

**CAPABILITY OF ADSORPTIVE EXPOXIFIED
POLY(ETHERSULFONE) MEMBRANE TO SEPARATE
CHROMIUM IONS**

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**CAPABILITY OF ADSORPTIVE EXPOXIFIED
POLY(ETHERSULFONE) MEMBRANE TO SEPARATE
CHROMIUM IONS**

by

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TABLE OF CONTENTS

ACKNOWLEDGEMENT	II
LIST OF TABLES	V
LIST OF FIGURES	VI
ABSTRAK	VIII
ABSTRACT	X
LIST OF SYMBOL	XII
LIST OF ABBREVIATIONS	XIII
CHAPTER ONE: INTRODUCTION	1
1.1. Water pollution.....	1
1.2. Membrane in heavy metal removal	2
1.3. Challenge of ultrafiltration PES membrane	2
1.4. Problem statement.....	3
1.5. Objective:	4
1.6. Scope of Study.....	4
1.7. Thesis organization.....	5
CHAPTER TWO: LITERATURE REVIEW	7
2.1. Industrial wastewater.....	7
2.1.1. Hazard contents.....	9
2.1.2. Conventional method to remove heavy metal	10
2.1.3. Membrane filtration to remove heavy metal	13
2.2. Membrane material used for wastewater treatment.....	15
2.3. PES membrane	17
2.3.1. Chemical and physical properties	17
2.3.2. Disadvantages of ultrafiltration PES membrane in removing heavy metal	18
2.4. Modification of PES	18
2.4.1. Modification method.....	19
2.4.2. Epoxy resin	22
2.5. Working mechanism of Epoxified-PES membrane in ultrafiltration of removal of chromium (VI) ions	24
2.6. Parameter that affect the epoxified process	27
2.6.1. Formulation	28

2.6.2. Casting condition.....	28
CHAPTER 3: MATERIALS AND METHODS	30
3.1. Material and chemicals	30
3.2. Research Flow Chart.....	31
3.3. Membrane preparation.....	32
3.4. Membrane characterization	33
3.4.1. Viscosity analysis.....	33
3.4.2. Porosity analysis	33
3.4.3. Fourier transform infrared spectroscopy (FTIR) analysis	33
3.4.4. Scanning electron microscopy (SEM) analysis.....	34
3.4.5. Porometer analysis	34
3.4.6. Membrane performance test.....	35
CHAPTER 4: RESULTS AND DISCUSSION	36
4.1. Neat (Polyethersulfone) PES membrane	36
4.2. Development of BADGE-PES composite membrane.....	41
4.3. Performance of BADGE/PES composite membrane.	44
4.4. Comparison of different Epoxy resin in PES membrane.	57
CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS	62
5.1. Conclusion	62
5.2. Recommendation	64
REFERENCES.....	65

LIST OF TABLES

Table 2. 1: List of heavy metals and their sources (Ahmad et al., 2016).....	8
Table 2. 2: The MCL standards for heavy metals (Usepa, 2009)	9
Table 2. 3 : Advantages and disadvantages of various method to remove heavy metals (Ahmad et al., 2016).	12
Table 3. 1: The material and chemicals used and their respective usage in this project.	30
Table 4. 1: Viscosity and porosity of the neat PES membrane.....	39
Table 4. 2: Area under the peak in Figure 4.6.....	43
Table 4. 3: Viscosity of different composition of BADGE/PES dope solution.....	51
Table 4. 4: Initial, steady flux and percentage of fouling for different composition of BADGE/PES membrane.	55
Table 4. 5: Chromium rejection of different composition of BADGE/PES membrane.	56
Table 4. 6: Permeate flux and solute rejection for neat PES, 30wt% BADGE/PES and GMA/PES membrane.....	58

LIST OF FIGURES

Figure 2. 1: Structural formula of PES (Razi et al., 2012).....	17
Figure 2. 2: Structural formula of sulfonated PES (Zhao et al., 2013)	19
Figure 2.3:Schematic representation of the methods of polymer modification (Bhattacharya and Misra, 2007).....	21
Figure 2. 4: Structural formula of epoxy group (Bhangale and M, 2017).	22
Figure 2. 5: Structural formula of Bisphenol A diglycidyl ether (Sigma-Aldrich-Co)	23
Figure 2. 6: Structural formula of Glycidyl Methacrylate (Dow-Chemical-Company, 2017)	23
Figure 2. 7: The PES membrane without modification.	25
Figure 2. 8: Adsorption of chromium ions on the PEI (Jan, 2017).....	26
Figure 2. 9: The adsorption and repulsion of chromium ions due to surface charge (Elveflow, 2015).	27
Figure 3. 1: Research flow chart	31
Figure 4. 1: FTIR spectra of neat PES membrane.	36
Figure 4. 2: SEM micrographs for surface and cross-sectional of neat PES membranes.	37
Figure 4. 3: Theoretical composition path during phase inversion.(Idris et al., 2017)	38
Figure 4. 4: Pore distribution curve of Neat PES membrane.	40
Figure 4. 5: Permeate flux of the neat PES membrane against time.....	41

Figure 4. 6: FTIR of different composition of PES-BADGE composite membrane.	42
Figure 4. 7: The FTIR analysis for the different composition of BADGE/PES at the sharp peak of 914 cm^{-1}	43
Figure 4. 8: SEM micrograph for top surface of neat PES and different composition of BADGE/PES membranes with 3.0k magnification.	45
Figure 4. 9: Example of porolux wet and dry curve analysis.	46
Figure 4. 10: Sample of membrane porolux with bad result.	47
Figure 4. 11: Pore distribution curve of 30wt%, 50wt%, 70wt% and 90wt% BADGE/PES membrane.	48
Figure 4. 12: SEM micrograph for cross-sectional of different composition of BADGE/PES membranes.	50
Figure 4. 13: SEM of different composition of BADGE/PES in 2.0 k magnification for Top and bottom side.	52
Figure 4. 14: Porosity of different composition of BADGE/PES membrane.	53
Figure 4. 15: Permeate flux of different composition of BADGE/PES membrane against time.	54
Figure 4. 16: Structural formula of BADGE and GMA (Sigma-Aldrich-Co;Dow- Chemical-Company, 2017).	57
Figure 4. 17: Permeate flux of 30wt% GMA/PES along the time.	58
Figure 4. 18: FTIR for 30wt% of BADGE/PES and GMA/PES membrane.	59
Figure 4. 19: SEM micrograph for surface and cross-sectional of 30wt% of GMA/PES membranes.	60

KEUPAYAAN PENJERAPAN POLY (ETHERSULFONE) MEMBRAN YANG DIEPOKSIKAN UNTUK MEMISAHKAN CHROMIUM ION

ABSTRAK

Mikropori Epoxified- polyethersulfone gabungan membran (EPES membran) telah disediakan melalui kering-basah fasa penyongsangan. Kajian ini bertujuan untuk mengaitkan perubahan dalam membran fizikal dan sifat kimia apabila komposisi yang berbeza (30wt%, 50wt%, 70wt% dan 90wt %) daripada BisphenolA ether diglycidyl (BADGE) telah ditambah ke dalam membran PES itu. Membran disintesis digunakan untuk memisahkan kromium (VI) karsinogen. Kemudian, analisis daripada spektroskopi inframerah transformasi fourier (FTIR) telah membuktikan kemunculan puncak epoksi yang menunjukkan kejayaan integrasi resin epoksi ke dalam matriks polimer. Mikroskop elektron pengimbas (SEM) telah menunjukkan struktur liang jari seperti dalam PES kemas dan span struktur liang dalam membran EPES. Oleh itu, macrovoid menjadi lebih serius dengan penambahan komposisi BADGE. Selain itu, kelikatan larutan bagi setiap formula didapati lebih rendah apabila lebih BADGE ditambah dan menjelaskan fenomena lihat di dalam SEM kerana kelikatan akan memberi kesan kepada kadar penyebaran NMP pelarut semasa fasa penyongsangan. Kelikatan yang lebih rendah membolehkan kadar resapan yang lebih tinggi dan dengan itu menambah serius fenomena macrovoid. Sebagai prestasi membran, meresap fluks meningkat dengan pengurangan fouling apabila komposisi BADGE telah meningkat. 30wt% daripada membran BADGE / PES menunjukkan penolakan tertinggi Cr (VI) ion di 83.73% dengan fluks meresap 1.52 L / m².min. Dalam karya ini, satu lagi jenis epoxy resin- Glycidyl metakrilat (GMA) juga digunakan sebagai bahan tambahan dan

membandingkan prestasi dengan membran BADGE / PES. Dengan itu, ia telah mendapati bahawa fluks awal yang sangat tinggi pada 89.312 L / m².min tetapi penolakan sangat rendah pada 19.08% telah ditunjukkan. Melalui analisis FTIR, GMA puncak telah gagal hadir, menunjukkan sebahagian besar daripada resin epoksi itu fluxed keluar semasa sintesis membran. Ia adalah disebabkan oleh kelarutan GMA yang tinggi dalam air berbanding dengan BADGE.

CAPABILITY OF ADSORPTIVE EXPOXIFIED POLY (ETHERSULFONE) MEMBRANE TO SEPARATE CHROMIUM IONS

ABSTRACT

A microporous epoxy resin epoxified-polyethersulfone (EPES) blend membrane (EPES membrane) was prepared through dry-wet phase inversion. This study attempts to correlate the changes in membrane physical and chemical properties when different composition (30wt%, 50wt%, 70wt% and 90wt %) of bisphenol A diglycidyl ether (BADGE) were added into the PES membrane. The synthesised membrane was used to separate the carcinogen chromium (VI). Analysis from fourier transform infrared spectroscopy (FTIR) has proved the present of the epoxy peak which indicated the successful integration of the epoxy resin into the polymer matrix. Scanning electron microscopy (SEM) showed the finger-like pore structure in neat PES and sponge structure pore in EPES membrane. Also, the macrovoid became more significant as the composition of BADGE increases. Moreover, the viscosity of the dope solution of each formula were found lower when more BADGE added which explain the phenomenon observe in SEM as viscosity will affect the rate of diffusion of NMP solvent during phase inversion. The lower viscosity allow the rate of diffusion higher and thus increased the macrovoid phenomenon. As the performances of the membranes, permeate flux increased with reduction of fouling when composition of BADGE was increased. 30wt% of BADGE/PES membrane show highest rejection of Cr (VI) ions at 83.734% with permeated flux of 1.52 L/m².min. In this work, another type of epoxy resin- Glycidyl methacrylate (GMA) was also used as the additive and compare the performance with BADGE/PES membrane. The GMA-PES membrane demonstrated very high initial flux of 89.312 L/m².min but very low rejection at 19.067%. Through FTIR

analysis, GMA peak was failed to appear, indicated most of the epoxy resin was fluxed out during the membrane synthesis. It was due to the high solubility of GMA in water as compared to BADGE.

LIST OF SYMBOL

Symbol	Description	Unit
Ld	Average thickness of the membrane	mm
m	Final weight of 2cm x 2cm size membrane.	g
P	Pressure for ultrafiltration	bar
Pr	Porosity	-
p	Density of the membrane which assume equal to standard density of PES.	g/cm ³
T	Temperature for casting membrane	° C
s	membrane area of 2cm x 2cm.	cm ²
J	Permeate flux	L/m ² .min

LIST OF ABBREVIATIONS

AA	acrylic acid
BADGE	Bisphenol A diglycidyl ether
BOD	Biochemical oxygen demand
CA	Cellulose Acetate
COD	chemical oxygen demand
Cr	Chromium
DMAc	Dimethylacetamide
ED	Electrodialysis
EDA	ethylene diamine
EPES	epoxified-Poly(ethersulfone)
ER	Epoxy resin
FTIR	Fourier transform infrared spectroscopy
GMA	Glycidyl methacrylate
HEMA	2-hydroxyethylmethacrylate
mPDA	1,3-phenylenediamine
NMP	N-Methyl-2-pyrrolidone

NF	Nanofiltration
PE	Polyethylene
PEI	Poly(ethyleneimine)
PES	Polyethersulfone
PEUF	Polyelectrolyte enhanced ultrafiltration
PLLA	Poly (L-lactic acid)
PPSU	Polyphenylsulfone
Psf	Polysulfone
PVA	poly(vinyl alcohol
PVDF	Polyvinylide fluoride
RO	Reverse osmosis
SEM	Scanning electron microscopy
UF	Ultrafiltration

CHAPTER ONE

INTRODUCTION

1.1. Water pollution

Water is the one of main essential resources for the human being. As population on earth continues to grow, people are putting ever higher demand on the water resources. Before the Industrial Revolution, people lived in more clean and less polluted environment. However, after industrialization has spread around the world, so the problem of pollution has spread with it. The industrial is the main source of the water pollution. It mainly consist of the acid, alkali, oil, heavy metals and even the radioactive material (Woodford and Chris, 2016). According to a report carrying out by Undesa (2013) , by the year of 2025, the two-third of the world population will face the water shortage problem. Water pollution is one of the main contributor for this phenomena.

Rivers have been associated with water pollution problems because of the discharging of untreated domestic and industrial waste into the river which leads to the increase in the level of heavy metals. The heavy metals are persistent environmental contaminants because they cannot be degraded or destroyed. Heavy metals such as copper, mercury, lead, and chromium are toxic even in small amounts. Chromium (Cr), one of the toxic metals, is used in a variety of applications including electroplating, nuclear power plant, water cooling and chromate preparation (Pang *et al.*, 2015). There are two stable oxidation state of Cr, which are Cr (III) and Cr (VI) in aqueous environment. It is well known that the Cr (III) is essential and safe for living organism, whereas the Cr (VI) is hazardous. For example, the hexavalent form

of chromium, Cr (VI), is toxic and has adverse effect like headache, diarrheal, and nausea, vomiting and carcinogenic when expose to it.

1.2. Membrane in heavy metal removal

There are a lot of chromium removal techniques available, such as adsorption, precipitation, electrodialysis, membrane separation and solvent extraction. Comparing to the conventional methods, membrane separation appeared as one of the effective method where is simple and economical for the removal of heavy metal ions from aqueous solution.

There are a lot of method to remove heavy metal though membrane filtration depends on its requirement of rejection. If very high rejection needed, Nanofiltration and reverse osmosis is suggested. According to Qdaisa and Moussab (2004), for the treatment of wastewater containing copper and cadmium ions was investigated, high removal efficiency of the heavy metals could be achieved by RO process (98% and 99% for copper and cadmium, respectively). NF, however, was capable of removing more than 90% of the copper ions existing in the feed water. While, for the application of very high rejection is not needed, ultrafiltration could be used. It can act as the pre-treatment which by lower down the concentration of heavy metal for NF or RO membrane application.

1.3. Challenge of ultrafiltration PES membrane

Currently, most of the heavy metal were remove by using either the reverse osmosis (RO) or Nanofiltration (NF) method. Unfortunately, higher pressure is needed as a driven force for NF and RO to work. Even though NF and RO will

achieved very high rejection, but sometimes very high rejection is not it will cost a lot of energy usage. For example, when there are very high concentration of heavy metal in the feed solution, directly using RO and NF might not worth for heavy metal removal.

So, the removal of heavy metal by using ultrafiltration (UF) method was suggested in this work. Unfortunately, in term of sieving, the heavy metal such as the chromium are found to be too small to be remove by ultrafiltration membrane. In order to use ultrafiltration membrane, chemical properties (adsorption) of PES have to enhance in order to remove the chromium. So, additive of other chemical in PES have to investigate.

1.4. Problem statement.

As mention by Papaevangelou *et al.* (2017), the hexavalent form of chromium, Cr (VI), is toxic and needed to remove from the wastewater before discharge. In order to remove chromium, membrane filtration by using PES membrane is suggested. While, the PES membrane have the problem of relatively high hydrophobicity which will lead to fouling problem. So, the added of epoxy to blend with the polymer to increase the hydrophilicity is suggested as mention by Mahendran *et al.* (2002). Meanwhile, different type of epoxy, formulation and casting condition will affect the membrane morphology and then lead to different performance of the membrane. Thus, the main challenge in this project is to study the type of epoxy resin, formulation and casting condition.

1.5. Objective:

In order to find a better type epoxy resin, formulation and casting condition to be able to achieve the optimum chromium removal performance, there are few goals needed to achieve in this project, which are:

- I. To synthesize the adsorptive epoxy cross linked polyethersulfone (PES) membrane.
- II. To characterize the physical and chemical properties of epoxy/PES membranes.
- III. To investigate membrane filtration performances through dead-end filtration set-up.

1.6. Scope of Study

In this work, the performance in terms of permeation and rejection for various compositions of epoxidized-polyethersulfone (EPES) was studied. BADGE and GMA were the epoxy resin materials to be studied in this work. So, different compositions (30wt%, 50wt%, 70wt% and 90wt %) of BADGE/PES membrane and the GMA/PES membrane with optimum composition were prepared and tested their performance with ultrafiltration unit.

In this work, non-woven support was used with membrane and compact with 7 bar of distilled water in the dead end filtration unit. 1 ppm of chromium was mixed with 1wt% of Poly (ethyleneimine) (PEI) which were used as feed solution in the dead end ultrafiltration in 3 bar operating pressure. For membrane characterization, SEM, FTIR, viscosity and pore size analysis were carried out for each membrane.

1.7. Thesis organization

This thesis consists of three main chapters and each chapter contributes to the sequence of this study. The following are the contents for each chapter in this study:

Chapter 1 introduces the water pollution cause by heavy metal, removal of heavy metal by membrane filtration, problem statement, research objectives, scope of study and organization of thesis.

Chapter 2 discusses the literature review of this study. First, an insight view into heavy metal and its adverse effect. Then, discuss about the technique to remove it and more detail on the membrane filtration method. In addition, the properties, advantage and the drawback of PES membrane were then discuss. The modification of the PES membrane are then discuss and more focus on the epoxified-PES method. Moreover, the working mechanism of the EPES was discuss. Last, the parameters that will affect the performance such as formulation and casting condition are included as well.

Chapter 3 covers the experiment materials and the details of methodology. It discusses on the description of chemical and materials used, research flow chart, membrane preparation and characterization.

Chapter 4 discuss about the result from the experiment. Firstly, discuss about the characterization and performance of neat PES. Then, the development of BADGE/PES membrane was cover as well. In addition, the performance of the BADGE/PES membrane was discussed. Last, compare with the different epoxy additive (GMA) was then discussed.

Chapter 5 had covers the conclusion and suggestion for improvement. Firstly, the conclusion for each part on chapter 4 were make. Last, the suggestion for improvement for this research were discuss as well.

CHAPTER TWO

LITERATURE REVIEW

2.1. Industrial wastewater

One of the most serious water pollution sources is from the industrial effluent. The industrial effluent may contain of Biochemical oxygen demand (BOD), Chemical oxygen demand (COD), oil, heavy metals, acids, and many other pollutant (Shi, 2009). Among the pollutants, the heavy metal is one of the most dangerous industrial pollutant because they are neither be degraded nor destroyed and thus will persistent in the environment (Duruibe *et al.*, 2007). As it can't be destroyed, the heavy metal will led to the contamination of soils and both surface and groundwater. For example, the surface and groundwater of many regions in Greece had detected exceeded legislative limit concentration of chromium (50 µg/L). As part of the groundwater is used for human consumption, this may lead to public health concern (Papaevangelou *et al.*, 2017).

Different industry may produce different kind of industry waste. For example, electroplating industry may generate significant quantities of wastewaters containing heavy metals such as cadmium, zinc, lead, chromium, nickel, copper, vanadium, platinum, silver, and titanium (Ajmal *et al.*, 2001; Algarra *et al.*, 2005; Rahman *et al.*, 2016). Besides, the printed circuit board manufacturing industry may produce the waste that contain Cu, Sn, Pb, Cd, Cr, Zn, Ni, and Mn (Jadhav and Hocheng, 2015). All this waste may lead certain kind of health effect to human which will be further discuss in Section 2.1.1. Table 2.1 has summarized the waste heavy metal produced by different industrial process.

Table 2. 1: List of heavy metals and their sources (Ahmad et al., 2016)

Metal	Sources
Aluminum	Food additives, antacids, buffered aspirin, astringents, nasal sprays, and antiperspirants, drinking water, automobile exhaust, tobacco smoke, aluminum foil, canes, ceramic and fire works
Arsenic	Rat Poisson, paints, fungicides and wood preservatives.
Barium	Tiles, glass and rubber brick, drilling mud, oil industries
Cadmium	PVC plastics, batteries, paints and pigments, insecticides, fungicides, fertilizers, dental alloys, electroplating and automobile exhaust.
Chromium	Alloys, leather tanning, dyes pigments, wood preservatives
Cobalt	Burning of coal and oil, found in soil, dust and sea water, car and truck exhaust
Copper	Industrial and domestic waste, metal plating mining mineral leaching.
Iron	Drinking water, iron pipes, cookware
Lead	Batteries, paints, PVC plastics, X-ray shielding, crustal glass production and pesticides.
Mercury	Mining operations, paper industries, thermometers, and aquatic food chains and fishes lakes.
Nickel	Electroplating industries, batteries coins, stainless steel and magnets.
Zinc	Paint industries, rubber, dye, wood, preservatives, galvanized iron objects, bronze and glass industries

2.1.1. Hazard contents

Most of the heavy metal found in waste stream are toxic and carcinogenic. The exposure to the heavy metal in a high dosage may cause serious health problem such as allergic dermatitis, kidney failure, children mental problem, increased the risk of getting cancer or many other serious health disease (Usepa, 2009). At a higher doses, heavy metals can even lead to fatality. Table 2.2 has tabulated the adverse impacts of some metal ions and its maximum contaminant level in drinking water.

Table 2. 2: The MCL standards for heavy metals (Usepa, 2009)

Heavy metal	Toxicities / adverse impacts to human	MCL* (mg/L)
Arsenic	Skin damage or problems with circulatory systems, and may have increased risk of getting cancer	0.01
Cadmium	Kidney damage	0.005
Chromium	Allergic dermatitis	0.1
Copper	Liver or kidney damage, Gastrointestinal distress	1.3
Nickel	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.2
Zinc	Depression, lethargy, neurological signs and increased thirst	0.8
Lead	Delays in physical or mental development for children, Kidney problems; high blood pressure	0.015
Mercury	Kidney damage	0.002

**Maximum Contaminant Level (MCL) –The highest level of a contaminant that is allowed in drinking water.*

2.1.2. Conventional method to remove heavy metal

The emission of the polluted water (especially heavy metal contamination) will pollute the surface and also underground water sources. This may lead the soil pollution and indirectly cause the polluted of the plant. When human intake those polluted water or the plant, it will cause significant of health effect as explain earlier. So, all this acquire the wastewater regulation to minimize the contamination. In order to minimize the human exposure to those hazardous metal variety of conventional heavy metal removal techniques have already been applied years ago include chemical precipitation, ion exchange, electro dialysis, membrane filtration and adsorption (Abas *et al.*, 2013).

Chemical precipitation is the most widely used method for heavy metal removal from inorganic effluents. The chemical precipitation is carry out by adding certain reagent in the waste water, which forms an insoluble compound in order to be settle out. For example, the most common method used is by added lime (CaO) or sodium hydroxide (NaOH) to waste stream to precipitate heavy metals in the form of metal hydroxides (Eddy, 2014). Its simplicity processes make it relatively inexpensive in capital cost. Moreover, this method is suitable to most of the heavy metal, since most of the metal can be precipitate out. However, the main disadvantages of chemical precipitation are the production of metal contained sludge. Thus, the sludge disposal cost and maintenance will be definitely higher.

As for the coagulation-flocculation process, it make used of the coagulant to separate the heavy metal from the wastewater. For example, the removal of heavy metals (Pb, Zn and Fe) by using Aluminium sulfate (alum), polyaluminium chloride (PACl) and magnesium chloride (MgCl₂) with Koaret PA3230 as the polyelectrolyte

through coagulation- flocculation method have been study by Pang *et al.* (2011). However, this process involved of huge chemical consumption.

Recently, adsorption have become one of the popular alternative treatment for heavy metal. Numerous approaches have been studied for the development of cheaper and more effective heavy metal removal (Uddin and Kashif, 2017). Adsorption make used of the attractive interaction between a surface and the species being adsorbed at certain molecular level in order to separate the heavy metal from the water. The process has a lot of advantages such as could be apply for a wide variety of target pollutants, high adsorption capacity, fast adsorption kinetics , efficient in removing metal ions even at ultra-trace level and cost effectively. However, the adsorption efficiency is highly dependent on the type of the adsorbent used. The advantages and disadvantages for those of heavy metal removal techniques are summaries in Table 2.3 (Ahmad et al., 2016).

Table 2. 3 : Advantages and disadvantages of various method to remove heavy metals (Ahmad et al., 2016).

Technique	advantages	disadvantages
Ion exchange	Metal selective Limited pH tolerance High regeneration	High initial capital cost High maintenance cost
Coagulation and flocculation	Bacterial inactivation capacity	Chemical consumption
Chemical precipitation	Process simplicity Not metal selective Inexpensive capital cost	Large amount of sludge containing metal Sludge disposal cost High maintenance
Adsorption	Wide variety of target pollutants High capacity Fast kinetic Efficient in removing metal ions even at ultra-trace level Cost effective Process simplicity Possible selective depending on adsorbent	Performance depends upon type of adsorbents Physical or chemical activation to improve its sorption capacity.
Membrane filtration	Low solid waste generation Low chemical consumption Remove wide range of dissolve species	Complex process High initial capital cost High maintenance and operation cost Membrane fouling Limited flow rated
Electrodialysis	Recover useful materials from waste water Remove heavy metals with high efficiency	High cost Process complexities Low permeable flux.

2.1.3. Membrane filtration to remove heavy metal

For the past few decades, membrane filtration has appeared as an attractive technique for heavy metal removal, due to their high efficiency and space saving. Depending on the size of the particle that can be retained, the membranes that can be used to remove heavy metals from the wastewater can be categorized into Ultrafiltration (UF), Nanofiltration (NF), reverse osmosis (RO), and Electrodialysis (ED) (Human-Press, 2005).

Electrodialysis (ED) is an electro-membrane process which transport ions through a selective membrane from one solution to another under the influence of electrical field. The electrical charges on the ions allow the solutes to be separated. Basically, there are two type of ED membranes which are the cation-exchange in which the cations move toward the cathode and anion-exchange in which the anions migrate to anode crossing the differently designed membranes (Khan *et al.*, 2017;Electrosynthesis Company, 2016). According to Öğütveren *et al.* (1997), the copper ions can be remove by using electrolysis method with IonacMA3475 anion and a Nafion423 cation as the exchange membranes.

Reverse osmosis, RO are essentially non-porous with pore size less than 2nm and works on the principle of size exclusion and solution diffusion with semipermeable membrane. In RO process, pressure is applied on the feed to reverse the natural osmotic flow. Normally, it operate at high pressure (usually 2000 to 10000kpa) and preferentially pass water and retain most solutes including ions. There are many works report about the removal performance of RO, under 8 bar operation pressure, RO can achieve up to 99.8% removal efficiency of contaminants from metal finishing industry. In the work carried out by Petrinic *et al.* (2015), the contaminant such as suspended solids, nickel, ammonium nitrogen, sulphate nitrogen,

chemical oxygen demand, and biochemical oxygen demand were completely removed. Usually, the RO unit is used for the desalination of sea water for domestic, but it also used for industrially purpose which needed high purity water.

As for the Nanofiltration membrane, it is a porous medium that commonly found with pore sizes of 2–5 nm. This membrane is suitable for partially retain ions. As compared with RO, small and monovalent ions or the low-molecular-weight organics tend to pass through the membrane. NF membranes usually have significantly higher water permeability than RO membranes and operate at lower pressures, typically 700–3,000 kPa. It have lower removal efficiency than RO but higher than UF unit. Under 8bar, the NF membrane with a pore size of 0.34 nm is able to remove Mg^{2+} ions up to 99.4% removal efficiency (Zhao *et al.*, 2016).

UF is a porous type membrane with a relatively large pore size (ranging 2–50 nm). It make used of the permeable membrane to separate the macro molecule and suspended which size are large than the pore size of the membrane. It is a relatively lower energy consumption process which work at lower transmembrane pressure for the removal dissolve and suspended materials. At 8 bar, the UF is able to remove the suspended solid from metal finishing industry up to 90% from the feed of 9.75 mg.L^{-1} of suspended solid (Petricin *et al.*, 2015).

Similarly to UF, microfiltration (MF) also a porous type membrane with the pore size ranging from 0.1-10 μm . MF is more economical process that usually operate at relatively low pressures (50–500 kPa), typically less than 100 kPa. However, it may performed the lowest removal efficiency due to big pores structure but MF retained the highest permeate flux as compared to other types of the membranes (Human-Press, 2005).

2.2. Membrane material used for wastewater treatment

Among the membrane type discussed in section 2.1.2, ultrafiltration membrane was in this work. As for the wastewater treatment, ultrafiltration and microfiltration are more attractive over Nanofiltration due to their lower operating pressure. The membrane configurations can be tubular, hollow fibre, or flat sheet depend on the application used.

The selection material is utmost important factor among the membrane selection criteria. Membrane materials can be classified in two major categories, which are organic and inorganic (metallic and ceramic) material. While, synthetic or natural polymers are the majority membrane material used in industrial today. Both polymer are known as organic membrane. There are variety of organic (polymeric) membrane such as Cellulose acetate (CA) , polyvinylidene fluoride (PVDF), polyethersulfone (PES), polyethylene (PE), and polysulfone (Psf) membrane which are common used in wastewater treatment application (Lin *et al.*, 2012).

The inorganic material are the membrane made from the material other than polymer, such as ceramic and metal. The ceramic membrane have several advantages over the polymeric such as the much higher chemical and thermal stability, higher mechanical strength and long reliable life. Chougui *et al.* (2014) have demonstrate a new type of a double-layer ceramic membrane used for the removal of cadmium, zinc, Methylene Blue and Malachite Green from water under a pressure of 5 bar with 99-100% of rejection rate was achieved. However, due to the high cost, low packing density and poor selectivity renders commercially available have hold wide practical used of ceramic membrane (Ivanets *et al.*, 2016;Li and Kang, 2007) .

On the other hand, polymeric membrane is more commercially available. The type of membrane used are strongly depend on its application and each of them have its' respective benefit and drawback. For example, Cellulose acetate (CA) was the first commercially available asymmetric membrane, and it is one of the most widely used filtration membranes. CA is relative hydrophilic in nature and have good fouling resistance properties as compared to others type of membrane. However, the CA polymer is suffered from drawback such as low chemical and thermal stabilities, narrow pH tolerance range, and weak mechanical strength if compared to the PES and Psf membrane (Ramli *et al.*, 2012;Riaz *et al.*, 2016).

Currently, there are many research on the PES membrane to improve its performance, such as additive of poly(vinyl alcohol) (PVA) in PES to make thin film composite Nanofiltration membranes for textile dyes waste treatment by Babu and Murthy (2017), blended aromatic polyamide PA-6 with PES to enhanced simultaneous permeability and fouling–resistance property by Shockravi *et al.* (2017) and sulfonated PES/PES blend proton exchange membrane for COD removal in microbial fuel cell by Zinadini *et al.* (2017). As state by Zinadini *et al.* (2017), PES is an attractive material for membrane preparation due to their low cost, good chemical, mechanical, and thermal stability. Thus, PES membrane is choose as the membrane material in this work and further discussion of PES will provided in next section.

2.3. PES membrane

Polysulfone are a family of thermoplastic polymers. The group of polysulfone includes polyethersulfone (PES), polysulfone (Psf) and polyphenylsulfone (PPSU). Figure 2.3.1 shown the structural formula of the PES monomer. As shown, PES contain the subunit aryl-SO₂-aryl, the defining feature of which is the sulfone group (Razi *et al.*, 2012).

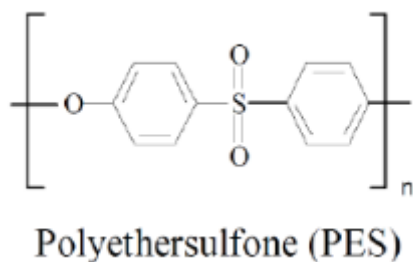


Figure 2. 1: Structural formula of PES (Razi et al., 2012).

2.3.1. Chemical and physical properties

As PES is the family of group of polysulfone, PES have almost similar properties same as the polysulfone. Polysulfone is the family of thermoplastic, which is well-known for their toughness and stability at high temperatures. So, PES also known as thermos-resistant polymer of good mechanical strength. Besides, PES also have the properties of high resistance to oxidation and hydrolytic stability. These feature is supported by the diphenylene sulfone group as shown in the Figure 2.1. While, the ether linkages have provide the extra thermal stability and flexibility in the backbone of the polymer. So, PES can be moulded, extruded, or thermoformed into a wide variety of shapes (Berins and L., 1991;Harper and Petrie, 2003).

Generally, PES are biological and chemical stability. It is highly resistant to aqueous mineral acids, bases, oxidizing agents and are fairly resistant to many

non-polar solvents. However, PES is having low resistant to the low polar solvents, such as esters, ketones, aromatic and chlorinated hydrocarbons (Poźniak and Poźniak, 2007;Subramanian and Gupte, 2014).

2.3.2. Disadvantages of ultrafiltration PES membrane in removing heavy metal

Besides the advance feature of PES, there are some drawback of PES which make it limited in its application especially used as membrane. One of the main drawback is about its relatively high hydrophobic characteristic (Erniza and Low, 2014). The high hydrophobic nature may leads to severe fouling due to the deposition of solute on the membrane.

Furthermore, Ultrafiltration PES membrane is not suitable to remove heavy metal. It is due to the pore size of any ultrafilter is too large to reject small molecules like inorganic ions especially chromium ions (Poźniak and Poźniak, 2007;Subramanian and Gupte, 2014).

2.4. Modification of PES

As discuss in 2.3.2, there are some limitations of PES membrane in heavy metal removal, especially the ultrafiltration PES membrane. Thus, it may not practical to be used for chromium removal. The relatively hydrophobic feature in PES polymer lead to the lower membrane flux (if the PES membrane is used for Nanofiltration or reverse osmosis) or which can then lead to fouling problem or lower selectivity (if the PES membrane is used for microfiltration and ultrafiltration). The pore size of any ultrafiltration membrane is too large to separate or reject the

small inorganic ions such as chromium. So, there is crucial to modify the PES membrane in order to overcome all these limitation (Pożniak and Pożniak, 2007).

Zhao *et al.* (2013) review the modification of polyethersulfone membranes and summarize few approach that could be applied to modify the PES membrane: 1) bulk modification of PES polymer, and used the modified PES polymer to prepare the membrane; 2) surface modification of PES membrane; and 3) blending PES with others functional or hydrophilic materials. These modification method may improve the hydrophobicity, permeate flux, fouling reduction, solute rejection or bio-compatibility of the membrane (Zhao *et al.*, 2013).

2.4.1. Modification method

The most common bulk modification of PES membrane is by sulfonation of PES. Sulfonation is a chemical reaction by introduce the sulfonic acid group SO_3H into the structure of molecule with replacing the hydrogen atom which localize in ortho-position of the aromatic rings as shown in the Figure 2.2.

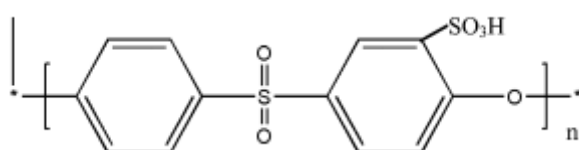


Figure 2. 2: Structural formula of sulfonated PES (Zhao et al., 2013)

In a sulfonation process, the PES polymer is first dissolved and stirred, then, the reagent is added drop by drop at constant temperature. After the sulfonation reaction, the solution will be cool down to precipitate the polymer. Precipitate is then separated by filtration, washed with deionized water, and dried. Through this bulk modification method, the sulfonated Polyethersulfone (SPES) membrane is expected

to have a better hydrophilicity with reduced water contact angle (Zhao *et al.*, 2013). In a study carried out by Rahimpour *et al.* (2010), different composition of SPES/PES membrane is used to remove the milk protein. As discuss by Rahimpour *et al.* (2010), the SPES have increase the pore size of the membrane if compared to the pure PES. Thus, the permeate flux found to be increase while the rejection of protein decreases.

Another popular method that used to modify PES membranes is through blending. This is a simple method without involving complicated procedure, harsh chemical reaction and usually is carrying out at room temperature. To improve the hydrophilicity, and the membrane antifouling capacity, PES polymer will be directly blended with hydrophilic or functionalized materials. Various kind of materials such as a compatible polymer, nanoparticles, or epoxy compound are suitable to use to be blend with PES polymer depends on the application. In the process, PES polymer was dissolved together with the paired materials and stirred to prepare the casting solution. Then, the cast membrane is undergoes solidification through phase inversion (Zhao *et al.*, 2013). While, in the study carried out by Jamshidi Gohari *et al.* (2014), Hydrous manganese dioxide (HMO) nanoparticles were blend with polyethersulfone (PES) to fabricate nanocomposite mixed matrix membranes (MMMs) for ultrafiltration (UF) to remove protein from feed protein solution containing 1000 ppm Bovine serum albumin (BSA). The hydrophilicity of the PES is greatly improve by the MMMs and then improve the performance and antifouling capability of PES.

Surface coating is also one of the surface modification method, where a functional thin film is directly deposited on the surface of the membrane. The deposited thin film will interacted with the support membrane through covalent or

non-covalent interactions. According to Madaeni *et al.* (2013) polydimethylsiloxane (PDMS) coated polyethersulfone (PES) composite membrane was prepared for gas separation (CO₂, CH₄, and N₂). PES did not provide any selectivity to the gases, while the PDMS provides desired permeability and selectivity for gases by intrinsic properties. So, coating of the support with PDMS layer on top have improves the permeability and selectivity for gas separation.

Furthermore, grafting is also an attractive surface modification method. Grafting is a method wherein monomers/ surface modifiers are covalently bonded (modified) onto the polymer chain as shown in the Figure 2.3. As compared to surface coating, both method are quite similar, which both involve of the covalent interaction. The main difference is about the deposition of functional layer. Surface coating involve the direct deposit of the thin film modifier on the prepared membrane, while the grafting involve the link or bond of the monomer on the backbone of the polymer. So, grafting show more permanent or long lasting surface modified compared to the surface coating method (Ni *et al.*, 2014;Bhattacharya and Misra, 2007).

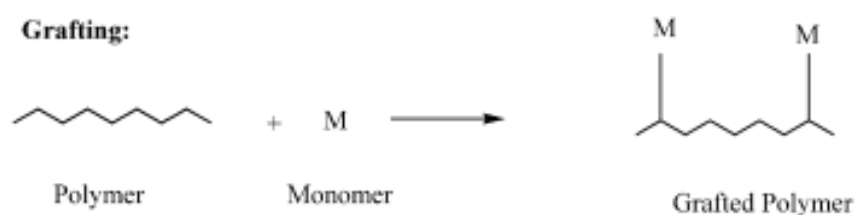


Figure 2.3:Schematic representation of the methods of polymer modification (Bhattacharya and Misra, 2007).

The grafting could be completed through chemical, radiation, photochemical, plasma-induced and enzymatic grafting techniques. Same as other method, grafting also can improve the membrane's hydrophilicity, anti-fouling feature, mechanical

stress, thermal and chemical stability depend on the additive and application requirement (Bhattacharya and Misra, 2007). For example, Rahimpour (2011) have study on the grafting PES membrane with hydrophilic monomers such as acrylic acid (Ahmed *et al.*), 2-hydroxyethylmethacrylate (HEMA), 1,3-phenylenediamine (mPDA) and ethylene diamine (EDA) using UV irradiation. In this study, the reduction in contact angle and pore size were achieved with the grafting method. Directly, the hydrophilicity and the protein rejection were improved.

2.4.2. Epoxy resin

Nowadays, simple and low cost manufacturing process are always the desirable choice. Among all the modification methods mention in section 2.4.1, blending method is the simplest and lowest cost. In this study, epoxy resin has been chosen as the blend material due to its hydrophilicity characteristic and possibility to have high affinity towards metal ions (Mahendran *et al.*, 2002;Hoffman, 1995).

Epoxy resin can be defined as a molecule that containing one or more epoxide groups, as shown in Figure 2.4. The epoxy group enables crosslinking reactions with amines, carboxylic acids, anhydrides and hydroxyl-containing polymers. Besides, it also allows structural modification of the polymer backbone that can result in differentiated properties and higher performance.

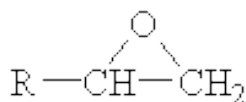


Figure 2. 4: Structural formula of epoxy group (Bhangale and M, 2017).

In this work, epoxy resin such as Bisphenol A diglycidyl ether (BADGE) and Glycidyl Methacrylate (Sigma-Aldrich-Co) will be blended with PES polymer to

improve hydrophilicity and adsorptive capacity of PES membrane. The structural formula for BADGE and GMA are shown below in Figure 2.5 and Figure 2.6 respectively.

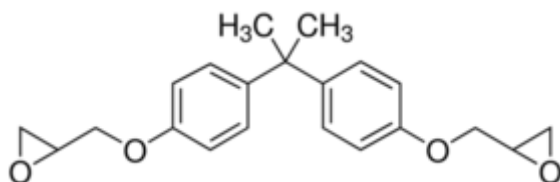


Figure 2. 5: Structural formula of Bisphenol A diglycidyl ether (Sigma-Aldrich-Co)

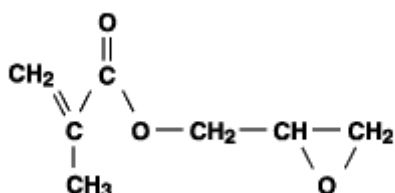


Figure 2. 6: Structural formula of Glycidyl Methacrylate (Dow-Chemical-Company, 2017)

BADGE have proven for its superior properties such as high porosity, relatively high hydrophilicity, and abrasion resistance. The resin is compatible to organic polymer, for example, a blending process with cellulose acetate polymer was demonstrated by Mahendran *et al.* (2002) and with PES polymer by Erniza *et al.* (2016). Both membrane modification with BADGE additive have shown a significant improvement in terms of the hydrophilicity, and solute rejection. For example, Mahendran *et al.* (2002) have study the performance of the membrane prepared from different blend composition of BADGE /CA for removal of protein of various molecular weight such as Bovine Serum Albumin (BSA), Egg Albumin (EA), Pepsin and Trypsin. It is then found that, the rejection of proteins was found to be

maximum for BSA (98%) and minimum for trypsin (58%), for the blend membranes. This have shown that the BADGE have improve the rejection of the protein.

Besides enhancing the membrane hydrophilicity, the embedded epoxy in polymeric membrane could have also improve the membrane zeta potential. The epoxy group have a net negative charge which contribute by the oxygen present in the functional group (Rimai *et al.*, 1995;Goharshadi *et al.*, 2015). As the higher negative charged on the surface, the rejection of the anions is enhanced. While, the chromium ions exits as in the form of oxide ions such as chromate ions (CrO_4^{2-}) when dissolve in water. This chromate ions is negative in charge. So, the rejection of chromium can then be enhanced by the Epoxified- Polyethersulfone (Brandhuber and Frey, 2015).

2.5. Working mechanism of Epoxified-PES membrane in ultrafiltration of removal of chromium (VI) ions

As discuss in section 2.1.3, ultrafiltration make used of pore size sieving method to retain/reject the molecule or ions that have a bigger size than the membrane pores. However, the Chromium ions is too small as it can easily pass through the pore of the ultrafiltration membrane as shown in Figure 2.7. Thus, the rejection of chromium is unsatisfied without any modification of the membrane.