglomeration of PVP reduce the effectiveness of the additive in handling fouling problem.

Besides PVP, PES membrane also being modified with PEG also being widely studied. One of the important factors in blending was the miscibility of the additive with the polymer and solvent in the casting or dope solution. Hence, Li et al. (2008a) fabricated PES casting solution blended with PEG of different molecular weight (PEG200, PEG400, PEG400) at different concentration. Based on the study, when PEG with lowest molecular weight (PEG200) being used, the stability of the casting solution is lowest at high PEG concentration. Thus, phase separation can occur easily in casting process. However, such high concentration can the transformation of macrovoid like structure in the membrane to sponge like form and reduced its water permeation. Nevertheless, blending it into PES membrane also increase its hydrophilicity. However, similarly as PVP, this only true up to 60 wt% of PEG200. Beyond that the dense sponge structure caused the membrane to be hydrophobic. Therefore, PEG also has the same fate as PVP to be used as pores forming agent.

On the other hand, the effect of PEG molecular weight on water flux also being reported by Krishnaiah et al. (2014). The research outlined that the pure water flux increase as the PEG MW blended to the membrane increase. This was highly related with the increase membrane porosity. Similar observation also being observed by (Mohammadi, 2009) where high MW PEG induced the formation of more finger like structure in the membrane as well as increased membrane average pore size and porosity. The effect of increased pore size and porosity was reflected by the higher