

**COPPER REMOVAL USING ION EXCHANGER
FLAT SHEET MIXED MATRIX MEMBRANE:
EFFECT OF POLYETHERSULFONE
COMPOSITION ON MEMBRANE PROPERTIES**

KIEW FONG FONG

**BACHELOR OF CHEMICAL ENGINEERING
UNIVERSITI MALAYSIA PAHANG**

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COMPOSITION ON MEMBRANE PROPERTIES**

KIEW FONG FONG

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

**Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG**

JANUARY 2015

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SUPERVISOR'S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

Signature :
Name of main supervisor : DR. SYED MOHD SAUFI
Position : SENIOR LECTURER
Date :

STUDENT'S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

Signature :
Name : KIEW FONG FONG
ID Number : KA11142
Date : 23 JANUARY 2015

Dedication

To my beloved family for their love and encouragement

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I would like to thanks the following people and organisations;

- My supervisor Dr. Syed Mohd Saufi for the guidance through an effective well-arranged weekly meeting.
- Lab owner, Mr Khairul for the guidance on the usage of Atomic Absorption Spectroscopy in the testing of the copper ions
- Technician, Mr Zainal Gimam for the fixing of the pressure valve on the flat sheet casting machine

ABSTRACT

Ion exchanger has been widely used and applied in removal of heavy metal in wastewater treatment. In the current study, mixed matrix membrane (MMM) ion exchanger was developed by incorporating Amberlite IR120H into polyethersulfone (PES) dope polymer solution for copper removal. The effect of PES composition in dope polymer solution was varied from 23wt%, 25wt%, 28wt% and 30wt% at constant amount of 20g Amberlite IR120. The performance of membrane was evaluated using batch binding and cross flow filtration. In batch binding, the highest static binding capacity of the copper removal was achieved by membrane prepared from 30wt% PES with the binding efficiency at a value of 64% from 500ppm standard solution of copper (II) sulphate pentahydrate. In cross flow filtration, 30wt% PES membrane has the maximum binding efficiency at 95%. Regeneration study was studied with 30wt% PES membrane using 10% HCL elution solution in three consecutive running cycles. The membrane can be regenerated with 97% binding efficiency in each 3 cycles meaning all the membrane produced can be regenerated. As a conclusion, the higher the composition of PES membrane, the higher the adsorptive performance, thus 30wt% PES membrane was the optimum PES composition.

ABSTRAK

Penyaring ion telah digunakan secara meluas dan digunakan dalam penyaringan logam berat di dalam rawatan air sisa. Dalam kajian semasa, membran matriks campuran (MMM) penyaring ion telah dibangunkan dengan menggabungkan Amberlite IR120H ke dalam larutan polimer polyethersulfone (PES) dadah untuk penyaringan kuprum. Kesan komposisi PES dalam larutan polimer telah diubah dari 23wt%, 25wt%, 28wt% dan 30wt% pada jumlah berterusan 20g Amberlite IR120. Prestasi membran telah dinilai menggunakan mengikat kelompok dan penapisan aliran silang. Dalam kelompok mengikat, kapasiti tertinggi statik mengikat penyaringan kuprum yang telah dicapai oleh membran yang disediakan daripada 30wt% PES dengan kecekapan yang mengikat pada nilai 64% daripada penyelesaian standard 500ppm kuprum (II) sulfat pentahydrate. Dalam penapisan aliran silang, 30wt% membran PES mempunyai maksimum yang mengikat kecekapan pada 95%. Kajian semula telah dikaji dengan 30W% t membran PES menggunakan 10% HCL penyelesaian elution dalam tiga consecutives berjalan kitaran. Membran yang boleh dijana semula dengan 97% kecekapan mengikat dalam setiap 3 kitaran yang bermaksud semua membran yang dihasilkan boleh dijana semula. Sebagai kesimpulan, komposisi yang lebih tinggi membran PES, lebih tinggi prestasi serapan yang, oleh itu 30wt% membran PES adalah komposisi PES optimum.

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LIST OF ABBREVIATIONS

AAS	Atomic Adsorption Spectroscopy
MLC	Maximum Contaminant Level
MMM	Mixed Matrix Membrane
MF	Microfiltration
NMP	N-methylpyrrolidone
PES	Polyethersulfone
PVP	Polyvinylpyrrolidone
PWP	Water Permeation Flux
SEM	Scanning Electron Microscope
Wt	Weight Fraction

1 INTRODUCTION

1.1 Motivation and statement of problem

Water of high quality is essential to human life and water of acceptable quality is essential for agriculture, industrial, domestic and commercial uses. Heavy metal contamination wastewater has turn into one of the most serious environmental problems. Heavy metal included ferrous metals and non-ferrous metals. Ferrous metals containing steel, casting and wrought iron while non-ferrous metals containing copper, brass, nickle and zinc (Gorilla, 2013). Differ from organic pollutants, almost all of the heavy metal are not degradable and toxic to living organisms. Heavy metal contamination exists in many industries for instance metal plating, mining operations, tanneries, chloro-alkali, radiator manufacturing, smelting, alloy industries and storage batteries industries (Hala Ahmed Hegazi, 2013).

Copper is one of the vital trace element required by humans for its role in enzyme synthesis, tissues and bone development. However, it becomes toxic and carcinogenic when a large amount is ingested (Sibel Tunali Akara *et al.*, 2009). Copper can be applied in a variety of product. It can be used as prevalent in water and wastewater systems, as algae controller in reservoirs, as common material in household plumbing and root killer in underground pipes (Less, 2012). Copper can also be found in industrial effluent in acid mine drainage, galvanizing plants, natural ores and municipal wastewater treatment plant which can constitute to serious health hazards. Since copper is non-biodegradable, its toxicity found at the level of 100-500ppm per day in human being could travel through food chain via bioaccumulation. According to World Health Organization 2006, the limitation for copper concentration that can reach its maximum in drinking water is 1.5ppm (Muzenda *et al.*, 2011) and only allowable for not exceeding 1.3ppm in industrial effluents (Muhammad Bilal *et al.*, 2013). In human, copper can cause liver deposition, vomiting, headache, nausea, respiratory problems, abdominal pain, liver, kidney failure and gastrointestinal bleeding. Large amount of copper in fresh water resources and aquatic ecosystem will damage the osmo-regulatory mechanism of fresh water animals and cause mutagenesis in human. Therefore, heavy metal wastewater needed to be treated for safer drinking water and discharged into freshwater bodies for safer human consumption. Table 1.1 showed the maximum contaminant level (MLC) standards of

hazardous heavy metal with copper ranked the second highest MCL in wastewater (Mukesh Parmar and Lokendra Singh Thakur, 2013).

Table 1-1: The MCL standards for the most hazardous heavy metals in wastewater

Heavy metal	Toxicities	MCL (mg/L)
Arsenic	Skin manifestations, visceral cancers, vascular disease	0.05
Cadmium	Kidney damage, renal disorder, human carcinogen	0.01
Chromium	Headache, diarrhea, nausea, vomiting, carcinogenic	0.05
Copper	Liver damage, Wilson disease, insomnia	0.25
Nickel	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.2
Zinc	Depression, lethargy, neurological signs and increased thirst	0.8
Lead	Damage the fetal brain, diseases of the kidneys, circulatory system, and nervous system	0.006
Mercury	Rheumatoid arthritis, and diseases of the kidneys, circulatory system, and nervous system	0.00003

There is growing concern about the pollution of heavy metals and residents are demanding for cleaner environment. The current review deals with all the available treatment technologies for copper removal to ensure environmental safety.

There are several technologies used to treat the copper waste water. These include chemical precipitation, chemical coagulation, ion-exchange, adsorption and membrane filtration. Each and every types of technologies has its own advantages and limitations. In the current study, a combination of ion exchange and membrane filtration was developed in the removal of copper in the study of PES composition toward the adsorption capacity.

Ion exchange is one of the methods that have been widely used in heavy metal waste removal as it is easily regenerated and has high removal efficiency with low running costs (Considine, 2005). Membrane filtration is providing high filtration efficiency with microfiltration (Fu & Wang, 2011). Microfiltration (MF) membranes have become the main focus as promising separation tool in several industrial processes, covering fractionation and concentration steps in pure water production and in water and

wastewater treatments (M.Cheryan, 1998) . Although many methods have been proposed to improve the separation performance, the heart of microfiltration processes is the membrane itself. Important characteristics for achieving high performance microfiltration are high flux in combination with desired selectivity and low fouling. Because of their mechanical strength, thermal and chemical stability as well as excellence film forming properties, sulfone polymer which is polyethersulfone (PES), have been used very often for the fabrication of high performance commercial microfiltration membranes (H.Susanto, 2009). The concept of ion exchanger using Amberlite IR 120 resin will be explained on how the uptake of copper ions by the hollow fiber membrane application. A grinded Amberlite IR120 cation resin were blended with Polyethersulfone (PES) polymer solution for the making of adsorptive hollow fiber membrane. The effect of PES concentration on the performance of the membrane were being investigated.

Adsorption is the most commonly used technology in treating effluent as it has been known as one of an effective and economic method for heavy metal treatment. Due to its reversible process, the potential adsorption by using mixed matrix membrane is economical as the adsorption agents increase its performance while decreasing treatment cost (Fu & Wang, 2011). In the current technique used, cation resins are the adsorbent due to its unique properties on ion exchange capability. Other than that, different types of adsorbent will be compared in the literature review.

Even though the technologies have large adsorption capacity, packed membrane chromatography in the module has high pressure drop, limited flow rate and flow channeling but it has been proved that it is a successful tool in separating ion effluents. Ion exchange chromatography is mostly applied in protein separation. The principle involved electrostatic interaction between macromolecules and adsorbents. There are two types of ion exchange membranes which are anion and cation exchanger. Cation exchange membranes has not been widely used in effluent treatment as it is still a new technology (Borneman, 2006). Therefore, in the current research, the feasibility of mixed matrix membrane for copper ions removal was studies.

1.2 Objectives

The objective of this research is to study the effect of PES concentration on the performance adsorptive flat sheet mixed matrix membrane for copper removal.

1.3 Scope of this research

The scopes of this research are as follow:

- i) To produce adsorptive flat sheet MMM by incorporating cation resin, Amberlite IR120 into a polymer solution consists of PES, NMP and PVP.
- ii) To characterize the MMM in term of pore structure, water permeability and static adsorption properties for copper removal.
- iii) To compare the performance of the membrane using batch binding and cross flow filtration.
- iv) To investigate the regeneration of MMM.

1.4 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 provides a description of the removal mechanism, principle of ion exchanger, membrane classification, mixed matrix membrane, selection of polymer and resin contents, types of adsorbents used and cross-flow filtration in flat sheet membrane. A general description on the technologies used and the ion exchange concept in adsorption of copper ions are presented with briefly describing the adsorption capacity. This chapter also provides a brief discussion of the types of membranes available for heavy metal removal, mentioning their strengths and limitations. A summary of the previous experimental work on preparation of dope solution is also presented.

Chapter 3 gives a review the methodology of the overall experiments. In this chapter, the chemicals used in preparation of dope solution with various types of concentration of PES on performances of flat sheet membrane is being reviewed with two different mechanisms which are batch experiment and cross flow filtration. The calculation for water flux using formula, morphological structure of membrane using Scanning Electron Microscope (SEM) and static adsorption capacity and cross flow filtration using Atomic Absorption Spectroscopy (AAS) are presented and compared.

Chapter 4 is devoted in testing the performance on different types of composition membrane being produced. A brief review of the morphological on pore structure is also presented. The adsorption capacity of copper ions by different PES concentration is being studied and compared by determining from its adsorption efficiency from both batch experiment and cross flow filtration. A detailed description of the water permeability testing is also outlined.

2 LITERATURE REVIEW

2.1 Overview

This paper presents the description of the removal mechanisms with their advantages and limitations, membrane classification, mixed matrix membrane, selection of polymer contents, types of adsorbents, selection of cation resins, principle of ion exchanger and cross flow filtration. A general description on the technologies used and the ion exchange concept in adsorption of copper ions are presented. This paper will present the reasons of using combination of ion exchange and membrane adsorption filtration membrane, types of membrane used, chemical usages and adsorbents used in the production of flat sheet membrane.

2.2 Removal Mechanisms

There are different types of wastewater treatment technologies which are chemical precipitation, coagulation, ion exchange, adsorption and membrane filtration. Table 2-1 showed a comparison of technologies used for heavy metal removal from wastewater.

Table 2-1: Comparison of technologies used for heavy metal removal from wastewater (Farooq *et al.*, 2010).

Technologies	Advantages	Limitations
Chemical Precipitation	<ul style="list-style-type: none">• Simple• Inexpensive• Most of the metals can be removed	<ul style="list-style-type: none">• Large amount of sludge produced• Disposal problem
Chemical Coagulation	<ul style="list-style-type: none">• Sludge settling• Dewatering	<ul style="list-style-type: none">• High cost• Large consumption of chemicals
Ion-exchange	<ul style="list-style-type: none">• High regeneration of materials• Metal selective	<ul style="list-style-type: none">• High cost• Less number of metal ions recovered

Adsorption using activated carbon	<ul style="list-style-type: none"> • Most of metals can be removed • High efficiency(99%) 	<ul style="list-style-type: none"> • Cost of activated carbon • No regeneration • Performance depends upon adsorbent
Membrane Filtration	<ul style="list-style-type: none"> • Less solid waste produced • Less chemical consumption • High efficiency (>95% for single metal) 	<ul style="list-style-type: none"> • High initial and running cost • Low flow rates • Percentage removal decreases with the presence of other metals.

Most of the heavy metal wastewater treatment industry is using ion exchange as the solution. Ion exchange is one of the methods that have been widely used in heavy metal waste removal as it is easily regenerated and has high removal efficiency with low running costs (Considine, 2005). Other than that, ion exchanger is one of the promising approach technique in effectively removing and recovery of targeted metal using ion exchange resins to exchange cation with wastewater metals (Bilal et al., 2013). Since ion exchange is a reversible chemical reaction, it will be used to study the adsorption and regeneration of ions using membrane (Mukesh Parmar and Lokendra Singh Thakur, 2013).

Not only that, the advantage in using ion exchange is contaminated ions can be regenerated. However, there are some limitations in ion exchange. (Practices, Treatment, Treatment, & Options, 1996). During regeneration, water that are not de-ionised containing calcium ions, when acid reacts with calcium ions will form calcium sulphate precipitates that can block the pipe. Therefore, cation resin must be washed with de-ionised water before usage. Not only that, iron fouling will occur since copper ions are using in the research which clogs resin beads and prevent ion exchange (Considine, 2005). Not to worry, ion exchange technology has high treatment and removal capacity and fast kinetic (Kang *et al.*, 2004) . Synthetic resin will be used as it has better adsorptive capacity in removal of heavy metal (Alyüz *et al.*, 2009).

Membrane filtration can be used for the treatment inorganic effluent, suspended solid, organic compounds and also inorganic contaminant heavy metals. Membrane filtration is defined as using membrane polymer with different properties using adsorption capability. Membrane filtration is a physical barrier that restricts the passage of materials. Membrane has four separation processes which are ultrafiltration, reverse osmosis, nanofiltration and microfiltration. In our study, microfiltration flat sheet membrane is selected as our ions are very tiny. Microfiltration (MF) is the technique in removing components in the range of 0.025 μm to 10.0 μm by using microporous membrane filter (Spring & Hashsham, 2006). Or in short, microfiltration is a conventional filtration that remove particles smaller than a micron such as colloids and bacteria that came with the definition on microfiltration refers to filtration process that use porous membrane to separate suspended particles with diameter between 0.1 to 10 μm (R.W. Baker, 2004). Membrane can be manufactured in flat sheet, hollow fiber, spiral and tubular in shape. Flat sheet membrane itself can withstand back pressure with high membrane packing density, providing high flexibility and high efficiency in filtering large volume of liquid while providing minimum space and energy (Chemical & Group, 2014)

Thus, membrane filtration is chosen with combining ion exchange technology in the research because of its high separation efficiency of more than 95% for a single ion metal removal with high regeneration of materials which can save cost (Farooq *et al.*, 2010), easy operation and space saving (Fu & Wang, 2011).

2.2-1 Principles of Ion Exchanger

Ion exchange is a reversible exchange of ions with ions in solution electrostatically bound to an insoluble support matrix. There are two types of ion exchangers named anion exchanger and cation exchanger as shown in Figure 2-1. Separation on ion exchange chromatography columns is based on charged density.

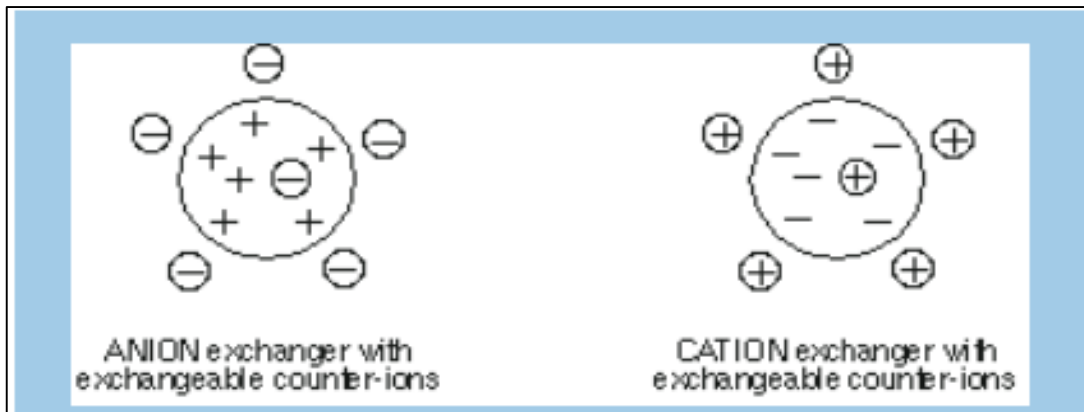


Figure 2-1: Types of ion exchanger.

The matrix is based on organic compounds and synthetic resins. There are five stages in ion exchange chromatography. There are starting conditions, adsorption of samples substances, start of desorption, end of desorption and regeneration.

In first stage, the ion exchanger allows the binding of desired ions molecules on the active site of cation resin. The negatively charged cation resin materials will be loaded with hydrogen ion in solution.

In second stage, sample application and adsorption where solute molecules carrying the charge displace counter-ions and bind reversibly to the resin. Ions, impurities and hydrogen ions that are not bounded to the resin binding site will be washed out from exchanger bed using starting buffer.

In third stage, ions are removed from column by changing to elution conditions unfavourable for ionic bonding of solute molecules. Desorption is achieved by the introduction of salt concentration gradient and solute molecules are released from column in order of their strengths of binding where weak bound substances are being eluted first. In fourth and last stage, elution will make the eluent will exchange and release the valuable cation. At the same time, the resin will be regenerated. The ions concentration before and after the process will be tested (Media, 2014) The overall stages are shown in Figure 2-2.

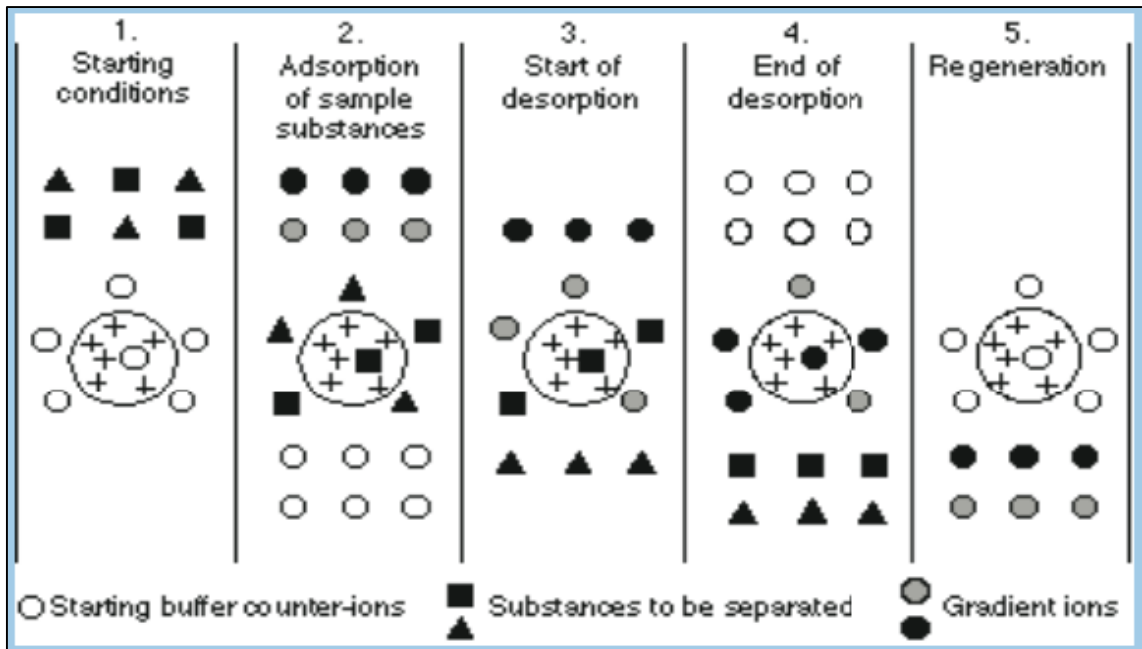


Figure 2-2: Principle of Ion Exchange Chromatography (salt gradient elution) (Media, 2014).

2.3 Membrane Classification

A membrane is a selective barrier between two phases. Depending on the application, different membrane morphologies were used and several types of membrane separation mechanisms exist. In membrane applications where the solution diffusion mechanism plays the major role, the membrane material is chosen based on the selective sorption and diffusion properties, membrane morphology will be not the main factor to affect the selectivity but it is still important as regarding to total flux (M.H.V. Mulder, 1996). Figure 2-3 showed the schematic representation of various morphologies.

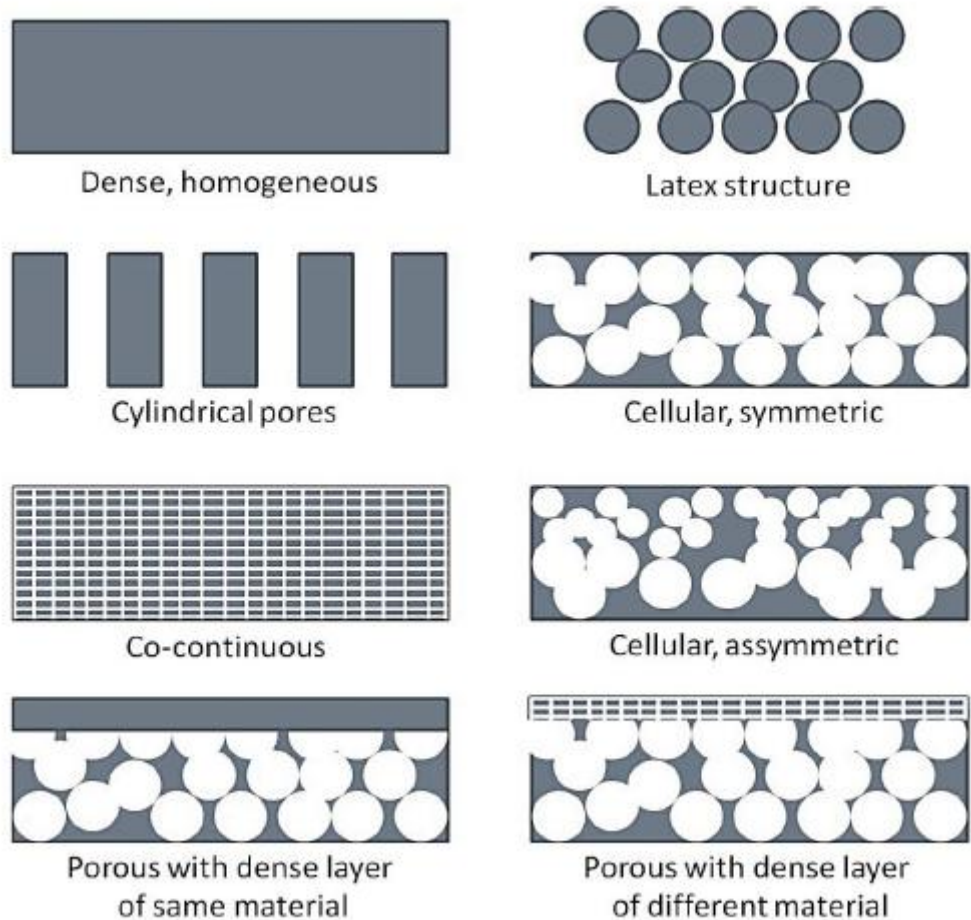


Figure 2-3: Schematic representation of various morphologies (M.H.V. Mulder, 1996).

In all the membrane processes, driving force is essential to deliver the energy to separate the feed molecules or particles; commonly applied driving force differences in pressure, concentration, partial pressure, temperature or electrical potential. The most widely used pressure driven processes are generally classified as microfiltration (MF), ultrafiltration (UF) and hyperfiltration, which is normally subdivided in reverse osmosis (RO) and nanofiltration (NF). Nevertheless, the difference between the processes is not always so sharp, as presents in Table 2-2, summarizing the main characteristics of various membrane processes, in which, typical permeability is for a typical permeate stream, i.e., with rejected species on the retentate side of the membrane.

Table 2-2: Pressure driven membrane processes(M.H.V. Mulder, 1996).

Membrane Process	Typical Pressure (bar)	Typical permeability (l/(m ² .h.bar)	Morphology of selective layer
Microfiltration	0.1-2	>50	Porous
Ultrafiltration	1-5	10-50	Porous
Nanofiltration	5-20	1.4-12	Porous/ Dense
Reverse Osmosis	10-100	0.05-1.4	Dense

2.4 Mixed Matrix Membrane (MMM)

Mixed matrix membrane is the latest membrane morphology comprising of organic polymer and inorganic particle phase as shown in Figure 2-4. Inorganic particles could be zeolite, carbon molecular sieve or nano-size particles. Mixed matrix membranes are known to have the ability of high selectivity, permeability or both relative to the existing polymeric membranes, resulting from the addition of inorganic particles with their inherent superior separation characteristics (Chung *et al.*, 2007).

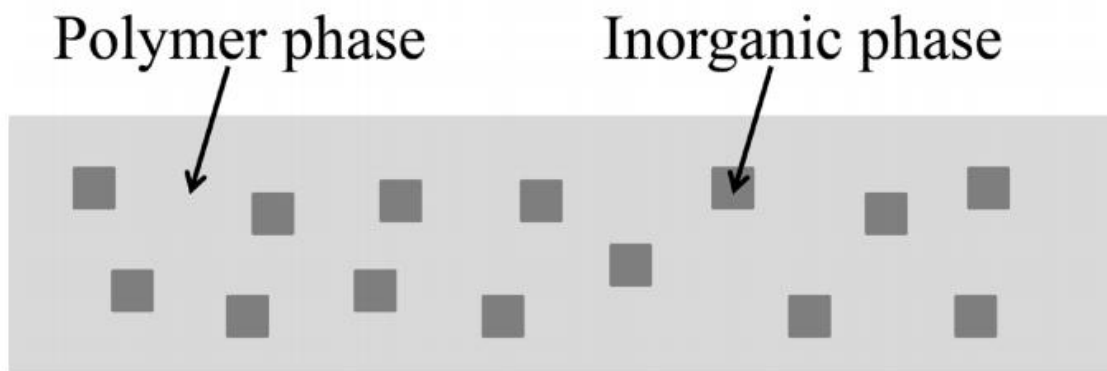


Figure 2-4: Mixed Matrix Membrane (Chung *et al.*, 2007).

In this study, PES/NMP/PVP is the polymer phase while cation resin is the inorganic phase. In olden time, mixed matrix membrane has been made in dense polymeric films in gas transport facilitation through the membrane. A dope polymer solution is mixed homogenized with cation resin before casting to produce flat sheet mixed matrix membrane (Joao Miguel de Sousa Andre, 2009). It is called mixed matrix membrane because of the mixing of dope polymer solution and cation resin. Mixed Matrix Membrane is chosen in the study because of its high separation of heavy metal with low

costs, and functionality will not be lost when mixed matrix membrane are incorporative with heavy metal (Joao Miguel de Sousa Andre, 2009).

2.4-1 Selection of Polyethersulfone (PES)/ N-methylpyrrolidone (NMP)/Polyvinylpyrrolidone (PVP) As Polymer Membrane Contents

In the preparation of membrane polymer content, Polyethersulfone (PES), N-methylpyrrolidone (NMP) and Polyvinylpyrrolidone (PVP) were being selected to be used. For the past of forty years, Polyethersulfone (PES) and Polysulfone (PSf) has been widely used in Microfiltration (MF) and Ultrafiltration (UF) separation technology. PES is more hydrophilic compared to PSf which is relatively hydrophobic (Lau *et al.*, 1991). Therefore, PES is selected as one of the element in membrane polymer. PES is the most suitable membrane materials to be used in the study as it has good film-forming properties and high thermal, chemical and biological resistance (Hofman & Pietrzak, 2013). Besides, it can withstand heat resistance regardless of short term or long term in dependence of half-life period of tensile strength, dimensional stability, creep resistance at high temperature, impact resistance to notches and chemical resistance (Pes, 2014.). However, PES has hydrophobic characteristic. But it can be overcome by adding additive such as Polyvinylpyrrolidone(PVP) to reduce the properties (Zhao, Xue, Ran, & Sun, 2013)

There are many different types of additives used in polymer membrane making. It includes glycerol, BuOH, PEG and PVP. Journal proved that glycerol was not a good choice to be used as additive and PEG has resulted sponge-like cross section (Ping Lan, 2012). In order to make a high performance of PES flat sheet membrane, it is recommended to use polyvinylpyrrolidone (PVP) as additive with low molecular weight of 10,000 with suitable content in between 2-5 wt%. The use of low molecular weight of PVP tends to produce high permeation flux and good solute rejection (Wang, Li, & Teo, 1999).

N-methylpyrrolidone (NMP) was used as membrane forming solvent (Lau *et al.*, 1991). NMP will be well miscible with non-solvent to be used in the phase inversion of the PES solution via the solvent-non solvent exchange process. Non-solvent is water was used as coagulant in the study. Due to its strong interaction with polymer and miscibility with water, NMP were chosen as solvent used (Choi *et al.*, 2006).

2.4-2 Types of Adsorbents

In the treatment of wastewater, there are different types of adsorbents used in the batch adsorption experiment in the study. Table 2-3 showed the comparison between different adsorbents used in the wastewater treatment.

Table 2-3: Comparison of different adsorbents used in the treatment of wastewaters (Lena Johansson Westholm, 2014)

Adsorbents	Cost	Availability	Advantages	Disadvantages
Chitin	Low cost 0.8–31 Euros/kg (1–40 USD/kg)	Abundant, especially China and India	<ul style="list-style-type: none"> –Efficient removal of metals –Neutralising agent –Sulfate removal –Efficient removal of metals 	<ul style="list-style-type: none"> –Variable composition –Swelling
Chitosan	12.2–230 Euros/kg (16–300 USD/kg)	Quite abundant, especially China, India, and Thailand	<ul style="list-style-type: none"> –Neutralising agent –Sulfate removal –Modification –Partial chemical regeneration 	<ul style="list-style-type: none"> –Variable composition –Swelling –Soluble in dilute acids
Commercial ion-exchange resins	2–100 Euros/kg	Abundant	<ul style="list-style-type: none"> –Large variety of specific resins available –Chemical regeneration 	<ul style="list-style-type: none"> –Different resins for anions and cations –High price in some cases –Swelling of polymeric resins –Loss of functionality during regeneration

Dairy manure compost	Low cost	Abundant	<ul style="list-style-type: none"> –Efficient removal of metals –Regeneration using acid 	<ul style="list-style-type: none"> –Variable composition –Leaching of elements
Lignite	Low cost	Abundant	<ul style="list-style-type: none"> –Efficient removal of metals –Neutralising agent –Regeneration using acid 	<ul style="list-style-type: none"> –Variable composition –Leaching of elements
Rice husk	Low cost	Abundant	<ul style="list-style-type: none"> –Efficient removal of metals –Regeneration using acid 	<ul style="list-style-type: none"> –Variable composition
Yeasts	Low cost	Abundant	<ul style="list-style-type: none"> –Efficient removal of metals –Regeneration –Easy to modify 	<ul style="list-style-type: none"> –Better in neutral conditions –Type of the wastewater has a significant effect

Commercial activated carbon	0.08–8 Euros/kg (0.1–10 USD/kg)	Abundant	<ul style="list-style-type: none"> –Known composition –Efficient removal of metals and organics 	<ul style="list-style-type: none"> –Thermal regeneration –Poor adsorption of anionic species
Biocarbon	Low cost, depends on the source and treatment temperature	Abundant	<ul style="list-style-type: none"> –Efficient removal of metals and organics 	<ul style="list-style-type: none"> –Thermal regeneration –Poor adsorption of anionic species
Fly ash	Low cost	Abundant	<ul style="list-style-type: none"> –Efficient removal of metals –Neutralising agent –Sulfate removal 	<ul style="list-style-type: none"> –Variable composition –Leaching of elements
Furnace slag	Low cost	Abundant	<ul style="list-style-type: none"> –Efficient removal of metals –Neutralising agent 	<ul style="list-style-type: none"> –Variable composition –Leaching of elements
Limestone	Low cost	Abundant	<ul style="list-style-type: none"> –Efficient removal of metals –Neutralising agent 	<ul style="list-style-type: none"> –Formation of sludge as secondary waste

Natural zeolite	Low cost 0.04–1.9 Euros/kg (0.05–2.5 USD/kg)	Abundant, especially China, Indonesia, and Turkey	–Efficient removal of metals and anions –Modification	–Variable composition
Olivine	Low-cost	Abundant, especially China, India, and Turkey	–Efficient removal of metals	–Variable composition –Leaching of elements
Synthetic zeolite	Low cost 0.2–2.3 euro/kg (0.3–3 USD/kg)	Abundant, especially China, Indonesia, and Turkey	–Efficient removal of metals and anions –Modification	–Variable composition

Among the different types of adsorbent used, commercial cation exchange resin will be used the adsorbent in the study in ion exchanger-adsorption mechanism due to its efficient adsorption and ability to regeneration using acid.

2.4-3 Selection Amberlite IR120H Cation Resin

Ion exchange resin is a type of polymer that is functioning in the exchanging of particular cation or anion within the polymer with ions in a solution that is passed through them. Ion exchange resins are applied in the purification of water including separating of elements. The use of resin is to remove unwanted ions for instance copper ions in the study from a solution that passed through it or accumulation of mineral which can be recovered from resin. Since copper ions are positively charged, cation resin is used in the research. Cation resin in the hydrogen form is used in the determination of total concentration of ions in solution (Considine, 2005). Ion exchange resins are used in the exchanged of non-desirable cations and anions with hydrogen and hydroxyl to form water (Anions, 2014). Table 2-4 showed the list of common ions found in wastewater.

Table 2-4: List of Common Ions in Wastewater (Anions, 2014).

Cations	Anions
Removed by cation resins	Removed by Anion Resins
Calcium (Ca ⁺)	Chloride (Cl ⁻)
Magnesium (Mg ²⁺)	Sulphate (SO ₄ ⁻)
Iron (Fe ²⁺)	Nitrates (NO ₃ ⁻)
Manganese (Mn ⁺)	Carbonates (CO ₃ ⁻)
Sodium (Na ⁺)	Silica (SiO ₂ ⁻)
Hydrogen (H ⁺)	Hydroxyl (OH ⁻)

Adsorption of heavy metal using ion exchange resin has proven efficient separation of metal from aqueous solutions. There are selection of commercial ion exchange resins availabilities shown in Table 2-5

Table 2-5: Characteristics of Commercial Cation Exchange Resin (E.Dabrowski *et al.*, 2004).

Resin	Ionic Form	Matrix	Density, (g/mL)	pH	Particle Size	Regenerant
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Amberlite IRC 86	H+	Gel Polyacrylic copolymer	1.17- 1.195	0-14	0.58- 0.78mm	2-5% HCL
Amberlite IR 120	H+	Styrene divinylbenzene copolymer	>1(vs air)	0-14	16-50 mesh	5-15% HCL
Amberlite IRN 150	H+	Styrene divinylbenzene copolymer	1.0-1.3	5-8	0.6- 0.7mm	NA
Dowex M-31	H+	Styrene divinylbenzene (macroporous)	0.76	0-14	16-40 mesh	4-8% HCL, 8- 12% NaCl
Dowex MAC-3	H+	Polyacrylic (macroporous)	1.18	5-14	300- 1200µm (50-16 mesh)	1-5% HCL
Dowex Marathon MSC	H+, Na+	Styrene divinylbenzene (macroporous)	1.20, 1.28	0-14	520- 50µm, 500- 50µm	4-8% HCL, 8- 12% NaCl
Lewatit Monoplus SP112	Na+	Cross linked polystyrene	1.24	0-14	0.65 mm	HCl, H2SO4, NaCl
Lewatit Monoplus TP214	Na+	Cross linked polystyrene	1.1	0-10	400- 1250µm	NA

Selectivity is a guideline to the new types of ion exchangers with specific affinity to definite metal ions or groups of metals. Higher selectivity can give a great exchangeability as well as reversibility of the sorption-elution process. It should be emphasized that in most cases ion exchange enables replacing the undesirable ion by another one which is neutral within environment. Amberlite IR 120 Resin will be used in the research as it has good physical, chemical and thermal stability with the characteristics

summarised in Table 2-6. It has good ion exchange kinetics making it has high exchange capacity (Company, 1978). However, addition of more resin will decrease the tensile strength of flat sheet membrane formation. Thus, the resin has to be grinded to as tiny as possible in the range of 38-45 μm .

Table 2-6: Characteristics of Amberlite IR120 (Alguacil, Alonso, & Lozano, 2004)

Polymer matrix	Styrene-DVB
Functional group	Sulfonic acid
Ionic form	H ⁺
Exchange Capacity	4.4meq/g (dry)
Operation temperature	120°C (maximum)
Effective size	0.45-0.60mm
Swelling	5-7%

2.5 Cross Flow Filtration in Flat Sheet Membrane

Flat sheet membrane initially in applying on dead end microfiltration only. Microfiltration has applications in dead end filtration for wastewater treatment where it has been captured by crossflow. Microfiltration system was operating at low pressure and are configured based upon the application (Chemical & Group, 2014). Comparatively, in industrial process for example heavy metal removal in commercial industry, flat sheet membrane was used more relevant in cross flow filtration than batch adsorption (Zhao *et al.*, 2013). In cross flow-filtration, fouling can be happened. Fouling is defined as the accumulation of unwanted materials for instance living organism or non-living organic or inorganic substances on membrane that resist the passage of heavy metals from adsorption of flat sheet membrane thus decreasing separation efficiency. Meanwhile, in cross flow microfiltration it does not create much fouling as it has a unique filtration surface which is continuously sweeping by flowing water non-stop where it provides almost steady state operation while decreasing the build-up of unwanted particles by the shear-force of the flowing liquid inside the module. Unlike dead-end filtration, solids layer will build up in flat sheet membrane which decreased in filtration efficiency (Orporation, 2002) while causing the permeate water flux to decrease and requires the stopping in filtration process for cleaning and replacing purposes of new flat sheet membrane (Spring & Hashsham, 2006). This phenomena is known as fouling. Fouling will result in less clean water at the

effluent. Figure 2-5 and Figure 2-6 showed the schematic diagram of dead end and cross flow microfiltration.

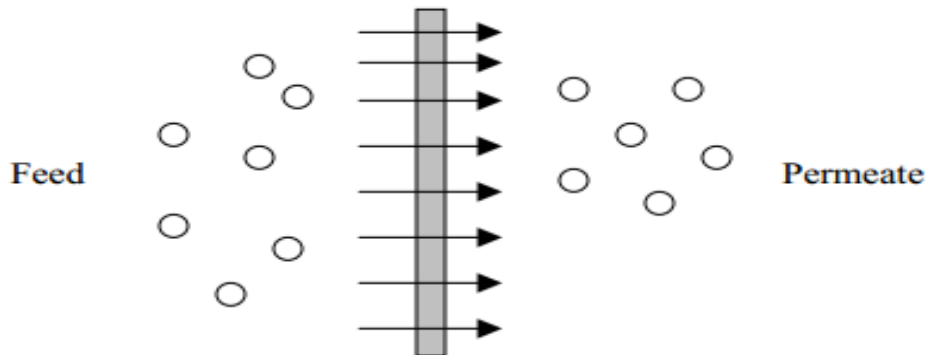


Figure 2-5: Dead End Microfiltration (Spring & Hashsham, 2006).

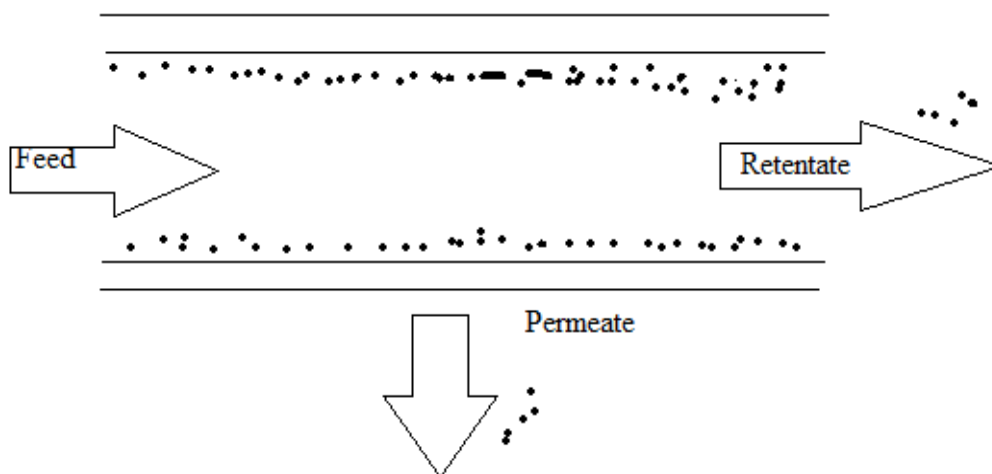


Figure 2-6: Cross Flow Microfiltration (Orporation, 2002).

In cross flow model, the permeate flow through the membrane diffuse through the membrane surface, where they will form a thinner layer when in contact with water causing permeability of membrane. At the lower pressure side, the permeate stream is assumed to be negligible force causing vacuum so that the flow is perpendicular to the membrane (Geankoplis, 2003).

2.6 Summary

This paper presents the overall literature review on the process of the technologies used in application of flat sheet membrane in heavy metal removal while explaining the theories of membrane filtration and ion exchange in copper removal. Chemicals to be

used for formation of flat sheet have been compared and selection of Amberlite IR120H as cation resin in uptake of copper ions, polyethersulfone(PES), N-methylpyrrolidone(NMP) and Polyvinylpyrrolidone(PVP) in the making of membrane polymer solution. Furthermore, the cross flow filtration module has been designed to allow the filtration using cross flow theory.

3 MATERIALS AND METHODS

3.1 Overview

This paper presents a production of flat sheet mixed matrix membrane for the treatment of copper ions. Various concentration of flat sheet mixed matrix membrane were produced from PES/NMP/PVP and Amberlite IR 120H cation resin using dry-wet spinning method. The 4 samples of different concentration of mixed matrix membrane were undergo characterization. This involved scanning of pores size and morphological of mixed matrix membrane, water permeability, static adsorption and lastly regeneration. The main testing equipment used including Atomic Absorption Spectroscopy (AAS). From the results that obtained, we determined which concentration of PES has the maximum adsorption of copper ions from batch experiment and cross flow filtration.

3.2 Introduction

This paper presents the overall methodology of the formation of mixed matrix membrane with various concentration to determine which concentration in effectiveness in ion exchange uptake of copper ions. All the chemicals and methods used were briefly explained on how to conduct the experiment. Furthermore, pictures have been presented to ease the understanding of methodology.

3.3 Chemicals

Radel Solvay Advanced Polymer polyethersulfone (PES) was used as a base membrane polymer. Amberlite IR120H, polyvinylpyrrolidone (PVP), Hydrochloric acid was obtained from Sigma-Aldrich. N-methylpyrrolidone, NMP and copper (II) sulphate pentahydrate from Mercks Malaysia and hydrochloric acid from AR&MJ. The dope polymer solution is prepared from PES/NMP/PVP with various weight concentration and fixed amount of Amberlite IR120H cation resin. The Amberlite IR120H cation resin from *Fluka* used to uptake of copper ions. Copper ion solution used in binding experiment was prepared by diluting copper (II) sulphate pentahydrate. Hydrochloric acid (37%) was used for elution in batch binding and regeneration of flat sheet mixed matrix membrane in cross flow filtration.

3.4 Production of Flat Sheet Membrane

In the production of flat sheet membrane, the procedures including preparation of Amberlite IR120H, mixed matrix membrane dope solution preparation and membrane casting process.

3.4-1 Preparation of Amberlite IR120H

Amberlite IR120H was washed with de-ionised water in order to remove the impurities and dried at 80°C for 24 hours in drying sample oven as shown in Figure 3-1(Dizge *et al.*, 2009). Dried resin was ground using *Retsch* branded ultracentrifuges grinder and sieved the resin in the range of 38-45 μm using stainless steel siever as shown in Figure 3-2.



Figure 3-1: Drying of Amberlite IR120 resin.



Figure 3-2: Grinded and sieved resin.

3.4-2 Mixed Matrix Membrane Dope Solution Preparation

PES and NMP were used as membrane forming material and solvent respectively while PVP was used as additive. Since the research is studied on the effect concentration of PES toward the adsorption capacity, the composition of PES were varied in the range of 23wt% to 30wt% in Table 3-1(Zhen-Liang Xu, 2004). The use of molecular weight of PVP at 10,000wt with suitable content at 2-5wt% tends to produce high permeation flux and good solute rejection (Wang *et al.*, 1999). Therefore, PVP used was fixed at 5wt% for every dope polymer concentration. Each solution was made in 500ml of SCHOTT reagent glass bottle. The formula (3.4-1) used on how to obtain the quantity of dope polymer content using 500mL of dope polymer solution is equivalent to 500g of PES.

$$PES \text{ content} = 500g \text{ PES} \times 23wt\% = 115g \text{ PES}$$

$$\text{Since PVP is fixed at 5wt\%, PVP content} = 500g \text{ PES} \times 5wt\% = 25g \text{ PVP}$$

$$\text{Therefore, NMP content} = 500g \text{ PES} \times 72wt\% = 360mL \text{ of NMP} \quad (3.4-1)$$

The formula were repeated for the rest of dope polymer concentration from 25wt% to 30wt%.

Table 3-1: Various concentration of PES concentration in polymer membrane solution

Polymer Concentration (by weight %)	Function	Dope A	Dope B	Dope C	Dope D
	Membrane forming material				
PES		23	25	28	30
NMP	Solvent	72	70	67	65
PVP	Additive	5	5	5	5
Amberlite IR120(g)	Cation resin	20	20	20	20

*Amberlite IR120H loading was calculated from (3.4-2)

The PES and PVP were dissolved in NMP at 60 °C using *IKA C-MAG HS 7* branded motorized stirrer with high speed (Shung, 1997) was shown in Figure 3-3. The solution was continuously stirred for about 5-6 hours until homogenous solution was formed. The grounded and sieved resin was then mixed with polymer solution to form brick colour solution in order to be prepared for spinning purposes in Figure 3-4. The amount of resin used was kept constant for 20g per 500mL dope polymer solution with the formula (3.4-2).

Assuming cation resin loading at 20% with M_{pes} used at 80g:

$$R = \frac{M_{cat}}{M_{cat} + M_{pes}} \times 100\% \quad (3.4-2)$$

Where,

R is resin loading in 20 %

M_{cat} is the mass of cation resin in g

M_{pes} is the mass of PES in g



Figure 3-3: PES/NMP/PVP solution

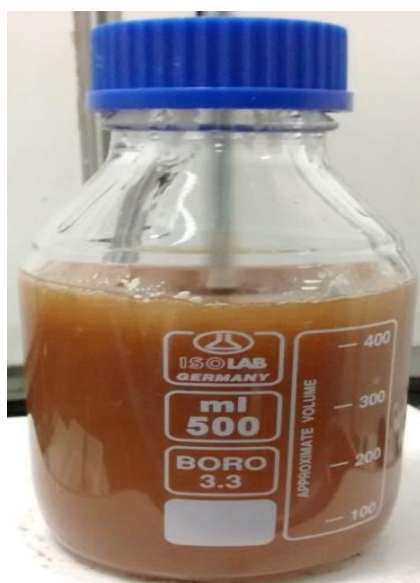


Figure 3-4: Mixed Matrix Membrane after mixing of 20g of Amberlite IR120 with PES/NMP/PVP.

3.4-3 Membrane Casting

After the mixed matrix membrane solution was being prepared, the solution is ready for casting. Since Amberlite IR120 is non-homogenous compound, the mixed matrix membrane solution must be stirred before the spinning process to avoid wastage as the the resin will sink at the bottom of the bottle. Figure 3-5 showed the picture of casting

membrane machine. The dope solution prepared is fed to the casting plate to let it flows to the bottom of the casting itself. The casting machine will be moving forward to evenly cast the membrane on top of the glass plates. The casted membrane will be stored for 24 hours in water filled basin in order to remove residual NMP thoroughly (Shung, 1997). The 4 different composition of flat sheet membranes are then treated for further characterization and application.



Figure 3-5: Casting Process

Table 3.4-2 showed the summarised casting parameter for flat sheet membrane.

Table 3-2: Summary parameters for casting membrane

Parameters	Conditions
Membrane casting thickness (mm)	0.02mm
Water bath volume in detaching of membrane (mL)	4500
Time in completing one move of casting (s)	24.76
Length of the flat sheet membrane (cm)	30
Casting speed (cm/s)	1.21 cm/s
Pressure (bar)	4.5

Figure 3-6 and Figure 3-7 showed the detaching process of membrane from casted glass and immersing of membrane for a night to remove residual NMP.

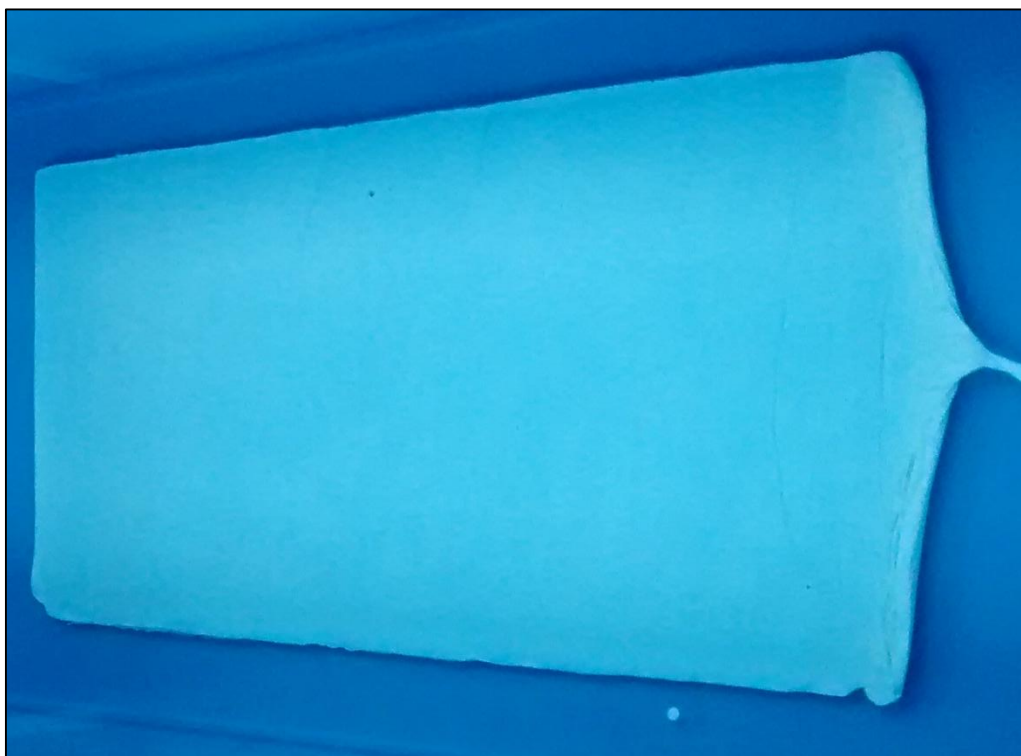


Figure 3-6: Detaching Process after casting for 1.5 minutes

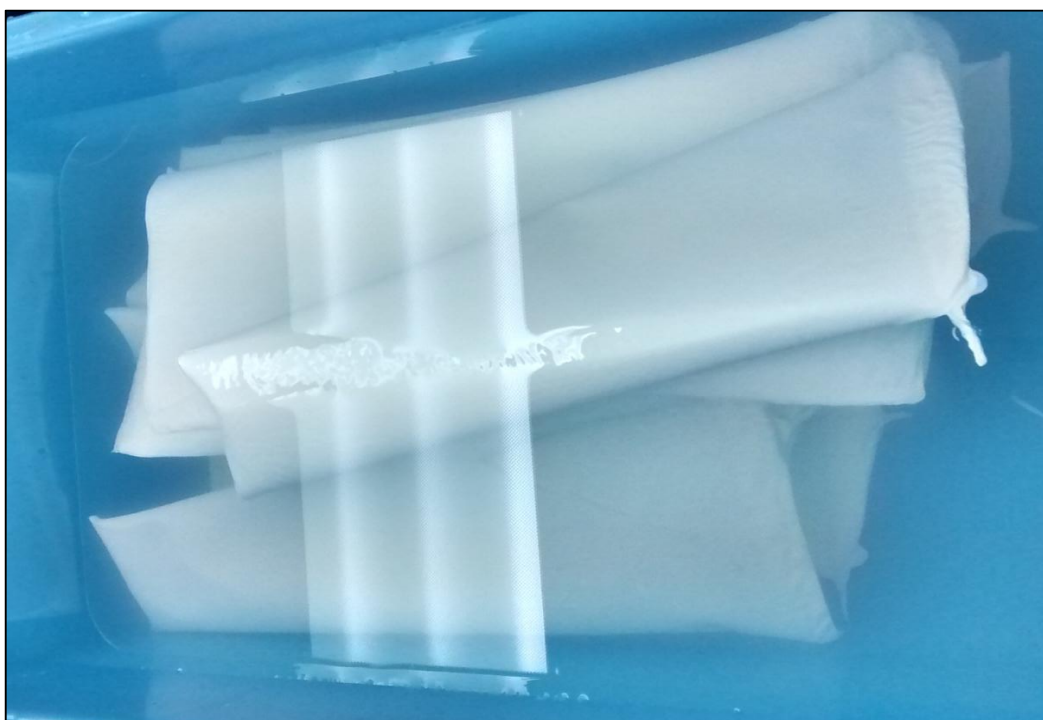


Figure 3-7: Membrane after detached immersed in water-bath.

3.5 Membrane Structure Characterisation/Morphology of Flat Sheet

All the 4 different concentration of PES solution flat sheet mixed matrix membrane were being scanned using scanning electron microscope (SEM) in order to obtain the scanning electron microscopy (SEM) images (Hofman & Pietrzak, 2013). Scanning electron microscopy (SEM) was used to investigate membrane morphology and molecular orientation in the flat sheet membrane active layer. The 4 samples of flat sheet membranes were dried and immersed for about 20 seconds in liquid nitrogen and then break to show the cross sectional structure (Ahmed, 2010). A commonly clean break was being snapped under the liquid nitrogen. Before viewed on a SEM, the sample was sputtered with gold by using an ion-sputtering (Biorad Polaron Division) with potential of 10kV under magnifications in the range of 500x to 5000x (Suhana Jalil & A.F. Ismail, 2014).

3.6 Batch Static Binding Experiment

3.6-1 pH of Copper (II) Sulphate Pentahydrate

The pH of the copper(II) sulphate pentahydrate is measured using METTLER TOLEDO pH meter. The pH meter is calibrated using the buffer solution at pH 4.01, pH 7.00 and pH 9.00 as shown from Figure 3-8 to Figure 3-11 before tested using prepared copper standard solution. 3 point of buffer calibration point was recommended and always start the first adjustment with pH 7.00 buffer solution (Steward Fuller, 2014). The probe must immersed inside the KCL solution to hydrate the pH probe. The pH values are taken three times in obtaining the average values. The results for copper standard solution was read.



Figure 3-8: Buffer solution for calibration.



Figure 3-9: Buffer solution for pH 4.01.

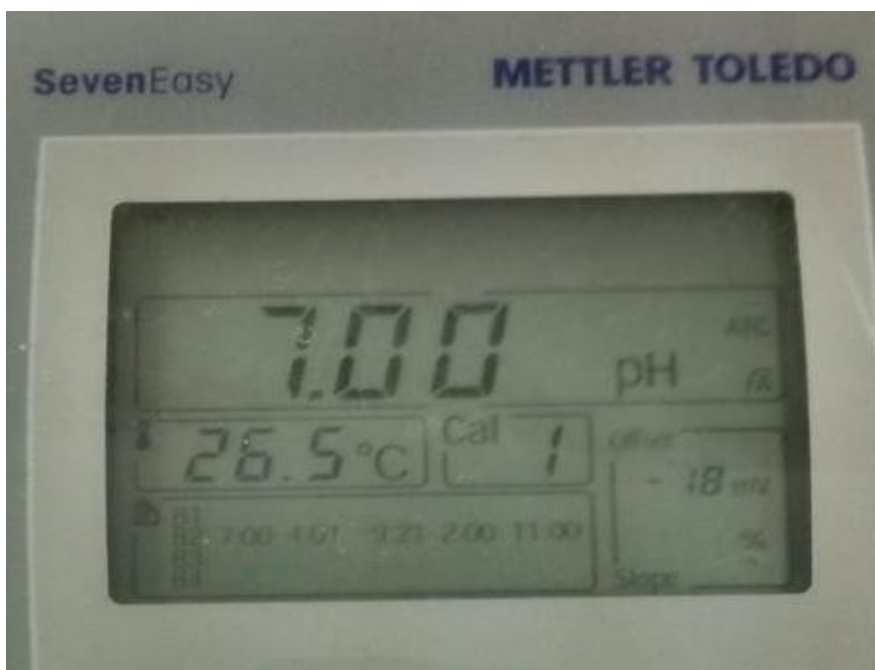


Figure 3-10: Buffer solution for pH 7.00.



Figure 3-11: Buffer solution for pH 9.00.

3.6-2 Binding Capacity

All the 4 different types of flat sheet membranes will be cut into 2cm X 1cm sample sizes for copper binding purposes. Triplicate samples for each membrane were experimental in order to obtain the average reading. The binding process will take up 24 hours for maximum batch binding. The 500ppm of copper(II) sulphate pentahydrate was used to prepare the standard solution in 15mL of centrifugal tubes. Each 15mL of copper solution will be pipetted while 2cm X 1cm sized of 23%, 25%, 28% and 30% PES membrane will

be deposited in for binding experiment. The remaining copper solution in the centrifugal tubes will be checked using Atomic Absorption Spectrometer Analyst 400 Perkin Elmer (AAS). For minimising the error in binding capacity, deionised water and ultrapure water are encouraged to use only. The blank water sources used has to be checked for copper composition as well to prevent the error occurred if the piping system or membrane filter for the water sources are contaminated. All R-square values of calibration data fitted by linear regression method are greater than 0.99 for copper when performing blank reagent. The errors of measurement for experimental samples are very small and acceptable. The calibration blank curve was attached at Appendix after Table A-4. Dilution factor of 150 will be used in diluting the copper sample as the AAS machine has the maximum concentration in detecting ions at 4ppm. The formula (3.6-1) were used in calculating the mass of copper remaining in the solution:

$$\begin{aligned} \text{Copper Feed (mg)} &= \text{volume of binding solution} \times 500\text{ppm} = \frac{15\text{L}}{1000} \times \frac{500\text{mg}}{\text{L}} \\ &= 7.5\text{mg} \end{aligned}$$

$$\text{Copper remained in the solution (mg)} = Cf(\text{AAS}) \times \text{Dilution Factor} \times \frac{15\text{L}}{1000}$$

$$\begin{aligned} \text{Copper binded on the membrane (mg), } m_1 &= \text{Copper Feed (mg)} - \\ &\quad \text{Copper remained in the solution (mg)} \end{aligned} \quad (3.6-1)$$

Adsorption capacity, q will be calculated from this formula (3.6-2) (Salehi et al., 2012).

$$\text{Adsorption Capacity, } q = \frac{(C_0 - C_e)V}{w} \quad (3.6-2)$$

Where,

q is equilibrium adsorbed on membrane (mg/g)

C₀ is the initial concentration of copper (mg/L)

C_e is the final concentration of copper (mg/L)

V is the volume of solution (L)

W is the Weight of membrane (g)

3.6-3 Batch Elution

According to (Considine, 2005), the hydrochloric acid is used in elution process to observe the effectiveness of membrane to regenerate in membrane usage. Triplicate samples straight after batch binding experiment from four different PES composition were used to study the batch elution. In this experiment, 10% HCL was used as elution buffer. After batch binding experiment in 3.7-2, the 2cm X 1cm of membrane that immersed in the solution were clipped away from the solution, dried it before transferred to the 10% hydrochloric acid for 24 hours elution process. The final concentration after 24 hours were tested with Atomic Absorption Spectrometer Analyst 400 Perkin Elmer (AAS) on eluted copper ion in hydrochloric acid. Dilution factor of 50 will be used and the water sources that were used in dilution has to be checked as well to minimise the copper error in contributing the copper concentration reading in AAS. Only ultrapure water and de-ionised water were recommended to use. The formula (3.6-3) was used in calculating the mass of copper eluted in elution:

$$\text{Copper remained in the solution (mg), } m_2 = Cf(AAS) \times \text{Dilution Factor} \times \frac{15L}{1000} \quad (3.6-3)$$

In order to find the elution efficiency, it is calculated using formula (3.6-4):

$$\text{Elution Efficiency} = \frac{m_2}{m_1} \times 100\% \quad (3.6-4)$$

Where,

m_2 is the copper remained in the solution in elution process (mg).

m_1 is the copper remained in the solution in batch binding process (mg).

3.7 Cross Flow Filtration

Cross-flow filtration was used to study the comparative maximum adsorption capacity of copper ions of membrane from batch binding experiment. On the other hand, cross flow filtration was used to double confirm which PES composition has higher adsorptive efficiency. Cross flow filtration were done with single cycle on each produced membrane on binding experiment and triplicate cycle on selected membrane on binding and elution process in order to study the regeneration of the membrane.

In single cycle cross flow filtration, continuous binding were studied with the four different PES composition to observe the performance adsorptive of membrane. Water permeability flux for de-ionised water and copper solution were obtained from permeate and retentate. In single cycle, 100ppm of copper solution were used after water compaction for 30minutes. The final concentration of copper ions from the tank will be obtained for AAS analysis.

After single cycle of cross flow filtration, repeated binding and elution of 3 cycles were done on a selected membrane to study the regeneration of one membrane on how the performance adsorptive of membrane. The 10% HCL were be used as the elution buffer solution in cross flow filtration. Water compaction, water flux, binding capacity, cleaning of membrane to prevent fouling and lastly elution process to run on 3 cycles at the most number of copper bounded membrane found from batch experiment and single cross flow filtration for regeneration.

3.7-1 Water Permeability Flux

Four different concentration of PES flat sheet mixed matrix membrane were tested with cross flow filtration. Each membrane are treated with de-ionised water for 30 minutes and 1 bars (Jasiewicz & Pietrzak, 2013) using cross flow machine shown in Figure 3-12.



Figure 3-12: Cross flow machine.

The flow rate of the permeate and retentate will be calculate using formula of permeation flux. The water permeation flux (PWP) were calculated based on this formula (3.7-1) (Suhana Jalil & A.F. Ismail, 2014).

$$\mathbf{PWP} = \frac{V}{t \times P \times A} \quad (3.7-1)$$

Where,

PWP is the de-ionised water flux (mL cm⁻² bar⁻¹sec⁻¹)

V is the volume of permeated water (mL)

t is the permeation time (sec)

A is the effective area of membranes (cm²)

3.7-2 Regeneration of Membrane

Study on the adsorptive performance of a membrane was not enough to clarify the performance of the membrane. Thus, regeneration study was being studied also. In regeneration experiment, adsorptive capacity and efficiency binding of selective membrane were being compared in three cycles in repeated binding and elution cycle to observe the performance of membrane.

3.8 Comparison Binding Efficiency Between Batch Binding and Cross Flow Filtration

Four different PES membrane were being compared from batch binding and cross flow filtration by using formula (4.3-2) to observe the efficiency using two different methods.

3.9 Summary

This paper presents the overall methodology from the beginning of the preparation of MMM to the end of the methodology testing on the performance of membrane and the adsorption capacity with the various composition of flat sheet using batch binding experiment and cross flow filtration. All the parameters were being analysed properly in order to suit the experiments. The results are being compared in chapter 4.

4 RESULTS AND DISCUSSION

4.1 Overview

This paper presents a screening study on the effect of PES concentration on the performance of Ion Exchange MMM for copper removal in flat sheet configuration using the batch and cross flow adsorption capacity. Morphological study and water permeability flux were presented as well.

4.2 Production of Flat Sheet Mixed Matrix Membrane

Flat sheet membrane with 23wt%, 25wt%, 28wt% and 30wt% of PES were being produced based on the parameters mentioned in Table 3-2.

In the preparation of 35wt% of mixed matrix membrane solution with 20g Amberlite IR120H resin, it was indication of limitation maximum concentration of PES added could be prepared as the stirring process cannot be done smoothly as the solution was too viscous to be stir. Not only that, the solution was too viscous until the bottle needs to be hold tightly while stirring with the minimum speed at 100rpm and hardly to be pour to the flat sheet casting machine. Therefore, in the study, 30wt% was made the maximum PES concentration could be prepared to be study. This experiment has proven almost the same with literature reviewed stated optimum PES concentration to be used was 15wt% (B.K. Chaturvedi *et al.*, 2001) but in the research the concentration were varies from 23wt% to 30wt% to study the effect of adsorption of copper ions with the concentration of PES. The maximum PES concentration based on journal was in between 30wt% to 35wt% of PES (Shung, 1997). Therefore, in the research, 30wt% was made the maximum concentration of PES as even higher PES composition the viscosity was too hard to perform the casting process.

4.2-1 SEM Analysis

Scanning electron microscopy (SEM) was used to investigate membrane morphology and molecular orientation in the flat sheet membrane active layer. The 4 samples of flat sheet membranes were dried and immersed for about 20 seconds in liquid nitrogen and then break using forceps to expose the cross sectional structure for SEM analysis (Ahmed, 2010). A commonly clean break was being snapped under the liquid nitrogen. Before

viewed on a SEM, the sample was sputtered with gold by using an ion-sputtering (Biorad Polaron Division) with potential of 10kV under magnifications in the range of 500x to 5000x (Suhana Jalil & A.F. Ismail, 2014.). From Figure 4-1 until Figure 4-4, the SEM images are shown below with magnifying factor of 500.



Figure 4-1: SEM of 23% PES

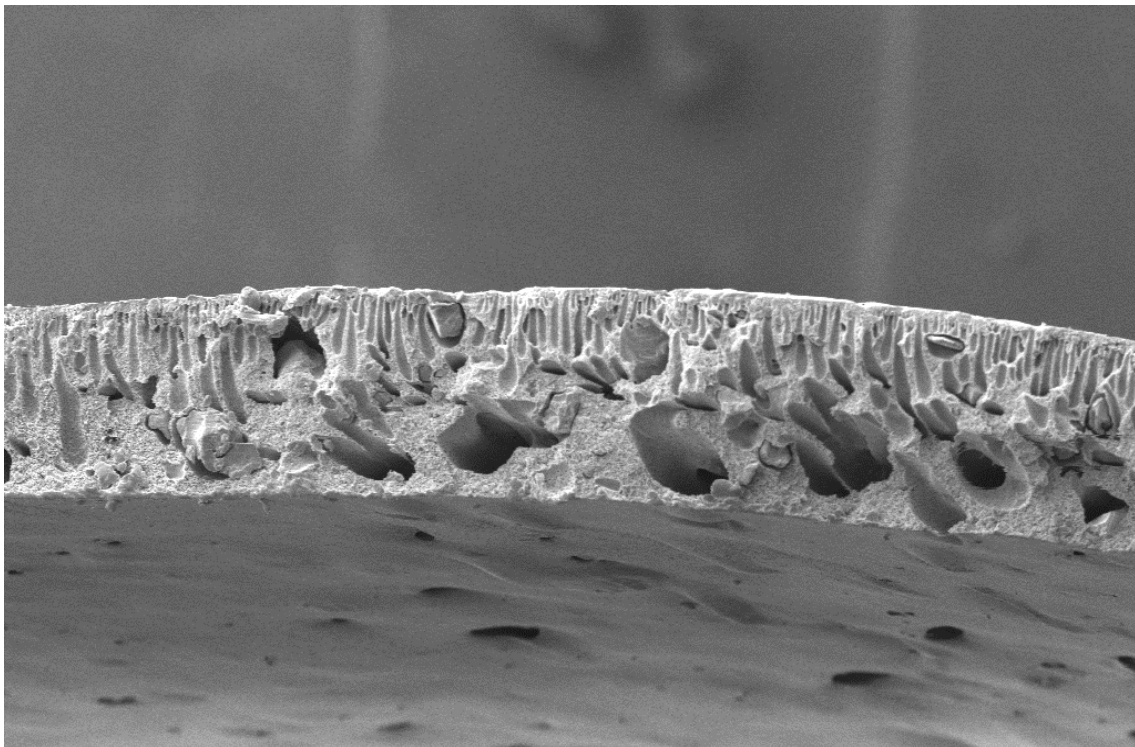


Figure 4-2: SEM of 25% PES

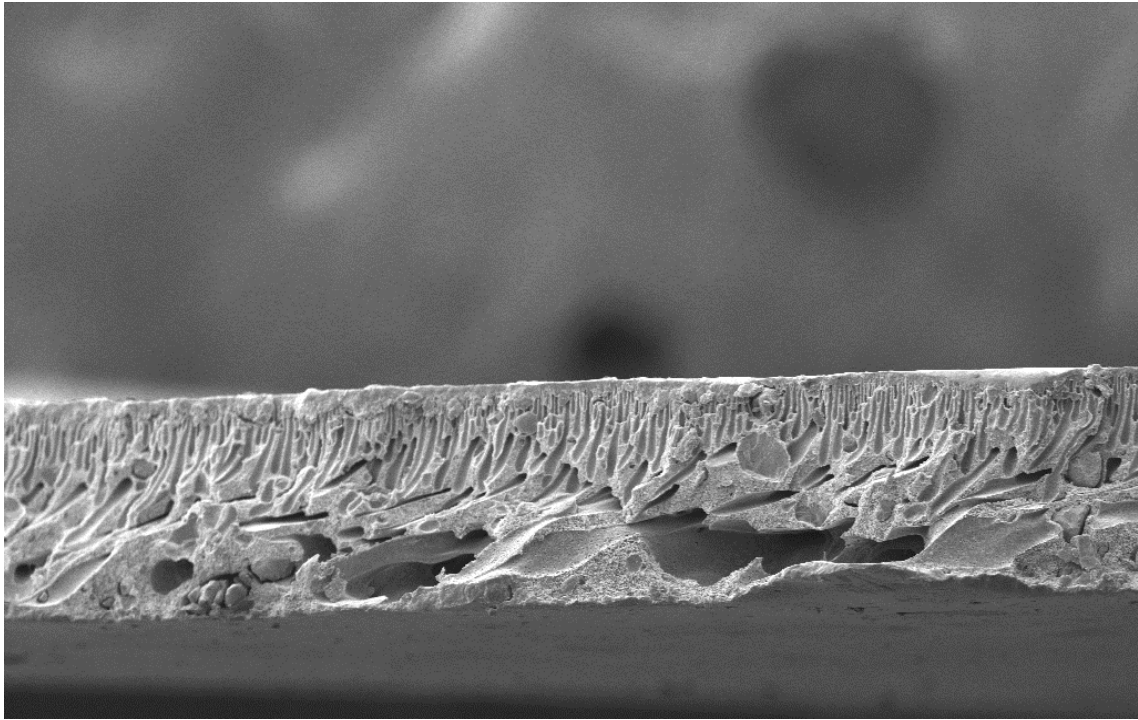


Figure 4-3: SEM of 28% PES

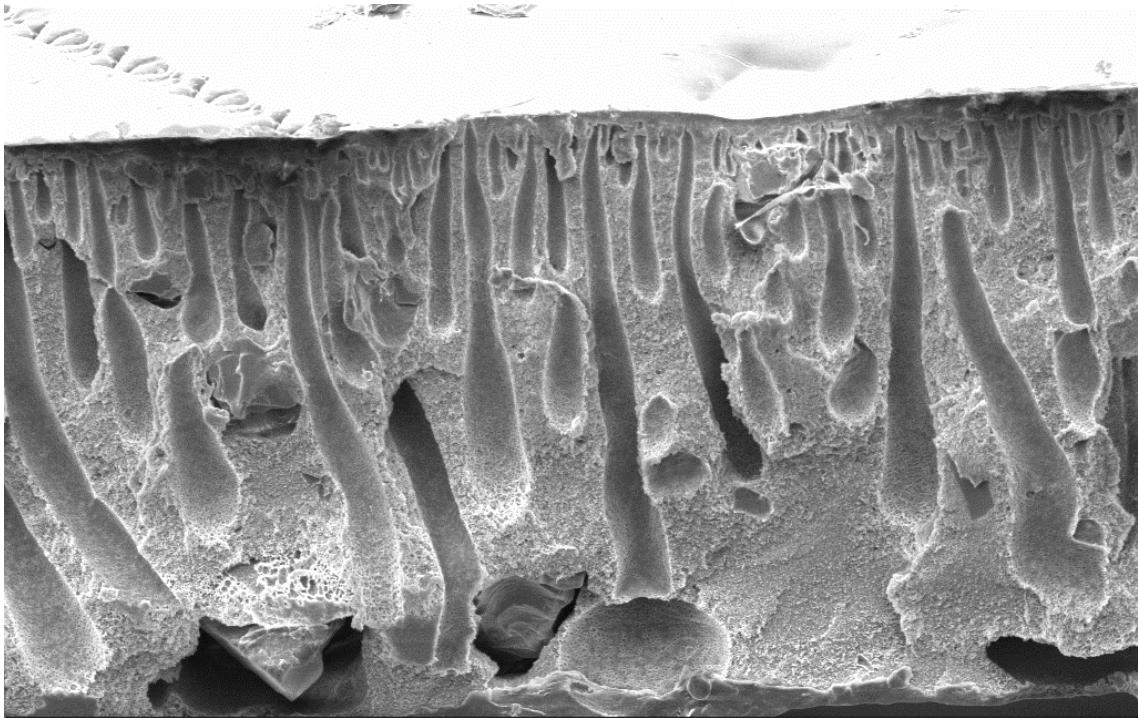


Figure 4-4: SEM of 30% PES

4.3 Batch Static Binding Capacity

4.3-1 pH of Copper(II) Sulphate Pentahydrate

The pH value of copper (II) sulphate pentahydrate found after calibrated with pH7.00, pH4.01 and pH9.00 obtained read as pH 5.00 as shown in Figure 4-5. The optimum adsorption of copper ions was in the range of pH 4-pH 7 (Abdel Salam *et al.*, 2011) since the standard copper solution prepared in the experiment was read at pH 5.00, it is acceptable.

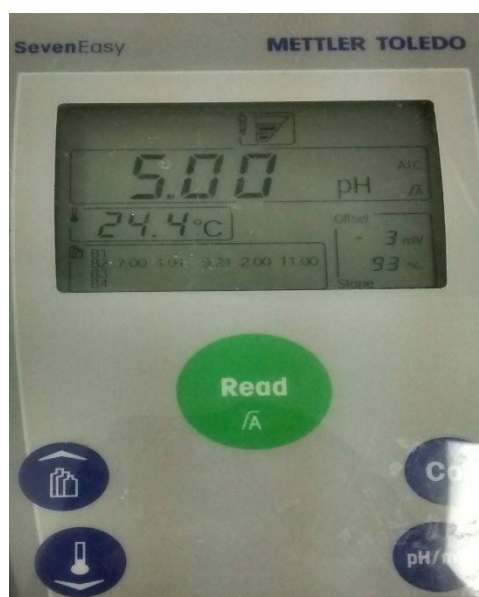


Figure 4-5: pH of copper (II) sulphate pentahydrate

4.3-2 Analysis of Binding Capacity

The 23wt%, 25wt%, 28wt% and 30wt% different in PES flat sheet membrane are being cut into 2 cm X 1cm each to be put into 15mL from 500ppm of copper (II) sulphate pentahydrate for batch binding. The formula in calculation for the mass of copper needed in producing 250mL of 500ppm $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ standard solution for batch binding is shown in formula (4.3-1).

$$\frac{250\text{mL}}{1000} \times \frac{500\text{mg}}{\text{L}} \times \frac{1\text{g}}{1000\text{mg}} \times \frac{249.68\text{g CuSO}_4 \cdot 5\text{H}_2\text{O}}{63.546\text{g Cu}} = 0.49\text{g of Cu} \quad (4.3-1)$$

About 0.49 g of Cu is needed to produce 250mL of copper solution. 15mL of 250mL of solution were pipette into 15mL of centrifuge tubes. Each cut of membrane from different

concentration was immersed in the copper solution for 24 hours and spin using *biosan* Multi rotator RS-60 as shown in Figure 4-6.



Figure 4-6: *biosan* Multi rotator RS-60

After 24 hours of batch binding, each solution was diluted using dilution factor of 150 by pipetting 50 μL of final concentration inside the centrifuge tubes and 7450 μL of ultrapure water before being testing using AAS. The diluted concentration of copper solution was membrane filtered using Titan3™ 0.45 μm of reg cellulose membrane filter with syringes to remove any impurity. Figure 4-7 and Figure 4-8 showed the examples of centrifuged tubes and Titan3™ 0.45 μm of reg cellulose membrane filter respectively.

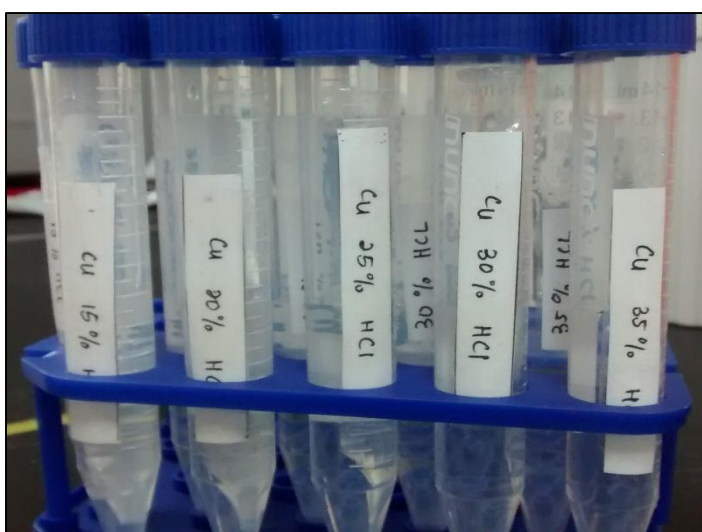


Figure 4-7: Centrifuged tubes



Figure 4-8: Titan3™ 0.45 µm of reg cellulose membrane filters

After preparation for dilution and membrane filtration of the samples, each samples was dropped with a drop of nitric acid functioning in stabilising the copper ions when tested with AAS. Table 4-1 showed the result for the batch binding of copper in the mixed matrix membrane in 4 different PES concentration with the adsorptive capacity, q and binding efficiency. From the experimental data, 30wt% PES was made the highest adsorptive capacity, q at 476.67mg copper/g membrane comparing to other composition with the standard deviation of 0.1. From the highest binding of copper ions which is 30wt% PES membrane with higher efficiency removal of copper at 64.83% calculated with formula (4.3-2). The calculation (4.3-2) was repeated with the rest of the PES composition.

$$\text{Binding Efficiency (\%)} = \frac{4.469\text{mg}}{7.5\text{mg}} \times 100\% = 59.585\% \quad (4.3-2)$$

Table 4-1: Average of Triplicate Batch Adsorption of Copper

Composition	Weight of membrane(g)	Average Triplicate of Copper binded in the membrane per 7.5mg (mg)	q (mg Cu/g)	Standard Deviation	Binding Efficiency (%)
23%	0.0102	4.469	438.14	0.388	59.59
25%	0.0102	4.734	464.12	0.060	63.12
28%	0.0113	4.709	416.73	0.360	62.78
30%	0.0102	4.862	476.67	0.100	64.83

*7.5mg was obtained from formula (3.6-1) and q was obtained from formula (3-6.2)

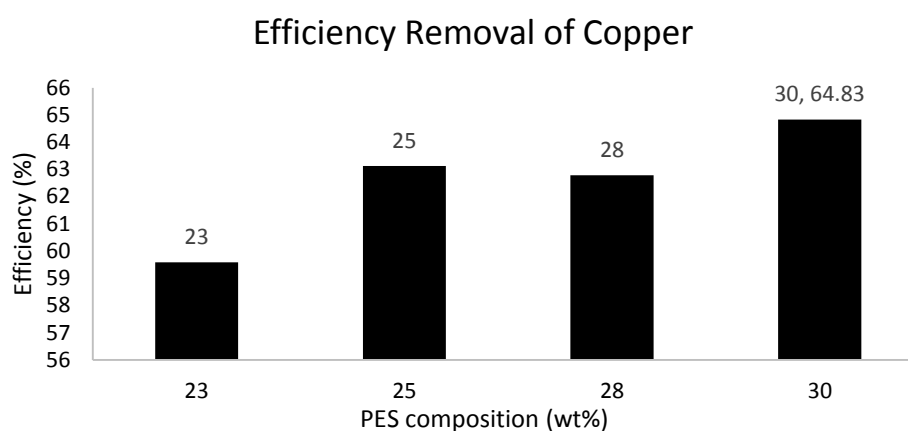


Figure 4-9: Comparison Removal Efficiency of Cu with different PES compositions

The raw data for batch binding analysis were attached at Appendix Table A-1.

4.3-3 Analysis of Static Elution Buffer

After undergo batch adsorption for 24 hours from 4.3-2 and the adsorbed membrane of copper were transferred into 15mL of 10% HCL solution. The acid solution was used for regeneration of copper ions from membrane to observe the performance of membrane. The samples were left 24hours and spin as shown in Figure 4-6. After 24hours, the procedures of dilution factor of 50 by pipetting 1000 μ L from final concentration in the centrifuge tubes with 4000 μ L of ultrapure water were done and proceed with membrane filtration shown in

Figure 4-8. The Table 4-2 showed the average of triplicate batch elution buffer for copper using 10% HCL on 4 different PES composition.

Table 4-2: Average of Triplicate Batch Elution Buffer for Copper using 10% HCL

PES Concentration(wt%)	Copper eluted in HCL (mg)	Elution Efficiency (%)
23	1.451	32.6521
25	1.397	29.5126
28	1.457	31.0456
30	1.655	34.0678

*Elution efficiency calculated from formula (3.6-4)

From the finding, the highest eluted mass of copper using 10% HCL with highest copper eluted at 1.655mg of copper and 34% efficiency in elution. Thus, the 10% HCL is used as the elution buffer solution for cross flow filtration in single and continuous cross flow filtration.

It was proven that 30wt% PES membrane has better performance of adsorptive and elution in batch experiment. The raw data were attached at Appendix Table A-2.

4.4 Cross Flow Filtration

Single cross flow and triplicate cross flow filtration were done in the investigation to compare the batch binding experiment and cross flow binding. In single cross flow filtration, all the four different PES composition membrane were undergoes cross flow filtration to observe the performance of continuous binding. From the most cross flow binding membrane, the membrane was used to study the regeneration of membrane in 3 cycles to double confirm the effectiveness of the adsorptive performance of 30wt% PES membrane.

4.4-1 Single Cycle Binding

Four different PES composition from 23wt%, 25wt%, 28wt% and 30wt% were experimental tested with cross flow filtration on the continuous binding in single cycle to observe which PES composition has higher binding efficiency while comparing with batch static binding. Firstly, 23wt% pf PES membrane was used. Before 1L of 100ppm of copper (II) sulphate pentahydrate was used, water compaction procedure was first run by cross filtration using de-ionised water for 30 minutes to open up the pore of the membrane. Water permeation flux for the permeate and retentate were record for 40 seconds. The equation for water flux is shown in formula (3-7.1). The process was proceeded by changing the de-ionised water with copper(II) sulphate pentahydrate and

run for 30 minutes. The flow rate of copper(II) sulphate pentahydrate was recorded and final concentration from the tank was kept to observe the remaining concentration of copper ions left inside the tank. The experiment was repeated with 25wt% PES to 30wt% PES composition. The adsorptive capacity, q and binding efficiency were tabulated in Table 4-4. The formula (3.7-1) was used to calculate the water compaction flux and tabulated in Table 4-3.

$$\mathbf{PWP} = \frac{V}{t \times P \times A} \quad (4.4-1)$$

Where,

PWP is the pure water flux (mL cm⁻² bar⁻¹sec⁻¹)

V is the volume of permeated and retentate water (mL)

t is the permeation time (sec)= 40

A is the effective area of membranes (cm²)= 66

Table 4-3: Water Compaction Flux,PWP for Single Cycle Cross Flow Filtration
(ml/bar.cm²sec)

PES composition	Permeate		Retentate	
	De-ionised water	Copper(II) Sulphate Pentahydrate	De-ionised water	Copper (II) Sulphate Pentahydrate
23	0.01047	0.00667	0.2145	0.1683
25	0.01167	0.00633	0.225	0.1683
28	0.00165	0.00583	0.2104	0.1683
30	0.01042	0.0075	0.2145	0.1683

*PWP calculated from formula (3.7-1)

From Table 4-3, the permeate water flow rate is lower than retentate due to the solution needed to diffuse across the pores of the membrane whereas the binding of copper in the membrane causing the flow of solution restricted in permeate. The more the number of cycles, the slower the flow rate.

Table 4-4: Cross Flow Filtration Binding for Single Cycle using 100ppm of Copper
(II) Sulphate Pentahydrate

PES Composition (wt%)	Weight of membrane(g)	Average Triplicate of Copper binded in the membrane per 100mg (mg)	q (mg Cu/g)	Binding Efficiency (%)
23	0.3366	93.523	277.846	93.52%

25	0.3366	95.250	282.977	95.25%
28	0.3729	94.743	254.071	94.74%
30	0.3366	95.015	282.783	95.02%

*q calculated from formula (3-6.2) and binding efficiency obtained from formula (4-3.2).

From the finding, the experiment data showed that almost all of the different composition membranes has effective removal adsorption up to 90% removal. Since both 23wt% and 30wt% PES composition has the highest efficiency at 95% binding and adsorptive capacity, q at 282mg Cu/g. Thus, 30wt% PES membrane was used in the triplicate cycles of the membrane to study for regeneration of membrane.

Thus, it can be double confirm that from two different binding mechanism used, 30wt% PES membrane had the highest binding efficiency at 64% and 97% respectively compared to other smaller composition of PES membrane. However, the study on the binding on membrane itself was not enough to determine the effective performance of membrane. Hence, regeneration study was studied as well in triplicate cycle using cross flow filtration to observe the usage of membrane on each cycle will have the same binding efficiency after each run. The raw data of this experiment were attached at the Appendix Table A-3.

4.4-2 Triplicate Cycles for Regeneration of Membrane

Next, experiment was proceeded with repeated binding and elution with 3 cycles using 30wt% PES membrane and 10%HCL elution buffer. The experiment procedures were the same when using single cross flow filtration. After single binding, it is followed with elution process using HCL after cleaning of membrane for 10 minutes. After 30 minutes of elution, the membrane was washed with deionised water for 10 minutes. The overall process was repeated for another 2 cycles with water permeability, copper solution, cleaning of membrane, elution and cleaning of membrane. The flow rate for permeate and retentate were recorded as well in Table 4-5. The Table 4-6 showed the results of the 3 cycles of repeated binding and elution readings using 30%PES flat sheet membrane and 10%HCL.

Table 4-5: Water Compaction Flux,PWP Cross Flow Filtration (ml/bar.cm²s)

	Permeate		Retentate	
	De-ionised water	Copper(II) Sulphate Pentahydrate	De-ionised water	Copper (II) Sulphate Pentahydrate
Run 1	0.01515	0.00946	0.1560	0.1484
Run 2	0.01439	0.00833	0.1515	0.1439
Run 3	0.01212	0.00681	0.1484	0.1393

*PWP calculated from (3.7-1).

From Table 4-5, the permeate water flow rate is lower than retentate due to the solution needed to diffuse across the pores of the membrane whereas the binding of copper in the membrane causing the flow of solution was being restricted in permeate. The more the number of cycles, the slower the flow rate. It has the similar trend with single cycle binding.

Table 4-6: Triplicate Cycle Cross Flow Filtration for Adsorption and Elution

Cycle	Weight of Membrane	Copper binded in the membrane per 100mg (mg)	q (mg Cu/g)	Binding Efficiency (%)	Elution efficiency using 10% HCL(%)
1	0.3364	97.145	288.78	97.15	1.582685676
2		97.065	288.54	97.07	1.468088394
3		97.123	288.71	97.12	2.059255064

*q, binding efficiency and elution efficiency were calculated from calculated from formula (3.6-2), (4.3-2) and (3-6.4) respectively.

From Table 4-6, 30wt%PES membrane had effective copper adsorption capability with averagely same amount of copper ions at 97% binding efficiency in 3 cycles. From the finding, since after each cycle, the adsorption capacity kept maintained meanings all the membrane produced can be regenerated even for only 3 cycles. The raw data were attached at the Appendix Table A-4.

4.5 Comparison Binding Efficiency Between Batch Binding and Cross Flow Filtration

Table 4-7 showed the comparison results from batch binding and cross flow filtration.

Table 4-7: Comparison Binding Efficiency From Batch Binding and Cross Flow

PES composition (wt%)	Binding Efficiency	
	Batch Binding (%)	Cross Flow Filtration (%)
23	59.59	93.52
25	63.12	95.25
28	62.78	94.44
30	64.83	95.02

*Binding efficiency calculated from (4.3-2)

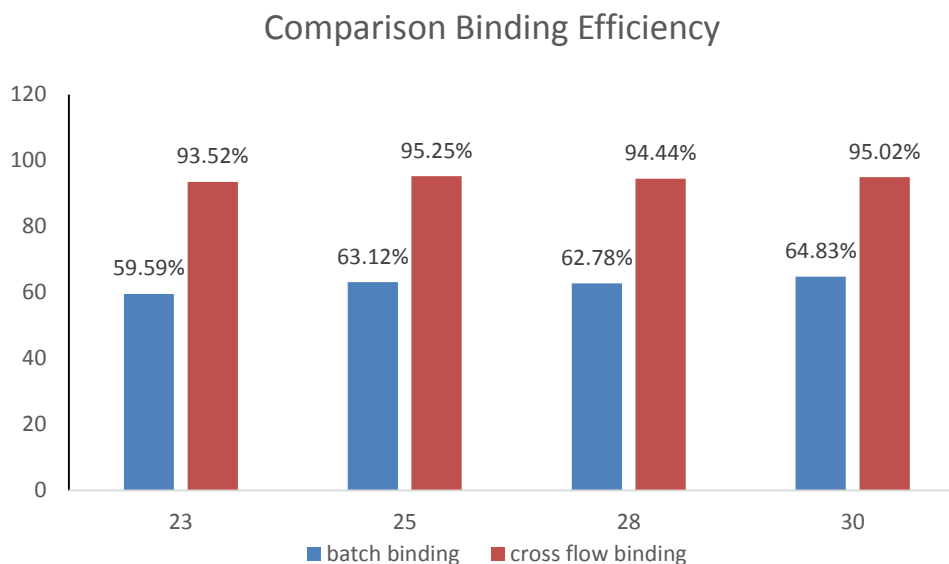


Figure 4-10: Comparison Binding Efficiency Using Batch Binding And Cross Flow Filtration

From the comparison data in Table 4-7 in both batch binding and cross flow filtration, cross flow filtration indeed was more efficient in copper removal than batch binding. In cross flow filtration, since that only 100ppm of copper solution was used, it is efficient in removing of copper ions up to 95% compared to 500ppm. Thus, cross flow is more relevantly used in most of the industry rather than batch experiment as it is faster in removing capability.

5 CONCLUSION

5.1 Conclusion

In the study, the objective of the experiment has been achieved in investigating the adsorptive performance with different PES composition. The scopes studied on production of adsorptive flat sheet MMM by incorporating cation resin-Amberlite IR120 into a dope polymer solution consisting of PES, NMP and PVP, studying the effect of PES concentration in the PES-Amberlite IR120 dope polymer solution from 23-30wt% on the performance of adsorptive MMM for copper removal and characterize the MMM in term of pore structure, water permeability and static adsorption properties for copper removal and regeneration of MMM.

With the first scope, it is found that the maximum composition of PES used in the production of membrane was made optimum at 30wt% as the preparation of 35wt% was too viscous and having difficulty when preparation of membrane. Besides, the drying of 30wt% PES indeed is very difficult to control as it will shrink easily. Therefore, the preparation of 30wt% was made the maximum.

From the experimental finding, it is found that the higher the PES composition is used, the more the copper ions being adsorbed by the membrane. From batch static binding analysis, the binding efficiency of copper bounded on the membrane increased from lower PES composition to highest PES composition used from 60% to 65%. Not only that, the cross flow filtration also showed a satisfactory result with the binding of all the different PES composition could reach up to 90% to 95% binding efficiency. From both of the binding efficiency, 30wt% PES membrane was made the highest binding efficiency at 64% and 95% in batch experiment and cross flow filtration respectively. Thus, two mechanisms used were double confirm 30wt% PES was the best adsorptive membrane from the study.

In second scope, characterisation of pore structure, water permeability flux and static adsorption capability were also being studied with SEM analysis, calculation of PWP and adsorption capacity. In term of water permeability, the permeate water flow rate is lower than retentate due to the solution needed to diffuse across the pores of the membrane whereas the binding of copper in the membrane causing the flow of solution was being

restricted in permeate. The more the number of cycles, the slower the flow rate. It has the similar trend in single cycle binding.

From the study, the membrane itself can be regenerated. In triplicate cycle of cross flow filtration, the adsorptive capacity still can be reached up to the same efficiency after each run of adsorption and elution meaning the membrane can perform well after undergo repeated adsorption and elution.

Hence, the objectives of the study had been achieved. The higher the PES composition, the better the adsorptive performance of membrane until it reached its optimum PES composition at 30wt%PES. Cross flow filtration indeed has better adsorptive performance at 97% efficiency than batch binding at only 64% efficiency.

5.2 Future work

For recommendation, future work can be carried out in the studying the elution buffer. Sulphuric acid is the cheapest cation resin regenerant for demineralisers and is used where possible. Some water supplies contain a high proportion of copper and when this acid is used copper sulphate precipitates can form during regeneration. Copper fouling can occur. Thus, under such circumstances, hydrochloric acid should be substituted (Considine, 2005). Thus, for future work, the concentration of HCL can be varies from the range from the concentration of 2%HCL to 15%HCL in order to study the regeneration through elution process using HCL(E.Dabrowski *et al.*, 2004), (Company, 1978).

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APPENDICES

Table A-1: Batch Binding For Different PES Composition

Static Adsorption (static binding)						23% PES				25% PES				28% PES				30% PES			
Repeat	cm ²	V, ml	Ci, mg/L	Fe feed, mg	Dil Factor	Cf, AAS, mg/L	mg Fe		Mg Fe Bound to MMM	Cf, AAS, mg/L	mg Fe		Mg Fe Bound to MMM	Cf, AAS, mg/L	mg Fe		Mg Fe Bound to MMM	Cf, AAS, mg/L	mg Fe		Mg Fe Bound to MMM
							Cf, Real, mg/L	Remained in Soln			Cf, Real, mg/L	Remained in Soln			Cf, Real, mg/L	Remained in Soln			Cf, Real, mg/L	Remained in Soln	
1	2	15	500	7.5	150	2.696	404.4	3.033	4.467	2.397	359.55	2.697	4.803	2.358	353.7	2.653	4.847	2.245	336.75	2.526	4.974
2	2	15	500	7.5	150	2.349	352.35	2.643	4.857	2.485	372.75	2.796	4.704	2.241	336.15	2.521	4.979	2.372	355.8	2.669	4.832
3	2	15	500	7.5	150	3.038	455.7	3.418	4.082	2.494	374.1	2.806	4.694	2.845	426.75	3.201	4.299	2.417	362.55	2.719	4.781
						Average Cf	404.15			Average Cf	368.8			Average Cf	372.2			Average Cf	351.7		
						w (g)	0.0102	Ave Bound, mg	4.469	w (g)	0.0102	Ave Bound, mg	4.734	w (g)	0.0113	Ave Bound, mg	4.709	w (g)	0.0102	Ave Bound, mg	4.862
						Std Dev			0.388	Std Dev			0.060	Std Dev			0.360	Std Dev			0.100

Table A-2: Batch Elution For Different PES Composition

Static Adsorption (elution)			23%				25%				28%				30%					
Repeat	V, mL	Dil Factor	Cf, AAS		mg Fe eluted,		Cf, Real,		mg Fe		Cf, AAS		mg Fe eluted,		Cf, Real,		mg Fe elu		% elution	
			mg/L	Cf, Real, mg/L	m ²	% elution	mg/L	mg/L	mg/L	% elution	mg/L	mg/L	mg/L	% elution	mg/L	mg/L	mg/L	% elution		
1	15	50	1.964	98.2	1.473	32.97515111	1.863	93.15	1.397	29.08892	2.007	100.35	1.50525	31.05369	2.194	109.7	1.6455	33.07953		
2	15	50	1.893	94.65	1.420	29.2287501	1.901	95.05	1.426	30.3069	1.913	95.65	1.43475	28.816751	2.166	108.3	1.6245	33.6231		
3	15	50	1.946	97.3	1.460	35.75234246	1.824	91.2	1.368	29.14204	1.907	95.35	1.43025	33.266463	2.263	113.15	1.69725	35.50082		
			Ave Elution		32.65208122		Ave Elution		29.51262		Ave Elution		31.045635		Ave Elution		1.65575		34.06782	
			Std Dev		3.273773807		Std Dev		0.688377		Std Dev		2.2248671		Std Dev		1.270431			

Table A-3: Single Cross Flow Filtration on Binding

Cross flow filtration (binding)						23% PES				25% PES				28% PES				30% PES			
Repeat	cm ²	V, ml	Ci, mg/L	Fe feed, mg	Dil Factor	Cf, AAS, mg/L	mg Fe		Mg Fe Bound to MMM	Cf, AAS, mg/L	mg Fe		Mg Fe Bound to MMM	Cf, AAS, mg/L	mg Fe		Mg Fe Bound to MMM	Cf, AAS, mg/L	mg Fe		Mg Fe Bound to MMM
							Cf, Real, mg/L	Remained in Soln			Cf, Real, mg/L	Remained in Soln			Cf, Real, mg/L	Remained in Soln			Cf, Real, mg/L	Remained in Soln	
66	1000	100	100	25	2.591	64.775	6.4775	93.523	1.9	47.5	4.75	95.250	2.103	52.575	5.2575	94.743	1.994	49.85	4.985	95.015	

Table A-4: Triplicate Cross Flow Filtration in Regeneration Study

Cross flow filtration (binding)										
	cm ²	V, ml	Ci, mg/L	Fe feed, mg	Dil Factor	Cf, AAS, mg/L	Cf, Real, mg/L	mg Fe Remained in Soln	Mg Fe Bound to MMM	Efficiency
Run1	66	1000	100	100	25	1.142	28.55	2.855	97.145	97.145
Run2	66	1000	100	100	25	1.174	29.35	2.935	97.065	97.065
Run3	66	1000	100	100	25	1.151	28.775	2.8775	97.1225	97.1225
Elution										
	V, mL	Dil factor	Cf, AAS, mg/L	Cf, Real, mg/L	mg Fe eluted, m ²	% elution				
Run1	250	50	0.123	6.15	1.5375	1.582685676				
Run2	250	50	0.114	5.7	1.425	1.468088394				
Run3	250	50	0.16	8	2	2.059255064				

* All the AAS analysis data were attached