EFFECT OF AIR GAP DISTANCE ON THE STRUCTURE, CHARACTERISTIC AND PERFORMANCE OF PES/PVP AND PES/PVP/ZnO HOLLOW FIBER MEMBRANE

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by

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LIST OF ABBREVATION

Abbrevation	Description
HA	Humic Acid
HF	Hollow Fibre
MM	Mixed Matrix
HAR	Humic Acid Rejection
PWF	Pure Water Flux
DI	Deionised
NPs	Nanoparticles
ZnO	Zinc Oxide
PES	Polyether Sulfone
CA	Contact Angle
DMAc	Dimethyl Acetone
PVP	Polyvinylpyrrolidone
MF	Microfiltration
UF	Ultrafiltration
NF	Nanofiltration
RO	Reverse Osmosis

LIST OF SYMBOL

Symbol	Description
Ww	The wet membrane weight (g)
Wd	Dry membrane weight (g)
ρ_w	Pure water density (1.0 g/cm^3)
l	Thickness of membrane
η	Water viscosity
Q	Pure water flow rate (m^3/s)
A	Area of membrane
P	Operating pressure(bar)
J_{WF}	Pure water flux (L/m^2.h)
V	The permeate volume (L)
Am	Effective filtration area
t	The measurement time
RFR	Relative flux reduction
J_{TS}	Tested solution (HA solution) permeate flux (L/m^2.h)
Jws	Initial water flux
μ	The permeate viscosity (Pa.s)
TMP	Transmembrane pressure (Pa)
Rt	Total resistance (cm^{-1})
Rf	Fouling resistance
Rr	Reversible fouling resistance

KESAN JARAK RUANG ANGIN TERHADAP STRUKTUR, CIRI-CIRI DAN PRESTASI MEMBRAN SERAT BERONGGA PES/PVP DAN PES/PVP/ZNO

ABSTRAK

Membran polietersulfone (PES) yang biasa digunakan dalam aplikasi rawatan air untuk penghapusan asid humik. Kemerosotan membran adalah salah satu kesan yang tidak baik semasa proses pemisahan yang menggunakan membran. Untuk mengatasi kesan kemerosotan prestasi pada membran, beberapa kajian telah menyatakan bahawa meningkatkan hidrofilisiti membran boleh mengurangkan kesan kemerosotan prestasi membran ini. Penambahan zarah nano zink oksida (ZnO) dalam membran PES dan memvariasikan panjang jurang udara semasa proses fabrikasi membran serat berongga adalah teknik untuk meningkatkan hidrofililiti membran.Serat berongga PES dengan penambahan zarah nano ZnO telah melalui kajian yang sistematik atas kesan panjang jurang udara pada morfologi membran dan prestasi pemisahan. Larutan yang terdiri daripada PES, ZnO dan polivinilpirolidon (PVP) digunakan untuk fabrikasi membran serat berongga dengan menggunakan proses berputar basah jet-kering. Pada masa yang sama, penggunaan panjang jurang udara adalah berbeza-beza (5cm, 10 cm, 15cm) untuk menambah baikkan hydrofilisiti. Morfologi membran serat berongga dianalisis dengan menggunakan mikroskopi daya atom (AFM) dan pengimbasan mikroskop elektron (SEM) untuk penilaian permukaan dalaman dan luaran membran dan struktur rentas keratan. Penambahan nanopartikel ZnO ke membran PES terbukti dapat meningkatkan hidrofilisiti dan mengurangkan kesan kemerosotan prestasi membran kerana penyebaran zarah nano ZnO dengan baik pada seluruh membran. Untuk penilaian membran serat rongga, 50 mg / L larutan humik asid pada pH 7.7 digunakan sebagai larutan masuk ke membrane dan ia menghasilkan fluks tertinggi yang diperolehi pada jurang udara yang

semakin tinggi manakala penolakan HA yang semakin tinggi pada panjang jurang udara rendah. Nisbah pemulihan fluks (FRR) berupaya meningkat sehingga 99.522% dan nisbah fluks pemulihan (RFR) berupaya dikurangkan sehingga 7.182% dipanjang jurang udara tertinggi. Selain itu, membran Z1-15, iaitu panjang jurang udara 15 cm menunjukkan fluks HA yang paling tinggi iaitu 124.675 kg/m^2.h di bawah tekanan transmembran 1 bar dan ini menunjukkan membran ini mempunyai antifouling paling rendah berbanding membran lain. Walau bagaimanapun, penolakan asid humik tertinggi didapati di membran Z1-5 yang pada panjang jurang air 5cm dengan 96.6%.

EFFECT OF AIR GAP DISTANCE ON THE STRUCTURE, CHARACTERISTIC AND PERFORMANCE OF PES/PVP AND PES/PVP/ZnO HOLLOW FIBER MEMBRANE

ABSTRACT

Polyethersulfone (PES) membrane commonly used in the application of water treatment for humic acid removal. Fouling of membrane is one of unfavourable effect during membrane separation process. To overcome this fouling effect on membrane, some research as stated improving hydrophilicity of the membranes can lead in reducing this unfavourable effect. An addition of ZnO-NPs in PES membrane and varying the air gap length during fabrication process of hollow fibre membrane is techniques to improve the hydrophilicity of the membrane. This PES hollow fiber with addition of ZnO-NPs undergoes systematic study of the air gap length effect on the membrane's morphology and the separation performance. The dope solution consist of PES, ZnO and Polyvinylpyrrolidone (PVP) is used for fabrication of the hollow fibre membrane using dry-jet wet spinning process. At a same time the air gap length parameter are varies (5cm, 10 cm, 15cm) to provide further hydrophilicity enhancement. The morphology of the hollow fibre membrane is analysed by using atomic force microscopy (AFM) and scanning electron microscopy (SEM) for evaluation of inner and outer surface of membranes and their cross-sectional structure respectively. An addition of ZnO nanoparticle into PES membranes is proven to improve the hydrophilicity and lead to reduce fouling effect of the membrane due to well disperse of ZnO-NPs through membrane. For hollow fibre membrane evaluation, 50 mg/L of humic acid solution at pH 7.7 is used as feed and it result at highest flux obtained at higher air gap meanwhile higher HA rejection at low air gap length. The flux recovery ratio (FRR) can increase up to 99.522 % and the recovery flux ratio (RFR) can reduced to 7.182% for the highest

air gap length. Besides, the Z1-15 membrane with 15 cm air gap length shows the highest HA permeate flux of 124.675 kg/m^2.h under 1 bar transmembrane pressure and it show the lowest antifouling compared to other membrane. Nevertheless, the highest humic acid rejection was found at Z1-5 membrane which at 5cm air gap length with 96.6%.

CHAPTER 1: INTRODUCTION

1.1 Research Background

Humic acid plays a fundamental role in many ecosystems since it interacts with toxic metal ions present in the system, resulting in a decrease in the bio-availability of such ions. Moreover, the availability of humic acid in water can react with other chemical compounds, such as chlorine to form trihalomethanes (including chloroform) and causes an increasing risk of cancer and may be linked to heart, lung, kidney, liver, and central nervous system damage. Therefore, humic acid removal in water treatment processes is very important in order to achieve the drinking water standards (Terdkiatburana,2007). Hence, its make the removal of humic acid (HA) from wastewater is vital. Thus there are few techniques or ways to remove HA from the wastewater body which are electrocoagulation, ultrasonic, bioabsorption of HA by white fungi and oxidation process (Terdkiatburana, 2007, Wu, 2011). However, these methods prone to electrodes fouling, high operating cost, maintaining cost and energy requirement (Teow, 2016). Hence, in order to provide same effect on removal of HA from the wastewater and at a same time have more cost effective compare to previous techniques that had been stated, the membrane separation technique can be applied in this matter. But the main problem about membranes is fouling. In order to make good membranes for HA removal, the membrane should be high resistance towards the fouling effect of the membrane for the membranes can be reusable in long period of time. Thus, extensive research about this membrane need to be conducted.

1.2 Problem Statement

Nowadays, membrane technology has become well known and efficient technique for wastewater treatment and production of clean water due to its high removal capacity, ease in operation and cost effective. Membrane separations are commonly based on polymeric membranes because of their higher flexibility, easily pore mechanism, low cost and lower space installation as compared to inorganic membranes. The main configurations of polymeric membranes can be group as flat sheet, spiral wound, tubular and hollow fiber. Hollow fiber membrane is one of the potential configurations in membrane technology due to its advantages such as compact design with very high membrane surface areas, high productivity per unit volume and self-support properties which can be backwash for liquid separation to provide good flexibility as well as easy handling during module fabrication and in the operation.

Many studies have been investigated to improve the filtration behaviour of hollow fiber membranes in order to optimize its filtration performance. The studies include to optimize the parameters during spinning process. During the spinning process, several spinning parameters include take up speed, air gap distance, residence time, bore fluid chemistry, dope extrusion rate, extrusion temperature and pressure, external coagulation type and temperature, travelling distance, and spinneret design will have influenced the hollow fiber membrane properties such as structures, dimensions and separation performance. Air gap distance during the spinning greatly affected the performance of membranes and increase in air gap resulted in significance decrease in membrane permeation (Chung and Hu, 1997).

Other aspect that are equally important concern is the membrane fouling. Fouling resistance of the membrane is very important properties for membrane, as this property is one of the factor that determine the lifespan of the membrane. There are three ways to

upgrade or modified membrane in order to obtain our desired properties of the membrane which are bulk modification, surface modification and blending. This modification of the membrane is required to maximize the fouling resistance of the membrane as it will prolonged the lifespan of the membrane. Presence of polymer in membrane will gave significant effect toward fouling resistance of the membranes. There is abundant polymeric material can be used in this fabrication membranes, but polyethersulfone (PES) is chosen as the polymeric material due to its excellent thermal and mechanical stability and rarely swell when had a contact with water. Regardless how excellent the stability of the PES, its fouling resistance also can deteriorate due to presence of the hydrophobicity in PES during HA adsorption (Shao et al., 2011). The irreversible fouling that caused by HA adsorption is worsen the membranes. As the fouling will induce plug on the membrane pore which could reduce the performance of the membranes and might be taken more energy if want to maintain high filtration performance. Due to this circumstances, the introduction of the various ZnO-NPs into membranes is required to help the membrane on achieving high fouling resistance. The combination of this polymeric membrane and the nanoparticle is known as mixed matrix (MM) membrane.

Therefore, in this work, ZnO-NPs has been chosen to reduce the hydrophobicity of the PES membrane and, hence, enhance the anti-fouling behaviour of PES membrane. Furthermore, based on author finding, there is no published work dedicated to study the effect of the air gap distance on PES/PVP and PES/PVP/ZnO hollow fiber membrane's morphology and performance.

1.3 Research Objectives

i. To study the effect of different air gap distance on the structure and physical properties of the fabricated PES/PVP and PES/PVP/ZnO hollow fiber membrane

ii. To investigate the effect of air-gap distance on the performance of the fabricated PES/PVP and PES/PVP/ZnO hollow fiber membrane

iii. To examine the fouling resistance behaviour of PES/PVP and PES/PVP/ZnO hollow fiber membrane at different air-gap distance.

1.4 Scope of Studies

In this study, two different formulated hollow fiber membranes (PES/PVP and PES/PVP/ZnO) were fabricated at three different air gap distances (5, 10 and 15) by using dry-jet wet phase inversion technique. Effect of air gap distance on the structure and characteristics of the fabricated hollow membranes were studied in term of physical properties which are surface morphology, surface roughness, hydrophilicity, surface charge, pore size group using SEM, AFM and CA. The performance of the fabricated hollow fiber membranes were also being tested via the pure water flux (PWF) and humic acid rejection (HAR). The data obtained from the performance test of the hollow fiber membranes were used to evaluate the FRR for fouling resistance evaluation.

CHAPTER 2: LITERATURE REVIEW

2.1 Membrane Technology

Separation, purification and the recovery process are main goals in membrane technology, where this technology is very favourable to industries that want to achieve high quality desired product. A study state that the membrane technology processes able to achieve high stability and efficiency, which result in low energy usage and easy operation involved, also potentially better for the environment since the membrane approach require the use of relatively simple and non-hazardous materials (Chai, 2017).

There is significant involvement of membrane technology in the wastewater treatment industry. This is because membrane is used to filter or purify impurities from the water body before being supplied to people as a drinking water. According to Mulder, in term of membrane filtration process for drinking water production, a pressure driven process in which membrane acts as selective barriers to restrict the passage of pollutants such as organics, nutrients, turbidity, microorganisms, inorganic metal ions and other oxygen depleting pollutants, and allows relatively clear water to pass through. Based on demand of quality water and presence of high technology , membrane process become most favourable solution for achieving high quality water and make it possible the water to be reuse back (Shannon and Marinas, 2008). Thus, it shown that, the drinking water quality also could be differ based on the type of filtration method used. Hence. The membrane filtration process is divided into categories as depending on their pore sizes as: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) membranes. This paper briefly reviews the application of NF for water and wastewater treatment including for water reuse (Shon et al., 2013).

There are many types of membrane processes that could be used as filtration method. For instance RO membrane is known as non-porous membrane, and its only allow its suitable liquid or ions pass through the membrane at a same time forbid all solute and also including ions. The RO is characterized by high operating pressure (20 to 100 bar). NF has pore size 1–5 nm and it can retains ions, and low molecular weight organics. It has significantly higher water permeability than that of RO membrane and operates at lower pressure (typically 7 to 30 bar). Similarly, UF membrane has pore size typically 5 to 20 nm and retains fine colloids, macromolecules, and microorganism. The UF operates with pressure range of 1 to 10 bar. Microfiltration (MF), electrodialysis (ED), liquid membrane (LM), pervaporation (PV), vapour permeation (VP), and gas permeation (GP) are other choice or way for liquid filtration process (Shon et al., 2013). The types of membrane processes, the particle size typically removed by the membrane, and the driving force of the processes are illustrated in Figure 2.1.

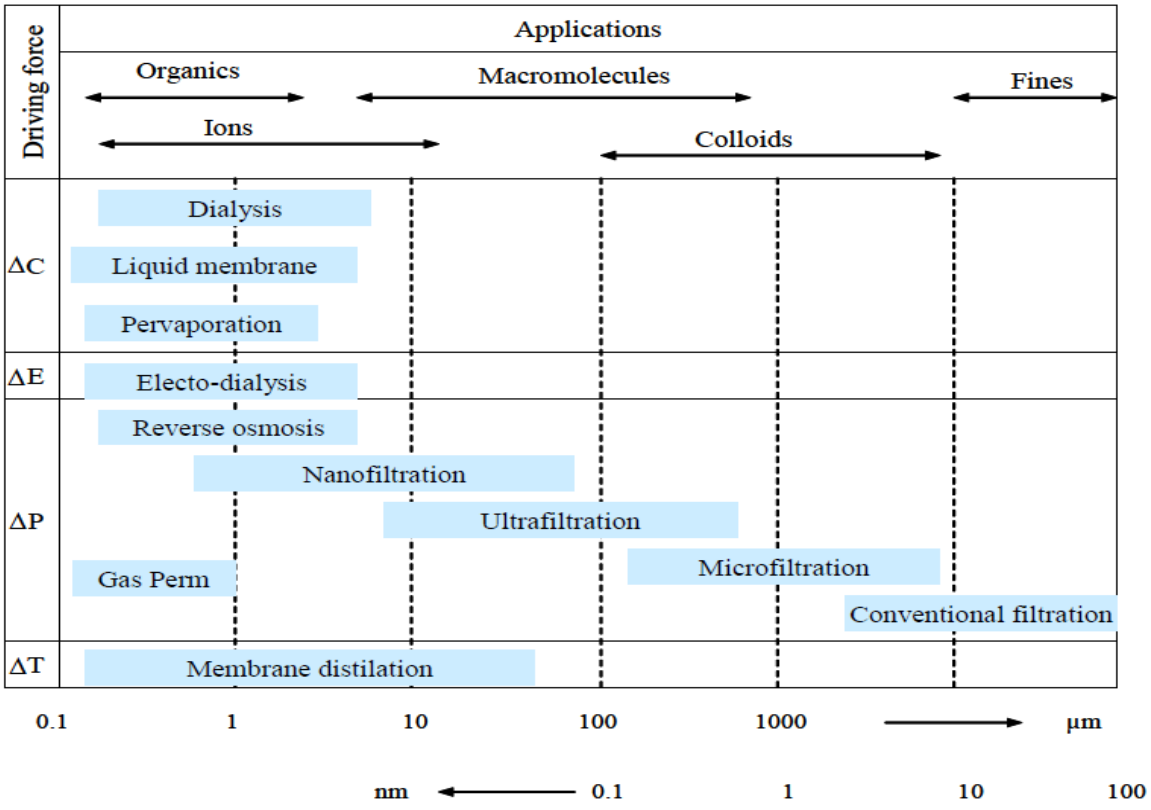

Figure 2.1: Effective range of membrane processes (Shon et al., 2013)

Ultrafiltration is one of the promising technologies for the treatment of natural organic matter and inorganic pollutants in surface water. The conventional treatment like sedimentation, adsorption, filtration and chemical precipitation is required for the production of clean and clear water which is safe from any diseases (Anselme et al., 1996). Recently, ultrafiltration is become favourable treatment to replace clarification step in conventional water treatment likes sedimentation, coagulation and filtration (Clever et al., 2000).This replacement will provide shortest path for producing clean water and a good way save cost.

Ultrafiltration membranes are known as very porous membrane which able to reject all particulate contaminant which cause disease such as bacteria, viruses and macromolecules. There is no need of chemical and size exclusion filtration is one of the advantages ultrafiltration membranes compared to conventional clarification and disinfection processes as the ultrafiltration membrane capable to produce good and constant quality of water which free from particulate and microbial. This ultrafiltration pressure-driven membranes able to operate at it optimum performance regardless raw feed water quality and low pressure (Anselme et al., 1996).

2.2 Polyethersulfone (PES) Membrane Properties

Membrane processes are one of the most effective separation processes and they are steadily under development leading to new prospects of their applications (Biotech, 2010). Development of membrane also make it possible to recover drinking water from unexpected sources (Nicolaisen, 2002). The selection of polymeric materials in fabrication of membrane is depending on the types of filtration process such as microfiltration, nanofiltration and reverse osmosis. This is due to each polymeric

materials will produce pore size of the polymeric membrane (Nicolaisen, 2002). It shown that every different type of polymeric material will induce different usage of membrane produced. There are many polymeric materials that can be used in order to produce polymeric membrane such as cellulose acetate and polysulfone (PS), polyethersulfone (PES), polyacrilonitrile (PAN), polyamide, polyimide, polyethylene and polypropylene (PEP), polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), polyvinylchloride (PVC). All these polymeric materiasl have their own unique characterises that will defined the properties of the polymeric membrane.

Among all these stated polymeric materials, there is one that has unique characteristic that could produce excellent polymeric membrane which is PES polymer. This is because PES polymer is available in a wide variety of different pore sizes and structures as well as surface properties to serve nearly unlimited selectivity of separation. Their superior intra and inter lot consistency guarantees for reliable results. Further outstanding features like their excellent gamma compatibility and high mechanical and thermal resistance make PES membranes the first choice for all major liquid and gas filtration applications, including medical devices (Biotech, 2010).

Major disadvantage of the PES membrane is consist high hydrophobicity (Burggen, 2009) which can lead to low fouling resistance of the membrane due adsorption process. Lots of studies had been done to PES membrane to increase hydrophilicity in order to increase the fouling resistance of the PES membrane. When the membrane surface become more hydrophilic, it will adsorb water molecule and form a 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, 2014).

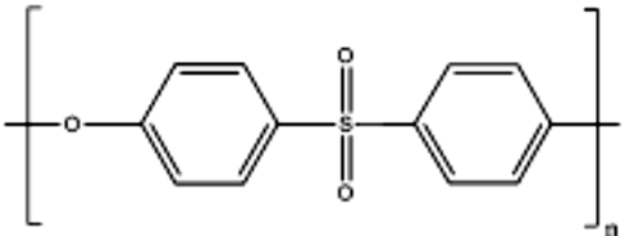

Figure 2.2: Structure of PES monomer (Burggen, 2009)

2.3 Inorganic and Nanomaterial Additives

Nanomaterial and nanotechnology have emerged as the best possible methods to develop high-performance separation membrane and help solve the expected global water crisis. These nanomaterial-based membranes, including nanoparticles, nanofibers, two-dimensional layer materials, and other nanostructured nanomaterials and their composites, exhibit extraordinary permeation properties as well as some additional properties (antifouling, antibacterial and photodegradation) (Yulong Ying, 2017).

The addition of inorganic nanomaterial into membrane is one of the method to improve the morphology and characteristic of the membrane (Madaeni, 2015). In the term of fouling resistance, the problem could be overcome by applying this method. The proper choice of additives may result in the formation of more desirable pore structures with better interconnectivity, an improvement in the surface properties such as wettability, and suppressing or encouraging the formation of macro-voids (Chung et al., 2017).A study shown that nanomaterial additives can promote and increase the antifouling characteristic for polyvinylidene fluoride (PVDF) membranes in addition of polymethyl methacrylate (PMMA) additive but unfortunately have resulted in a reduction in membrane strength (Ochoa, 2003).

Nanosized inorganic particles can be effectively used as additives in a membrane matrix due to their small size and high specific surface area (Goh, 2015). Due to high surface area of the respective additives, it enable to form great interfacial

interaction between partice in the membrane which can lead in increase mechanical stabilities and characteristic of the composite membrane. It has been revealed that using nanomaterials as additives in composite membranes could overcome material deficiencies, and improve permeate flux, surface wettability, and mechanical properties of the membrane (Hou, 2014).

Moreover, some researchers state the next generation membrane can be improved when there is hybrid membrane with polymeric emmbeded with inorganic filles (Celik, 2011) as the hybrid membranes combine the essential membrane forming capacity of organic polymers with some unique desirable features of selected inorganic additives (Koyuncu, 2015). There are few inorganic additives that commonly used in fabrication of membrane such as silica, carbon nanotubes (CNTs), titanium oxide (TiO_2) and graphene oxide (GO). For enhancing the mechanical stability, this salica particle could be introduce into the membrane (Kim, 2010) and the CNTs also able to improve the flux of the polymer membrane, , shape selectivity and specific sorption of zeolites would help the polymers improve the membrane salt rejection, meanhile the TiO_2 nanoparticles could solve the problem of fouling resistance and water flux of the membrane (Lee, 2013).

Out of all stated nanoparticle additives, ZnO-NPs membrane is one of nanoparticle that can improve the hydrophilicity of the membrane. In a study reported, concentration range ZnO-NPs, maximum pure water and HA fluxes is recorded when the ZnO-NPs in the casting solution is about 1.25 wt%. In their study, it been found out that at high ZnO concentration may eventually block the pore and the present of ZnO-NPs also reduce the membrane pore size (Ahmad and Mohd Shafie, 2017).It proven that ZnO-NPs could increase the performance of the membrane and increase the fouling resistance of the membrane as the hydrophilicity of the membrane is improved. Based

on this research, it giving us insight that the shape of the nanofiller may eventually affect the performance of the fabricated membrane too (Rajabi, 2015).

2.4 Enhancement Hollow Fiber membrane by air gap distance.

Hollow Fiber membrane is fabricated by using phase inversion technique, which means preparation of asymmetric hollow fibre membrane. This technique will produce a hollow fiber membrane with dense skin layer that is integrally bonded in series with a thick porous substructure. The importance of skin layer are containing the effective separating layer in determining membrane flux and separation factor for liquid separation (Chung, 2008).

The reason why hollow fiber membrane is better than flat sheet membrane are presence of large total surface area per unit volume of membrane module which resulting in a higher productivity of membrane module, self-mechanical support which the membrane able to reuse back after flushed for liquid separation. In term of flexibility also hollow fiber membrane has good flexibility and easy to handle during module fabrication, membrane reparation, and system operation (Kesting, 1985). During the hollow fiber fabrication process there are few parameters that need to be consider in order to obtain the desired hollow fiber membrane characteristics. The parameters are dope solution pressure, dope speed, spinneret internal and external diameter and the length of air gap. These parameters will influence in determining membrane's morphology and performance.

In the perspective of air gap distance used in fabrication of hollow fiber membrane, it is very an important parameter that will influence the outer skin layer (Liu, 2005).There is one report regarding polyvinylidene fluoride (PVDF) hollow fiber membranes that describe this membrane morphology and performance based on the different air gap distance in fabrication of hollow fiber membrane, where in this report

it state as increasing the air gap distance, the shrunken of wall thickness will occurred but the inner diameter of the hollow fiber membranes remain almost the same regardless how lower or higher air gap distance that been used (Khayet, 2003).

In a study of the polyether sulfone (PES)/polyvinyl alcohol (PVA) hollow fiber membranes are fabricated by using various distance of air gap (5 cm, 10 cm, 15 cm, 20 cm). The result of this membrane fabrication shown that in a presence low air gap, circulatory of inner lumen form oval lumen, meanwhile it became circular at higher air gap distance as shown in the Figure 2.4. Hence, that study indicate that dimension of the membrane will be reduced when there is increasing of air gap. The performance PES/PVA membranes is evaluate based on water flux and humic acid rejection process. According result that had been obtained, higher air gap distance will induce the higher water flux, but the lower air gap distance hollow fiber membrane achieve the highest rejection of humic acid (Ahmad and Mohd Shafie, 2017).

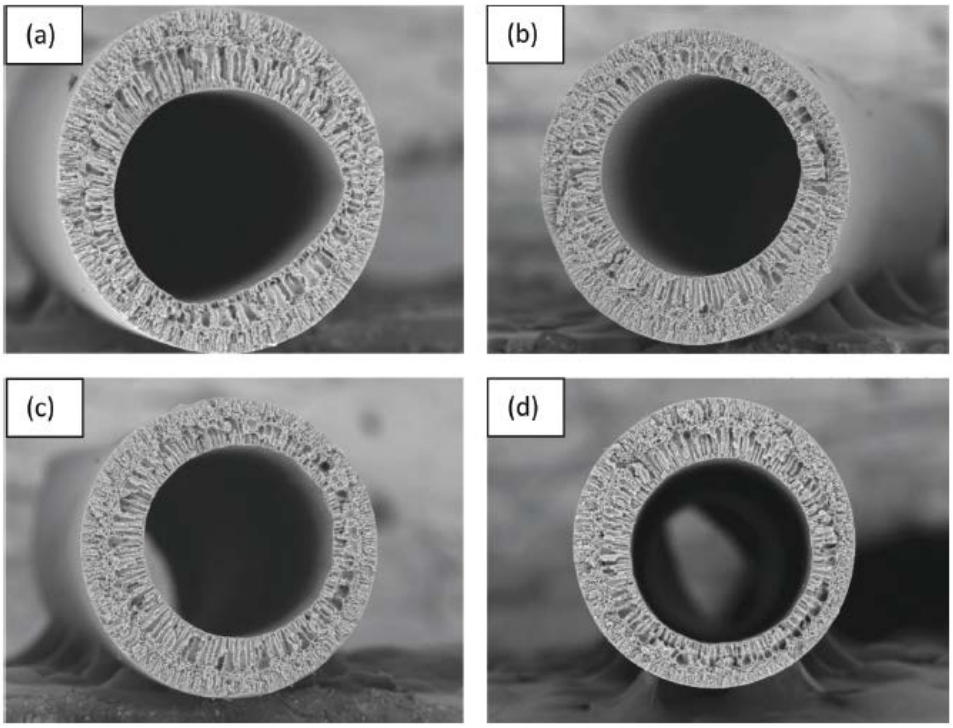

Figure 2.3: SEM cross sectional micrograph (×150 magnification) of hollow fiber membrane samples spun at (a) 5 cm, (b) 10 cm, (c) 15 cm, and (d) 20 cm respectively (Ahmad and Mohd Shafie, 2017).

There are many researches that had conducted by the researchers regarding this air gap distance parameter on the hollow fiber membrane as summarized at Table 2.1. This researches shown that different air gap distance used for different hollow fiber membrane will result various improving in hydrophilicity and pure water flux (PWF) permeation. Based on the table 2.1, it clearly shows that membrane morphology and the performance is affected by difference air gap length used.

Table 2.1: Summary effect of air gap for different hollow fiber membrane

Membrane configuration	Membrane type	Additive	Testing Method	Length of air gap (cm)	PWF ($l/m^2.h$)	Pore size (nm)	Description	Ref.
Hollow fiber	PSf/PVP	-	Cross flow	3	93.95($l/m^2.h$)	18.00	Performance of the membrane increase while maintaining excellent protein resistance.	(Noresah Saida, 2017)
				30	94.25($l/m^2.h$)	39.00		
				50	94.36($l/m^2.h$)	44.00		
Hollow fiber	PVP/PVA	LiCl	Cross flow	5	30.61($l/m^2.h$)	-	The hydrophilicity of the membrane improved as the higher length of air gap used	(Ahmad and Mohd Shafie, 2017)
				10	38.44($l/m^2.h$)	-		
				15	40.38($l/m^2.h$)	-		

Hollow fiber	PES/NMP/PEG	-	Cross flow	0	714(l/(m^2 .h.bar))	10.00	The pore size of the outside skin increases with increasing air gap length will result to higher permeate flux	(M. Rahbari-Sisakhta et al., 2016)
				1	1826(l/($m^{2.}$.h.bar))	40.00		
				6	1993(l/(m^2.h.bar))	-		
				10	8.50×10^{-4} (mol m^{-2} s^{-1})	88.61		
				15	2.10×10^{-3} (mol m^{-2} s^{-1})	21.27		
Hollow fiber	PVDF	-	Cross flow	1	9.62($10^{-9}m^2$/s)	126.64	Permeate flux decreased and the separation performance of a particular solute increased when the air gap was increased.	(Khayet, 2003)
				25	5.83($10^{-9}m^2$/s)	91.38		
				80	2.98($10^{-9}m^2$/s)	82.29		

The unit in bracket () mean the particular data follow the unit in the bracket instead on the one listed at the table title

CHAPTER 3: MATERIAL AND METHODS

3.1 Introduction

This chapter highlight the materials, chemicals and equipment used in the current researches. It also discussed the method used to synthesis the hollow fiber mixed matrix membrane via blending of Zinc Oxide. The method used to characterize the membrane chemically and physically being outlined in the subsequent subsection too. Finally, the detail calculation performed to evaluate the fouling resistance of the membrane was introduced at the end of the chapter.

3.2 Material and Chemicals

This section reports the raw materials and chemicals used in this research.

3.2.1 Chemical

The chemicals and reagents used for membrane fabrication, membrane characterization and membrane performance test are outlined in with detail of the purity, suppliers, and usage purpose in Table 3.1.

Table 3. 1: List of Chemical and Reagents

Chemical/Reagent	Purity/Grade	Supplier	Purpose
Ethanol	99%	Merck	Membrane wetting
Humic Acid(HA)	-	Sigma-Aldrich	Model solution
Liquid Nitrogen	-	Wellgas, Malaysia	Membrane fracturing
Nitrogen gas	-	Wellgas, Malaysia	Compress dope solution
Polyethersulfone (PES)	99%	BASF	Membrane polymer
N-N-dimethylacetamide (DMAc)	99.8%	Sigma-Aldrich (USA)	Solvent for membrane polymer
Zinc Oxide (ZnO)	99.5%	Sigma-Aldrich (USA)	inorganic filler in MM membrane
Polyvinylpyrrolidone (PVP)	99.5%	Sigma-Aldrich (USA)	Pore forming additives
Glycerol	99%	Merck , Malaysia	Preservation of hollow fiber membrane
Acetone	99%	Merck , Malaysia	Cleaning
Sodium hydroxide	99%	Merck	pH modification
Hydrochloric acid	99%	Merck	pH modification

3.3 Flowchart of Experimental Activities

The overall experimental activities performed in this study is simplified in the Figure 3.1:

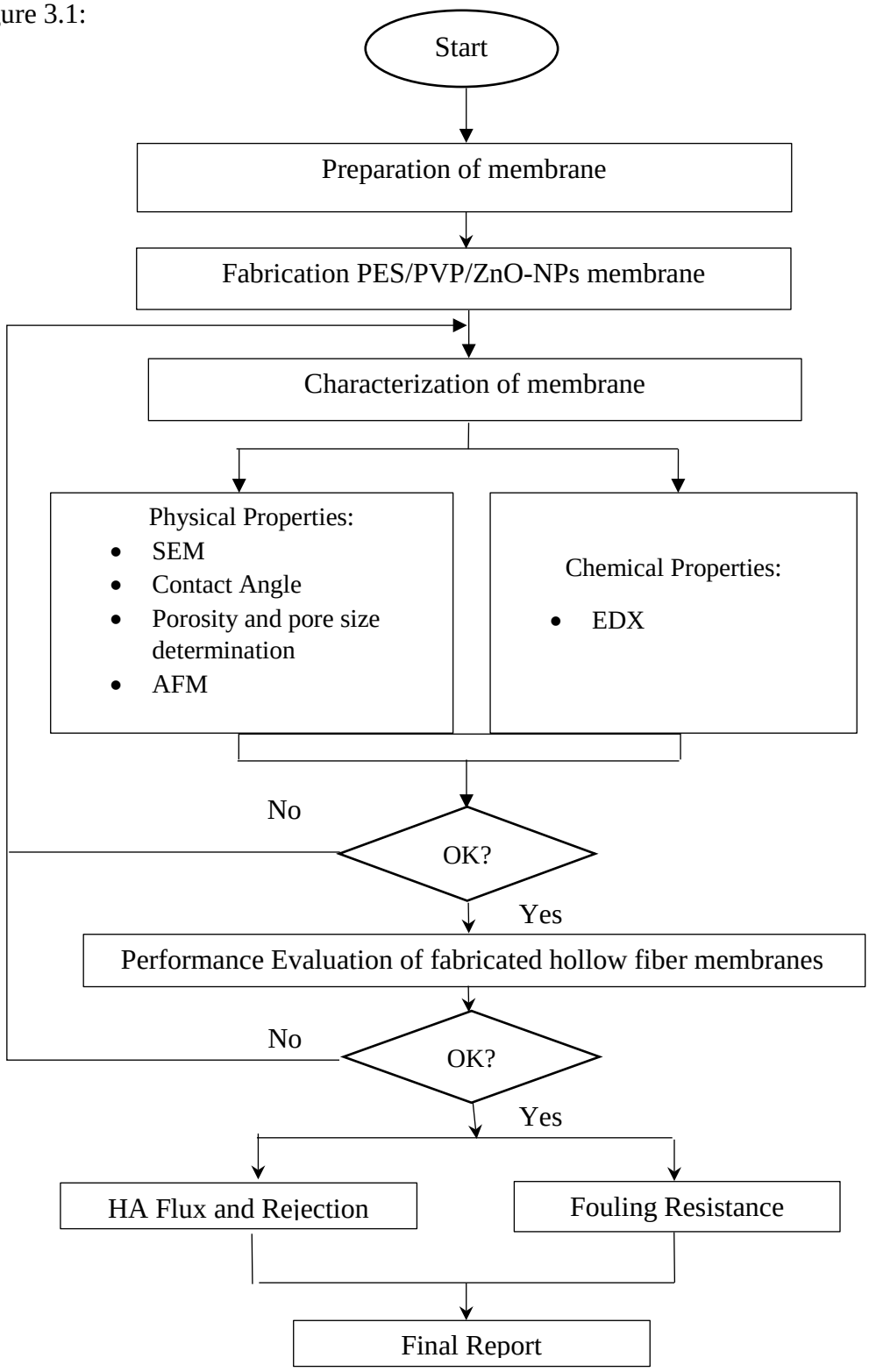

Figure 3.1: Flowchart of the overall experimental works

3.4 Fabrication of the PES/PVP and PES/PVP/ZnO membranes

The hollow fiber membrane was fabricated at two different formulations by dissolving (i) the PES with PVP and (ii) PES, PVP with ZnO-NPs in DMAc solvent. The composition of the dope solution is shown in the Table 3.2. For formulation contain ZnO-NPs, firstly, 600g of dope solution was prepared by dissolving the 2% of ZnO-NPs in the DMAc solvent. The solution was mechanically stirred at 600 rpm for 3 hours. Then, the mixture were sonicated for 10 minutes and stirred for another 3 hours at 600 rpm. The 3.75% of PVP was added into the mixture and stirring was continued for another 5 hours at 60^{o}C. Dried PES flakes were added into mixture and continued stirred the mixture using mechanical stirrer at 500 rpm and 60^{o}C for 24 hours. Once dope solution was well mixed, the dope solution was degassed for an hour by placing the solution in an ultrasonic bath before ready to be used.

Table 3.2: Composition of dope solution

Material	Composition of dope solution (wt%)	
	R1	Z1
PES	17.25	17.25
PVP	3.75	3.75
DMAc	79.00	77.00
ZnO	-	2.00

The hollow fiber membranes were fabricate by using dry-jet wet phase inversion. The degassed dope solution was filled into the polymer tank. Then, the dope solution and the bore fluid were extruded through the spinneret at fixed speed of 15 rpm with various air gap length (5, 10 and 15 cm) before entering the coagulation bath (cold water). The hollow fiber membrane was spun using distilled water as the bore fluid at room temperature (21±1^{o}C). The fabricated hollow fiber membranes were directly immersed

into distilled water for 5 days. The water need to be changed daily for removal of residual solvent. Half of fabricated membrane was air dried directly for characterization process. Meanwhile the other half was immersed into 50% of glycerol/water mixture for a day before air dried to preserve the membrane's pore structure.

Table 3.3: Spinning conditions

Parameter	Value
Dope Speed	15 rpm
Dope pressure (bar)	1.5
Draw ratio	1
Bore fluid composition	Distilled water
Bore fluid flow rate(L/min)	1.8
External Coagulant	Tap water
Coagulant Temperature (^oC)	10
Spinneret internal/ external diameter	0.5/1
Spinneret temperature (^oC)	21-22
Relative humidity (%)	63.67
Length of Air gap (cm)	5, 10, 15

Table 3. 4: Membrane sample with different air gap distance

Membrane Sample	Dope Solution	Air gap distance (cm)
R1-5	R1	5
R1-10	R1	10
R1-15	R1	15
Z1-5	Z1	5
Z1-10	Z1	10
Z1-15	Z1	15

3.5 Characterization of the membrane

Characterization of membrane is one of the important section in membrane study. This is because through membrane characterization important information about the fabricated membrane which able to relate to the performance of the fabricated membrane. Characterization of membrane can be separated into two categories that is physical and chemical properties. The information regarding the membrane surface and cross sectional morphologies, membrane pore size, membrane wettability or hydrophilicity, dispersion of nanoparticle, surface composition and functional group can be obtained via some analytical equipment and methods as described in the following sections.

3.5.1 Physical Characteristic

3.5.1.(a) Scanning Electron Microscopy (SEM) Analysis

The HITACHI Tabletop Microscope instrument(TM-3000-Japan) which operated at 15 kV was used to visualize the hollow fiber membranes surface and cross section and surface morphologies. In order to run cross sectional images test, the membrane samples was prepared by cutting the membranes sample into small size and immersed in the liquid nitrogen for 15 minutes and followed by fracturing. Then, the samples were mounted vertically on the double-sided carbon adhesive foil as the sample holder for the cross section imaging. While in case of the SEM image for membrane surface, the membrane samples were cut into small size and mounted horizontally on double-sided carbon adhesive foil as the sample holder. Prior sent into the sample chamber for SEM test, sputter coating (Quorum-SC7620) was used to coat the membrane surface and cross sectional area with a thin layer of the platinum under vacuum to avoid any electrostatic charging.

3.5.1.(b) AFM analysis

The surface topography and roughness of the hollow fiber was investigated using AFM (Atomic Force Microscope) SPA400 SH Technology. The membrane samples were observed with a scan size of `10 µm x 10 µm. Roughness parameters such as the mean roughness (R_a) and the mean difference in height between the highest peaks and the five lowest valleys (R_z) were obtained.

3.5.1.(c) Contact Angle

To evaluate the hydrophilicity of the membrane, the contact angle between water and the membrane surface is used. CA evaluation is done by using contact angle measuring system (Rame-Hart 25-FI, USA). Hollow fiber membrane mounted horizontally on the glass slide by using double sided tape and pressed using another piece of glass slide to make it flat. A drop of water (0.2 µL) was dropped on the surface of the membrane using a motor driven microsyringe at room temperature (21 ± 1^{o}C). CA between the water droplet and the membrane surface was calculated using a long working distance objective at high frequency (100Pcs/s). The captured image was analysed using DROP image software to obtain the contact angle value. To reduce experimental error, a series of 10 measurements for each membrane evaluation was considered.

3.5.1.(c) Porosity and Mean Pore Radius of Fabricated Hollow Fiber Membrane

The porosity of the hollow fiber membrane was determined through its dry-wet weight. The PES/ZnO-NPs hollow fiber membrane was immersed in DI water for 24 h. Then, the wet membrane weight was measured after discarded the excess water attached on both inner and outer membrane surface by using filter paper. To obtain the dried

weight of the membranes, the wet membranes were dried in an oven for 10 h at 30°C and the weight of the dried membrane was measured. The porosity was calculated using the following equation: -

$$\varepsilon\ (\%) = \frac{W_o + W_w}{(W_W - W_d)/d_w + W_d/d_p} x100\% \qquad (3.1)$$

Where ε is the membrane porosity, Ww is the wet membrane weight (g), Wd is the dry membrane weight (g), dw is the pure water density (1.0 g/cm^3) and d_p is the polymer density (1.37 g/cm^3). The mean pore radius size (r_m) size was calculated based of the pure water flux (PWF) and porosity data obtained previously using the Guereout-Elford-Ferry equation as follow (Hamid, et al., 2011):-

$$r_{on} = \frac{(2.91 - 1.75\text{Porosity})8\eta l Q}{\text{Porosity} x A x \Delta P} \qquad (3.2)$$

Where η is the water viscosity (8.9×10−4 Pa.s), l is the membrane thickness (m), Q is the pure water flux (m3/s), A is the area (m2) and ΔP is the operating pressure (1 bar).

3.5.2 Chemical Characteristic

3.5.2(a) Energy Dispersion X-ray Spectroscopy (EDX)

EDX analyser aimed to analyse the elemental and chemical properties of the hollow fiber membranes. EDX analysis was performed using FESEM equipped with an EDX spectroscopy (EDAX Inc., USA) under 5000× magnification. The dispersion of ZnO-NPs on the hollow fiber membrane in term of amount per unit tested area was evaluated.

3.6 Performance Evaluation of Hollow Fiber membrane

To study about HA rejection and flux on the performance of fabricated hollow fiber membrane in term of HA rejection and HA flux solution was used. No further

purification and treatment was done prior using the HA. The preparation of HA solution was started by dispersing 0.05 g of HA in 1 L of deionized (DI) water. In order to enhance HA particle dispersion in DI water, the solution was sonicated for 1 h. The 1 M of NaOH and 1 M of HCl was used to adjust pH bench to 7.70. the solution need to continuously stirred before HA rejection test.

3.6.1 Construction of Humic Acid Calibration Curve

For purpose of calibration, different HA solution with different concentration were prepared within the range of 0 to 50 mg/L using the procedure mentioned in the previous section. By using UV spectrophotometer (Pharo 300, Merck-Germany) at wavelength of 254nm, the absorbance of each HA solution concentration can be obtained. The calibration curve of humic acid concentration against respective absorbance obtained was plotted into a graph. The humic acid data and its calibration curve is shown at Appendice.

3.6.2 Membrane Permeation Test and Fouling Analysis for Hollow Fiber Membrane

Hollow fiber membrane permeation test is carried out using cross flow filtration unit shown schematically in with outside in configuration. Firstly, hollow fiber module is prepared prior running the permeation test. Four strand of hollow fiber with length of 53 cm is cut out and potted using araldite epoxy in the module holder. After curing the epoxy resin, the prepared samples were immersed in ethanol for 1 h. Then, the samples were immersed in distilled water for 1 day before used in the hollow fiber membrane test rig. The effective fiber length was about 47 cm while the effective filtration area is dependent on the outer diameter of the fiber.