

COPPER REMOVAL FROM AQUEOUS SOLUTION USING
AMBERLITE IR-120 CATION EXCHANGER MIXED MATRIX
MEMBRANE CHROMATOGRAPHY

ZURAIDAH BINTI MOHAMAD

UNIVERSITI MALAYSIA PAHANG

ZURAI DAH BINTI MOHAMAD BACHELOR OF CHEMICAL ENGINEERING 2013 UMP

COPPER REMOVAL FROM AQUEOUS SOLUTION USING AMBERLITE IR-
120 CATION EXCHANGER MIXED MATRIX MEMBRANE
CHROMATOGRAPHY

ZURAIDAH BINTI MOHAMAD

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

Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

FEBRUARY 2013

SUPERVISOR'S DECLARATION

I hereby declare that I have read this project and in my opinion, this project is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

Signature :

Name of Supervisor : Dr. Syed Mohd Saufi Bin Tuan Chik

Position : Supervisor

Date : 25th January 2013

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 : Zuraidah binti Mohamad
ID Number : KA09093
Date : 25th January 2013

Special dedication to my beloved family, especially my parents (Mohamad bin Piai & Saodah binti Omar) for their love and care.

And,

To my friends, that encouraged and fully supports me throughout completing this thesis.

ACKNOWLEDGEMENTS

In the name of Allah, the most beneficent, the most merciful. I would like to express my sincere gratefulness to Allah S.W.T. for giving me strength to complete my project.

I am grateful and would like to express my sincere gratitude to my supervisor, Dr. Syed Mohd Saufi Bin Tuan Chik for his germinal ideas, invaluable guidance, continuous encouragement and constant support in making this research possible. I am really thankful for his cooperation and commitment in assisting me from the beginning until the completion of this research. Also, I am thankful for his kindness to guide and correcting my mistake throughout this report.

I would like to extend my appreciation to all FKKSA lab staffs for their cooperation while facilitating me through this semester. Not forgotten I would like to thanks to Master students, Noor Fadilah Mohd Sabri that always give me full of guidance and support throughout this project work. I acknowledge my sincere indebtedness and gratitude to my parents and my family for their love, dream and sacrifice throughout my life and for their never ending support on me. Lastly I would like to thank to my fellow friends who always give me motivation and support for me to complete my research. I am truthfully grateful for all their kindness.

**COPPER REMOVAL FROM AQUEOUS SOLUTION USING AMBERLITE
IR-120 CATION EXCHANGER MIXED MATRIX MEMBRANE
CHROMATOGRAPHY**

ABSTRACT

Copper is one of the toxic heavy metals that contaminated in industrial wastewater. Cation exchange chromatography is widely used for the removal of copper (II) from the water. In this study, Amberlite IR-120 cation exchanger resin was used to prepare mixed matrix membrane (MMM) chromatography by blending the resin in ethylene vinyl alcohol (EVAL) base polymer solution. The EVAL composition was varied in the range of 15 to 20 wt% with fixed Amberlite IR-120 loading at 30%. The adsorption isotherm of cation MMM was determined from batch binding experiment. From the result, it shows that MMM15, prepared at 15 wt% EVAL gave high amount of copper binding of 5688.190 mg Cu/g adsorbent. In regeneration experiments using 0.1M HCl, more effective regeneration was showed by MMM20, prepared at 20 wt% EVAL, than EVAL membrane.

**PENYINGKIRAN TEMBAGA DARI LARUTAN AKUEUS
MENGUNAKAN AMBERLITE IR-120 PENUKAR KATION CAMPURAN
MATRIX MEMBRAN KROMATOGRAFI**

ABSTRAK

Tembaga adalah salah satu logam toksik berat yang tercemar dalam air sisa industri. Kromatografi pertukaran kation digunakan secara meluas untuk penyingkiran kuprum (II) dari air. Dalam kajian ini, Amberlite IR-120 resin penukar kation telah digunakan untuk menyediakan matriks membrane campuran (MMM) kromatografi dengan menggabungkan resin dalam etilena vinilalkohol (EVAL) polimer asas penyelesaian. Komposisi EVAL telah diubah dalam julat antara 15 hingga 20% berat dengan tetap Amberlite IR-120 loading 30%. Isoterma penjerapan kation MMM telah ditentukan dari eksperimen kelompok mengikat. Dari hasilnya, ia menunjukkan bahawa MMM15, disediakan pada 15% berat EVAL memberikan jumlah yang tinggi tembaga mengikat 5688,190 mg Cu / g adsorben. Dalam eksperimen semula menggunakan 0.1M HCl, lebih regenerasi berkesan telah menunjukkan oleh MMM20, disediakan di 20 wt% EVAL, daripada membran EVAL.

TABLE OF CONTENTS

	PAGE
SUPERVISOR'S DECLARATION	ii
STUDENT'S DECLARATION	iii
SPECIAL DEDICATION	iv
ACKNOWLEDGEMENT	v
ABSTRACT	vi
ABSTRAK	vii
TABLE OF CONTENTS	viii
LIST OF TABLES	xi
LIST OF FIGURES	xii
LIST OF SYMBOLS	xiii
LIST OF ABBREVIATIONS	xiv
CHAPTER 1 INTRODUCTION	
1.1 Background of Study	1
1.2 Problem Statement	3
1.3 Research Objectives	4
1.4 Scope of Study	4
CHAPTER 2 LITERATURE REVIEW	
2.1 Heavy Metal	5
2.1.1 Copper	7
2.1.2.1 Used of Copper	8
2.1.2.2 Health Affect of Copper	8
2.2 Current Technology for Removal of Heavy Metal	9
2.2.1 Precipitation	9
2.2.2 Electro-coagulation	9
2.2.3 Reverse Osmosis and Electro-dialysis	10
2.2.4 Cementation	10
2.2.5 Electro-winning	11
2.3 Adsorption	11

2.4	Adsorption Isotherm	12
2.4.1	Freundlich Isotherm	12
2.4.2	Langmuir Isotherm	13
2.5	Adsorbents for Removal of Heavy Metal	13
2.5.1	Diethylenetriamine-grafted Poly (glycidyl methacrylate) (PGMA- DETA)	13
2.5.2	Tea Waste	14
2.5.3	Membrane Bioreactor	14
2.5.4	Polyvinylalcohol Membranes	15
2.5.5	Novel Nanofiber Membrane (M-1)	15
2.6	Ion Exchange	15
2.7	Resin for Ion Exchange	18
2.8	Definition of Membrane	19
2.9	Types of Membrane Process	19
2.9.1	Reverse Osmosis	19
2.9.2	Nanofiltration	20
2.9.3	Ultrafiltration	20
2.9.4	Microfiltration	21
2.10	Mixed Matrix Membrane (MMM)	22

CHAPTER 3 METHODOLOGY

3.1	Materials	24
3.1.1	Chemicals	24
3.2	Preparation of Membrane Casting Solution	25
3.3	Flat Sheet Membrane Casting Process	26
3.4	Synthetic wastewater preparation	27
3.5	Binding Experiment	27
3.6	Regeneration of Adsorbent	29
3.7	Atomic Absorption Spectrophotometry (AAS)	29
3.8	Pure Water Flux Test	29

CHAPTER 4 RESULTS AND DISCUSSIONS

4.1	Introduction	31
-----	--------------	----

4.2	Copper Binding for Ground Resin, EVAL Membrane and Cation Exchange MMM	31
4.3	Effect of EVAL Composition on Copper Binding in MMM	33
4.4	Regeneration of Adsorbent	35
4.5	Pure Water Flux	36
CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS		
5.1	Conclusions	38
5.2	Recommendations	39
REFERENCES		40
APPENDICES		
	Appendix A	46
	Appendix B	50

LIST OF TABLES

	PAGE
Table 2.1 Example of heavy metal content in effluent samples collected from different industries of Taloja industrial estate of Mumbai	6
Table 2.2 Removal of heavy metal using different types of resin	18
Table 4.1 Copper binding capacity for ground resin, EVAL membrane and cation exchanger MMM	32
Table 4.2 Copper binding for MMM prepared using different EVAL content	34
Table B.1 Standard copper solution for calibration curve	50
Table B.2 Absorbance for each concentration	50
Table B.3 Preparation of CuSO ₄ .H ₂ O solution	53
Table B.4 Copper Binding for Ground Resin	54
Table B.5 Copper Binding for EVAL membrane	55
Table B.6 Copper Binding for 15% EVAL MMM	55
Table B.7 Copper Binding for 20% EVAL MMM	56

LIST OF FIGURE

		PAGE
Figure 2.1	Size exclusion membranes and their function	21
Figure 3.1	(a) Preparation of casting solution in fume chamber	25
	(b) Homogenous casting slurry of mixed matrix membrane	25
Figure 3.2	Flat sheet membrane after freezes dried	27
Figure 3.3	Rotate the centrifuge tube for copper binding	28
Figure 4.1	Graph of copper binding versus equilibrium concentration for ground resin, EVAL membrane and cation exchanger MMM	33
Figure 4.2	Copper binding versus equilibrium concentration for MMM15 and MMM20	35
Figure 4.3	Comparison of copper recovery between EVAL membrane and MMM20	36
Figure 4.4	Graph of water flux with MMM15 and MMM20	37
Figure A.1	Freeze dryer used to dry the resins.	46
Figure A.2	Ultra centrifugal grinder used to grind the resins	46
Figure A.3	Ultrasonic used to immersed homogenous casting slurry of MMM	47
Figure A.4	Freeze dryer used to dry the flat sheet MMM	47
Figure A.5	Centrifuge 5810 R used to separate the ground resin from the copper ion solution	48
Figure A.6	Atomic Absorption Spectrophotometer used to measure heavy metal concentration	48
Figure A.7	Amicon stirred cell used in water flux experiment	49
Figure B.1	Graph of standard curve	51

LIST OF SYMBOLS

°C	Degree celcius
g	Grams
L	Litre
mL	Millilitre
s	Seconds
w/w	Weight per weight
%	Percentage
q	Dynamic binding capacity
V	Volume
C _o	Initial concentration
C _f	Equilibrium Cu concentration
m	Mass
R	Percentage of resin loading
W _r	Amount of resin
W _p	Amount of EVAL
A	Area
t	Operation time

LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
Cu	Copper
Cr	Chromium
DMSO	Dimethyl Sulfoxide
EVAL	Ethylene vinyl alcohol
HCl	Hydrochloride acid
MMM	Mixed Matrix Membrane
Ni	Nickel
ppm	Parts per million
Zn	Zinc

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Industrial wastewater is one of the serious environmental problems in the natural eco-system because the wastewater contaminated with heavy metal due to the improper wastewater treatment. Heavy metals pollution occurs in a lot of industrial wastewater. For example the industrial wastewater produced by metal plating facilities, mining operations, battery manufacturing processes, the production of paints and pigments, and the ceramic and glass industries (Abdel Salam *et al.*, 2011). This industrial wastewater usually contains Cu, Pb, Zn, Cd, Ni, and Cr (Argun *et al.*, 2008). When the toxic heavy metals are bare to the natural eco-system, accumulation of metal ions in human bodies will occur through either food chains or direct intake. Hence, to solve this problem, heavy metals must be prevented from reaching the natural environment (Meena *et al.*, 2008).

Copper (II) is one of the toxic heavy metal. There are a lot of industrial that use of copper to produce product, due to its features like malleability, resistance to

corrosion, high conductivity and thermal conductivity. Copper is alloyed with nickel and used in form of cupronickel for shipbuilding. This is due to in this form it is highly resistant to corrosion. Besides, copper in liquid form is used as a wood preservative which can help in restoration of original structures that are damaged due to dry rot. Unfortunately, high dose of copper can cause liver impaired, kidney failure, gastrointestinal disturbance and other health problems (Futlan *et al.*, 2011). Maximum contaminant level of copper is 1.3mg/L according to US Environmental Protection Agency (Ghassabzadeh *et al.*, 2010).

Several conventional methods have been used in order to remove toxic heavy metals from wastewater, such as chemical precipitation, coagulation, solvent extraction and filtration, evaporation, ion exchange and membrane methods (Panayotova *et al.*, 2003). Adsorption is one of the generally economical and effective processes to remove heavy metal (Li *et al.*, 2012). Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of solid or a liquid, forming a molecular or atomic film. Ion exchange resins have been developed as a main alternative for treating wastewater over the past few decades (Muraviev *et al.*, 2000). Ion exchange process was defined as ion is removed out of an aqueous solution and is replaced by another ionic species (Neumann *et al.*, 2009). Selective resins will reduce the residual concentration of heavy metal to below maximum limits (Rauf *et al.*, 2000). Numerous studies on the adsorption of metal ions on ion exchange resins such as Duolite GT-73 (Shaha *et al.*, 2000), NKA-9 (Xingcun *et al.*, 1997), and Dowex A-1 (Mathur *et al.*, 1985) have been reported. In this study, Amberlite IR-120 mixed matrix membrane chromatography is used as the adsorbent to remove copper from aqueous solution.

1.2 Problem Statement

Heavy metals can be found in various concentrations in any natural source of water, however the major treatment problems exist in the process water in the industries such as metal mining and smelting operations, foundries, metal planting and finishing, and metal fabricating plants. Heavy metals such as copper, lead and mercury are micro-pollutants and of special interest as they have both health and environmental significance due to their persistence, high toxicity and bio-accumulation characteristics. These can accumulate in living tissue, also causing various disease and disorder.

Copper is one of the heavy metals that can be found in various sources of wastewater such as electronics plating, wire drawing, copper polishing and paint manufacturing. Copper is an important trace element to human being, however, high dose of copper can cause anemia, liver and kidney damage, and stomach and intestinal irritation. Therefore, study need to be conducted in order to find method to reduce the impact of heavy metal contamination in the industrial effluent which can contribute to major water pollution.

In order to remove heavy metal from wastewater, some methods have been suggested such as chemical precipitation, coagulation, solvent extraction, filtration, and evaporation. However, most of the methods have some limitations such as requirement of several pre-treatment as well as additional treatments. Besides, some of the methods are less effective and require high capital cost (Kam *et al.*, 2002; Kim, 2002; Volesky, 1990). Precipitation followed by coagulation has been widely

employed for removal heavy metals from wastewater but this technique typically produces large volumes of sludge consisting small amount of heavy metal (Amarasinghe *et al.*, 2007). Ion exchange is one of the effective methods for removal of heavy metal ions, and its operational and economic advantages for treating electroplating rinse water have been discussed (Weltrowski *et al.*, 1996). Several advantages of ion exchange are very compact facility, easy recovery of metals, more versatile than the others methods and no secondary pollutant (Lim *et al.*, 2002).

1.3 Research Objective

The objective of this research is to investigate the feasibility of using mixed matrix membrane (MMM) chromatography using Amberlite IR-120 for the removal copper (II) from aqueous solution.

1.4 Scope of Study

In order to achieve the objective of this study, the scope of the study has been determined as followed:

- i. To prepare Amberlite IR-120 MMM based membrane at different EVAL composition, between 15 to 20 % and at 30 % Amberlite IR-120 loading.
- ii. To determine the adsorption isotherm of MMM for copper (II) binding.

CHAPTER 2

LITERATURE REVIEW

2.1 Heavy Metal

Heavy metal elements usually exist in different oxidation states, such as soil, water and air. In the water, the ion charges, solubilities and reactivities of this metal are vary widely. For their short term or long term toxic effect, the maximum permissible concentration of this heavy metal in drinking water stated in municipal and industrial discharged are closely regulated through the legislation. There are several example of heavy metal, such as copper, aluminum, magnesium and cadmium. Each of heavy metal elements has their own characteristics. Yan *et al.*, (2003) state that heavy metal present in nature and industrial waste. The presences of heavy metals in surface and groundwater cause a major inorganic contamination problem because of their mobility in natural water and ecosystems and the toxicity. There are different types of heavy metal content for different industries as shown in Table 2.1.

Table 2.1 Example of heavy metal content in effluent samples collected from different industries of Taloja industrial estate of Mumbai
(Source: Lokhande, *et al.*, 2011)

Industries	Heavy Metals (mg/L)	Year-1999							Year-2000						
		February	April	June	August	October	December	Average	January	March	May	July	September	November	Average
Engineering	Cr	27.9	31.6	27.2	24.9	27.5	38.7	29.6	30.9	34.6	40.2	27.5	20.7	28.5	30.4
	Cd	24.9	30.7	25.5	20.4	27.8	26.4	26.0	22.7	28.4	34.9	27.5	15.6	17.1	24.4
	Ni	14.9	20.1	20.1	10.5	20.1	24.0	18.3	19.6	23.6	27.4	24.0	16.2	18.1	21.5
	Zn	27.0	31.6	27.1	20.0	24.0	31.4	26.9	26.9	29.5	32.1	25.2	20.0	26.2	26.7
	Cu	21.6	26.3	26.2	12.9	15.2	23.2	20.9	19.1	24.3	32.4	20.1	13.8	19.5	21.5
	Pb	21.6	22.8	19.9	11.8	13.2	17.0	17.7	19.2	23.0	27.4	20.4	17.1	19.4	21.1
	Fe	7.6	8.7	8.0	6.2	6.2	7.1	7.3	7.0	9.6	11.5	8.3	6.0	6.8	8.2
Paper Mill	Cr	35.0	40.0	30.0	32.5	29.5	45.3	35.4	28.3	27.9	39.3	26.9	18.9	26.1	27.9
	Cd	21.1	23.2	19	14.5	23.0	19.2	20.0	27.3	27.8	31.2	31.9	21.9	25.1	27.5
	Ni	15.3	21.4	20.9	11.2	13.2	20.5	17.1	21.7	27.2	29.7	24.8	21.2	23.5	24.7
	Zn	27.0	32.2	25.6	19.7	21.1	24.7	25.1	21.9	37.3	42.6	29.3	23.7	28.2	30.5
	Cu	28.2	31.5	29.5	19.7	21.4	30.4	26.8	29.2	33.4	37.5	22.8	19.3	27.1	28.2
	Pb	17.4	23.2	21.3	14.3	17.3	16.3	18.3	23.7	27.2	31.2	23.8	20.3	22.9	24.9
	Fe	7.0	7.9	6.9	5.3	6.0	6.4	6.6	6.1	7.9	4.9	6.3	5.7	6.4	6.2
Fine Chemicals	Cr	22.1	32.1	37.3	29.3	26.3	27.5	29.1	29.2	28.3	33.0	19.6	20.1	25.7	26.0
	Cd	33.9	41.2	43.2	29.9	26.3	28.9	33.9	30.2	25.3	41.4	15.2	29.1	31.7	28.8
	Ni	29.7	32.7	31.9	21.8	20.3	27.3	27.3	34.2	27.3	37.6	13.3	12.1	25.9	25.1
	Zn	28.1	29.8	27.8	20.7	22.2	26.2	25.8	31.1	20.4	37.7	18.3	19.7	22.7	25.0
	Cu	25.2	29.4	29.9	19.3	21.2	22.7	24.6	22.9	24.6	26.1	15.5	18.3	23.1	21.8
	Pb	26.0	37.2	36.7	28.5	27.7	28.3	30.7	27.4	19.2	35.3	21.4	19.2	24.1	24.4
	Fe	7.9	9.9	8.2	6.3	6.9	7.6	7.8	7.2	7.9	8.6	7.9	6.1	7.6	7.6
Dyes	Cr	14.5	18.2	12.5	9.2	13.2	20.3	14.7	17.3	19.5	23.4	18.7	14.7	21.6	19.2
	Cd	32.2	37.1	34.3	17.3	29.1	29.4	29.9	17.5	18.6	21.3	17.8	10.8	14.3	16.7
	Ni	19.4	25.5	21.0	17.6	21.0	25.2	21.6	8.4	9.3	12.7	7.7	5.6	7.5	8.5
	Zn	39.2	61.3	29.7	21.2	37.3	41.8	38.4	17.2	19.2	21.5	14.6	8.3	13.7	15.8
	Cu	21.3	17.6	21.0	16.3	19.7	17.5	18.9	36.7	61.3	77.0	44.2	31.9	34.9	47.7
	Pb	15.2	24.5	20.7	9.3	11.0	14.3	15.8	19.7	37.2	46.3	34.8	25.7	29.6	32.2
	Fe	5.4	5.4	5.3	4.5	4.1	4.6	4.9	7.3	7.9	8.8	7.4	6.0	7.5	7.5

2.1.1 Copper

Copper is a reddish metal that occurs naturally in rock, soil, water, sediment, and, at low levels, air. The average concentration of copper in the earth's crust is about 50 parts copper per million parts soil (ppm) or 50 grams of copper per 1,000,000 grams of soil (1.8 ounces or 0.11 pounds of copper per 2,200 pounds of soil). In the periodic table of the elements, copper has its own symbol which is Cu. Copper atomic number is 29, its atomic mass is 63.546, its fusion point is 1,803°C, its boiling point is 2,567°C and it is defined as a non ferrous transition metal. Besides, copper occurs naturally in all plants and animals. Copper is an essential element for all known living organisms including humans and other animals at low levels of intake. At much higher levels of copper, toxic effects can be occurring.

From Agency for Toxic Substance and Disease Registry, (ATSDR) copper can enter the environment through releases from the mining of copper and other metals, and from factories that make or use copper metal or copper compounds. Copper can also enter the environment through waste dumps, domestic waste water, combustion of fossil fuels and wastes, wood production, phosphate fertilizer production, and natural sources. Thus, copper is widespread in the environment. According to ATSDR, around 1,400,000,000 pounds which is 640,000,000,000 grams of copper were released into the environment by industries in 2000. In addition, copper is often found near mines, smelters, industrial settings, landfills, and waste disposal sites.

2.1.1.1 Used of Copper

There are many industrial uses of copper, due to its high ductility, malleability, thermal conductivity and resistance to corrosion. According to ATSDR, copper in liquid form is used as a wood preservative. It helps in restoration of original structures that are damaged due to dry rot. It is the main component of coins for many countries. Besides, about 65% of copper that is produced is used for electrical applications. The important uses of copper include, use in power generation and transmission of electricity. It is used in transformers, motors, bush bars, generators, and etc., to provide electricity throughout the country, safely and efficiently. In case of electrical equipments, copper is used in wiring and contacts for PC, TV, mobile phones and in the circuitry.

2.1.1.2 Health Affect of Copper

From ASTDR, copper is essential for good health. Nevertheless, when copper is exposure to higher dose it can be harmful. Long-term exposure to copper dust can irritate nose, mouth, and eyes, and also can cause headaches, dizziness, nausea, and diarrhea. In addition, when drink water that contains higher than normal levels of copper, it can cause nausea, vomiting, stomach cramps, or diarrhea. Purposely high intakes of copper can cause liver and kidney damage and even death. The Environmental Protection Agency (EPA) does not classify copper as a human carcinogen because there are no adequate human or animal cancer studies.

2.2 Current Technology for Removal of Heavy Metal

2.2.1 Precipitation

Precipitation is a process of addition of coagulants such as lime, iron salts, alum, and other organic polymers (Ahalya *et al.*, 2003). Precipitation process is the most familiar method for removing heavy metals up to parts per million (ppm) levels from water (Ahluwalia *et al.*, 2007). Precipitation is a simple and cost effective method for removal heavy metal. However, it is will produces large amount of sludge containing toxic compounds (Ahalya *et al.*, 2003). Besides, its efficiency is affected by low pH and the presence of other salts (ions). These precipitation method also requires an addition of others chemicals, which finally leads to the generation of a high water content sludge, which the disposal is cost intensive (Gray, 1999). Furthermore, the precipitation with lime, bisulphide or iron exchange is lacks on the specifity and ineffective in the removal of heavy metal ions at low concentrartion (Ahluwalia *et al.*, 2007).

2.2.2 Electro-coagulation

Electro-coagulation is an electrochemical approach, where in this process an electrical current was used to remove the metals from the wastewater (Ahluwalia *et al.*, 2007). Besides removing heavy metals, electro-coagulation is also an effective method in removing suspended solids, dissolved metals, tannins and dyes. The contaminants that presents in the wastewater are sustain in the solution by the electrica charges. When these ions and other charged particles are neutrilized with

ions of opposite electrical charges provided by electrocoagulation system, they become destabilized and precipitate in a stable form.

2.2.3 Reverse Osmosis and Electro-dialysis

Reverse osmosis is a process in which heavy metals are removed by a semi-permeable membrane at a pressure greater than the osmotic pressure caused by the dissolved solids in wastewater (Ahalya *et al.*, 2003). Meanwhile, electro-dialysis is a process in which heavy metals are removed through the use of semipermeable ion-selective membranes (Ahalya *et al.*, 2003). An electrical potential and the two electrodes will cause a migration of cations and anions towards respective electrodes. Because of the alternate spacing of cation and anion permeable membranes it will cause the cells of concentrated and dilute salts to be formed. For this reverse osmosis and electro-dialysis, both methods require the use of semi-permeable membranes for the removal of heavy metal ions from wastewater. Both methods have disadvantages for the removal of heavy metal. For reverse osmosis, it is an expensive method and for electro-dialysis the disadvantage is the formation of metal hydroxides, which clog the membrane.

2.2.4 Cementation

Cementation is another type of precipitation method implying an electrochemical mechanism in which a metal with a higher oxidation potential passes into the solution (Ahluwalia *et al.*, 2007). For example, the oxidation of metallic iron, Fe (0) to ferrous iron (II) to replace a metal having a lower oxidation potential. Copper is the most commonly separated by cementation along with noble

metals such as Ag, Pb and Au as well as As, Pb, Sb and Sn can be remove in this manner.

2.2.5 Electro-winning

Electro-wining is an extensively used in the mining and metallurgical industrial operations for heap leaching and acid mine drainage. Besides, it is also used in the metal transformation and electronics and electrical industries for removal of heavy metals (Ahluwalia *et al.*, 2007). Metals like Au, Cd, Cr, Ag and Zn present in the effluents can be recovered by electro-deposition using insoluble anodes (Gray, 1999).

2.3 Adsorption

According to Geankoplis (2003), adsorption processes is one or more components of a gas or liquid stream are adsorbed on the surface of a solid adsorbent and a separation is accomplished. Usually, in commercial processes, the adsorbent is on the form of small particles in a fixed bed. The fluid will passed through the bed and the solid particles will adsorb components from the fluid. When the bed is about to saturated, the flow in this bed is stopped and the bed is regenerated thermally. The adsorbed material is thus recovered and the solid adsorbent is ready for another cycle of adsorption.

Adsorption is commonly preferred for removal of heavy metal ions due to its high efficiency, easy handling, availability of various adsorbents and cost

effectiveness (Reed *et al.*, 1997). Besides, adsorption also gives advantages of less capital investment and land, simple design rules and operation (Markovska *et al.*, 2006). In addition, adsorption process can remove both organic and inorganic constituents even at very low concentration, it is relatively easy and safe to operate, both batch and continuous equipment can be used, no sludge formation and the adsorbent can be regenerated (Mohanty *et al.*, 2005). Furthermore, adsorption is economical because it requires low capital cost.

2.4 Adsorption Isotherm

2.4.1 Freundlich Isotherm

The Freundlich isotherm Equation (2.1), which is empirical, often approximates data for many physical adsorption systems and is particularly useful for liquids:

$$q = Kc^n \quad (2.1)$$

where K and n are constant and must be determined experimentally. If log-log plot is made for q versus c, the slope is the dimensionless exponent n. The dimensions of K depend on the value of n. The linear form of this equation is given as Equation (2.2):

$$\log q = \log K + n \log c \quad (2.2)$$

2.4.2 Langmuir Isotherm

The Langmuir isotherm has a theoretical basis and is given as (2.3):

$$q = \frac{q_o c}{K+c} \quad (2.3)$$

where q_o and K is constant. q_o is kg adsorbate/kg solid and K is kg/m^3 . The equation was derived assuming that there is only a fixed number of active sites available for adsorption, that only monolayer is formed, and that the adsorption is reversible and reaches an equilibrium condition. The linear form of this equation is given as (2.4):

$$\frac{1}{q} = \frac{K}{q_o c} + \frac{1}{q_o} \quad (2.4)$$

2.5 Adsorbents for Removal Heavy Metal

An adsorbent is a substance that is generally porous in nature and with a high surface area that can adsorb substances onto its surface by intermolecular forces. There are various types of adsorbent that has been studied for the removal of heavy metal.

2.5.1 Diethylenetriamine-grafted Poly (glycidyl methacrylate) (PGMA-DETA)

From Lui *et al.*, (2006), PGMA-DETA adsorbent achieved excellent adsorption performance in copper ion removal and the adsorption was most efficient

at pH 3. Besides, the adsorption isotherm data fitted the Langmuir-Freundlich model and the adsorption capacity reached 1.5mmol/g. The adsorption process was fast with adsorption equilibrium time less than 1 to 4 hr. The X-ray photoelectron spectroscopy (XPS) exposed that there were different type of amine sites on the surface of PGMA-DETA adsorbent. However, copper ion adsorption was mainly through forming surface complexes with the neutral amine groups on the adsorbent and was resulting in better adsorption performance at a higher solution pH value.

2.5.2 Tea Waste

Tea waste is a good adsorbent for removal of Cu and Pb from the wastewater. Amarasinghe *et al.*, (2007) showed that the adsorption capacity was highest at solution pH range 5 to 6. The equilibrium data for this study were fitted to Langmuir and Freundlich isotherms and the highest metal uptake for Cu and Pb is 48 and 65 mg/g respectively. The kinetic data for this study, it is revealed that Pb and Cu uptake was fast with 90% or more of the adsorption occurring within first 15-20 of the contact time.

2.5.3 Membrane Bioreactor

A membrane with suitable pore size can remove almost all pollutants without using any chemical. Moslehi *et al.*, (2008) showed that by using membrane bioreactor, the COD removal was increased in all conditions. The removal efficiency was shown to be about 95% with the concentration of chromium is below 50 mg/l and at these concentrations, chromium has no toxic effect on microorganism.

Membrane also showed an increase of efficiency from 44% to 65% in the case of having 50mg/l of lead.

2.5.4 Polyvinylalcohol Membranes

According to Denizli *et al.*, (2000) study, the maximum adsorption of heavy metal ions onto the Cibacron Blue F3GA-attached affinity membranes for non-competitive conditions were 16.9 mmol/m² for Hg (II), 19.2 mmol/m² for Cu (II), 25.8 mmol/m² for Pb (II), and 32.4 mmol/m² for Cd (II). The regeneration of polyvinylalcohol membranes was complete by using 0.1M HNO₃ in 30 minutes. The adsorption rates for this study were very high and the equilibrium was achieved within 10 minutes. In addition, the adsorption isotherm was fitted with Langmuir isotherm equation.

2.5.5 Novel Nanofiber Membrane (M-1)

From Sang *et al.*, (2008) study, it shows that the rejections of copper in the simulated groundwater by MEF using M-1 can reach more than 73 %, the rejection of lead more than 82 % and the rejection of cadmium is more than 91 %.

2.6 Ion Exchange

Many synthetic exchangers have been developed because of the understanding and the reputation of ion exchangers raise over the last few decades.

The first ion exchangers used natural zeolites, now there are synthetic zeolites and polymeric ion exchangers (Jorgensen, 2002).

Geankoplis (2003) state that ion exchange processes are basically chemical reactions between ions in solution and ions in an insoluble solid phase. The techniques used in ion exchange so closely resemble those used in adsorption that for the majority of engineering purposes ion exchange can be considered as a special case of adsorption process. In ion exchange process, certain ions are removed by the ion exchange solid. Since the electroneutrality must be maintained, the solid releases replacement ions to the solution. Usually it is used matrices for ion exchange is synthetic organic ion exchange resins (Ahluwalia *et al.*, 2007).

From Neumann *et al.*, (2009) study, ion exchange is an ion removed out of an aqueous solution and is replaced by another ionic species. There are synthetic materials (resin) available that have been specially designed to enable ion exchange operations at high performance levels. Resins are either cationic or anionic. Cationic resins are the materials that have reactive groups that can give up positive ions in exchange of other positive ions from the liquid phase. Meanwhile anionic resins are the materials that have reactive groups that can give up negative ions in exchange of other negative ions from the liquid phase.

Neumann *et al.*, (2009) state that the resins are typically beads or granular particles having a diameter of about 0.3 to 1.3 mm. The beads contain around 50% of water and since the water is dispersed homogenously through the bead, so the water soluble materials can move freely, in and out. For each of the monomer units of the

polymer, there is functional group that attached to it which is can interact with water soluble species such as ions (positively or negatively charged).

Because of the functional groups are also charged, so the interaction between ions and functional groups is exhibited via electrostatic forces. The functional groups that have positively charged such as a quarternary amine will interact with anions. Meanwhile the functional groups that have negatively charged such as a carboxylic acid group will interact with cations.

In addition, the binding force between the attached ion and functional group is relatively loose. The exchange can be reversed by another ion passing across the functional group. After that another exchange reaction can take place and so on and onward. One exchange reaction can follow another reaction (Neumann *et al.*, 2009).

There are several advantages in ion exchange for removal of heavy metal such as recovery of metal value, selectivity, less sludge volume produced and the meeting of strict discharge specifications (Rengaraj *et al.*, 2001). Besides, it has the ability to achieve ppb levels of clean up while handling a relatively large volume (Ahluwalia *et al.*, 2007). States by Lim *et al.*, (2002), ion exchange are very compact facility, easy recovery of metals, more versatile than the others methods and no secondary pollutant.

2.7 Resin for Ion Exchange

There are many types of resin for ion exchange in removal heavy metal such as Amberlite IRN-77, SKN1, Dowex M4195, Lewatit S 100 and Amberlite IR-120.

Table 2.1 shows the study of removal heavy metal using different types of resin.

Table 2.2 Removal of heavy metal using different types of resin.

Author	Adsorbent	Results
Kang <i>et al.</i> , (2004)	Amberlite IRN-77	<ul style="list-style-type: none"> The maximum amounts of metals adsorbed by Amberlite IRN-77 were 74.63 mg Co, 62.11 mg Ni, and 46.95 mg Cr per unit gram of wet resin. The adsorption behavior was fitted to the Langmuir isotherms.
Rengaraj <i>et al.</i> , (2001)	SKN1	<ul style="list-style-type: none"> SKN1 cation exchange resin is capable of removing 100 mg/l chromium from the aqueous solution to the extent of 98%. The adsorption process was fitted with the Freundlich isotherm.
Gode <i>et al.</i> , (2006)	Lewatit S 100	<ul style="list-style-type: none"> The ion-exchange process, which is pH dependent show maximum removal of Cr(III) in the pH range 2.8–4.0 for an initial Cr(III) concentration of 1.0×10^{-3} M. The maximum ion-exchange capacity of 0.39 mmol of Cr(III)/g was achieved at optimum pH values of 3.5.

2.8 Definition of Membrane

According to Mulder (2003), membrane is a selective barrier between two phases, the term 'selective' being inherent to a membrane or membrane process. Membranes also can be classified into different point of view. First is the classification by the nature. For example is biological or synthetic membrane. Besides, morphology or structure also is includes in the classifying of membrane.

Another definition of membrane that state by Munir (2006), membrane is a physical barrier that allows certain compounds to pass through, that depending on their physical and/or chemical properties. Membrane usually consists of porous support layer with a thin dense layer on top that forms the actual membrane.

2.9 Types of Membrane Process

Membrane process can be broadly placed into four categories, which is classification being dependent on the pore size of the membrane (Coppen 2004). Reverse osmosis, nanofiltration, ultrafiltration and microfiltration are the types of membrane process.

2.9.1 Reverse Osmosis

Reverse osmosis (RO) will separates salts and small molecules from low molecular weight solutes at relatively high pressures using membrane with NMWLs of 1 kDa or lower (Munir 2006). Reverse osmosis membranes are usually rated by

their retention of sodium chloride and it is generally used to purify tap water to purities that exceed distilled water quality, blood osmosis and blood filtration. The membrane size for reverse osmosis is $10 \lambda - 0.001 \mu\text{m}$ (Coppen 2004).

2.9.2 Nanofiltration

Nanofiltration usually was used for partial desalination, to remove for example sucrose and egg albumin (Coppen 2004). Besides, nanofiltration is used in high organic removal and moderate inorganic removal due to its characteristic that can operate at much lower pressure and passes some of the inorganic salt. Commonly nanofiltration can operate at higher recoveries but it is not effective at small molecular weight organics. The membrane size for nanofiltration is $10 \lambda - 0.001 \mu\text{m}$ (Coppen 2004).

2.9.3 Ultrafiltration

Ultrafiltration is the process of separating small particles and dissolved molecules from fluids (Munir 2006). Ultrafiltration can only separate the molecules which are differs by at least an order of magnitude in size. In addition, ultrafiltration is usually used for sterilization, clarification, and wastewater treatment (Coopen 2004). Ultrafiltration will dependent on the charge of the particles and it will more anxiety withthe size of the particles. Pressure differential is the driving force for the transport through the membrane. The membrane size for ultrafiltration is $1 \lambda - 0.01 \mu\text{m}$ (Coppen 2004).

2.9.4 Microfiltration

Microfiltration is the process of removing the particles or biological entities from fluids by passage through a microporous medium such as membrane filter (Munir 2006). This type of membrane is basically porous enough to pass the molecule of exact solution. Natural or synthetic, polyvinylidenedifluoride (PVDF), polyamides, polysulfone, polycarbonate and polypropylene are the several types of material that used to produce microfiltration membrane. Microfiltration is usually used for wastewater treatment. The membrane size for microfiltration is $0.1\mu\text{m}$ - $10\mu\text{m}$ (Coppen 2004).

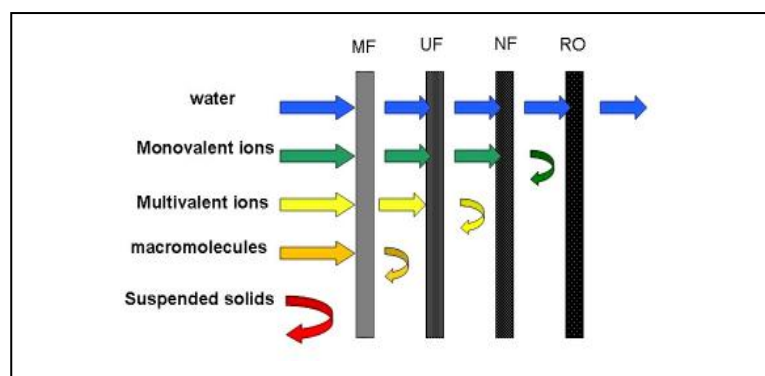


Figure 2.1 Size exclusion membranes and their function
(Source: Mulder 2003)

2.10 Mixed Matrix Membranes

Mixed matrix membranes (MMM), consist of inorganic materials such as metal oxide, zeolite, metal or carbon particles is fixed in organic polymer matrix, have been developed to improve the performance of membrane by synergistic combination of the properties of both components (Drioli *et al.*, 2009). The improvement that have been developed such as the respect to separation performance which higher selectivity or permeability and respect to membrane stability which mechanical, thermal or chemical.

The preparations of mixed matrix membrane and the resulting properties are strongly will dependent on the interactions between the different materials, and homogeneous, regular distribution and interface compatibility. The preparations of mixed matrix membrane consist of a few steps. First step is needed to separate preparation of a polymer solution and a suspension of inorganic materials. Secondly is mixing of both resulting in a mixed-matrix solution. Next is casting or spinning the solution and lastly is inducing the phase separation, basically in the framework of the NIPS process. Besides it is also an alternative method for the preparation of mixed matrix membrane that mainly will applied for the preparation of advanced reverse osmosis, nanofiltration and pervaporation membranes. The steps are mixed matrix membrane that containing inorganic oxides such as silica is the *in situ* synthesis of nanoparticles within a polymer solution via the sol-gel method. Then, it is followed by phase separation. In a special case only the separation performance of the barrier really determine by the added of inorganic (nano) materials such as by zeolites or carbon nanotubes (Sholl *et al.*, 2006).

For development of mixed matrix membrane, the proper material selection for both the matrix and the inorganic phase is essentially important. Chang *et al.*, (2007) state that the polymer properties and inorganic phase properties can affect the mixed matrix membranes morphology and separation performance. Basically, highly selective polymers can result in mixed matrix membranes with better separation performance (Mahajan *et al.*, 2000). Hence, glassy polymers with superior gas selectivity are preferred to highly permeable but poorly selective rubbery polymers (Mahajan *et al.*, 2002).

In addition, the dispersed inorganic phase as well as the continuous phase can affect the mixed matrix membrane separation properties and morphology (Aroon *et al.*, 2010). As mentioned above, porous and non porous fillers are the two main inorganic phase material that have been used for mixed matrix membrane fabrication. When a porous material is used in the polymeric matrix, its pore size distribution, surface chemistry and functional groups must be consistent with the gas molecules pairs. For example, activated carbon is appropriate for carbon dioxide/methane separation. It is because it has higher adsorption selectivity for CO₂ and the CH₄ (Anson *et al.*, 2004).

In contrast, for nonporous material on mixed matrix membrane separation, the interaction between polymer-chain segments and nanofillers as well as functional groups on the surface of the inorganic phase must be considered when these materials are added to polymer matrix (Cong *et al.* 2007).

CHAPTER 3

METHODOLOGY

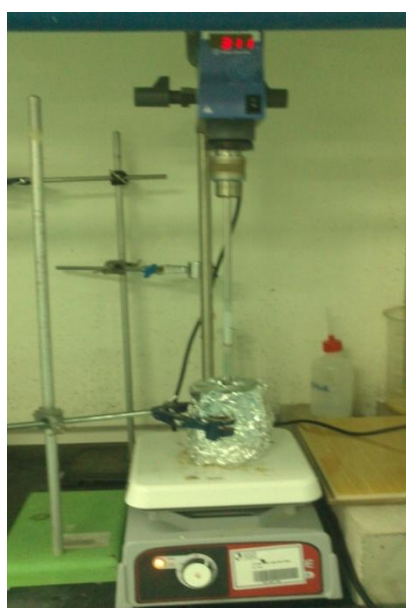
3.1 Materials

3.1.1 Chemicals

Ethylene vinyl alcohol (EVAL) with an average ethylene content of 44 mol% was purchased from Sigma Aldrich. Dimethylsulfoxide (DMSO) from System as the EVAL solvent and 1-octanol from Fluka as a non-solvent additive. Amberlite IR-120 was used as the ion exchanger resin was purchased from Sigma Aldrich. Copper (II) sulfatepentahydrate used in binding experiment was purchased from Merck. Hydrochloride acid (HCl) was purchased from Fisher Chemical used for regeneration of resin and membrane.

3.2 Preparation of Membrane Casting Solution

A polymer solution that consists of 15% of EVAL polymer and 15% 1-octanol in DMSO was prepared (Saufi *et al.*, 2009). The mixture was continuously stirred around 60°C and between 200 to 300 rpm for several hours until the EVAL pellets were fully dissolved. Amberlite IR-120 resin was ground using an ultra centrifugal grinding machine and sieved to obtain resin particles less than 45 µm. The ground resin with 30% resin loading was added to the prepared polymer solution. Then, the mixture was stirred until homogeneous casting slurry was obtained as shown in Figure 3.1(b). The steps were repeated using 20% of EVAL.



(a)



(b)

Figure 3.1 (a) Preparation of membrane casting solution in fume chamber.
(b) Homogenous casting slurry of mixed matrix membrane.

The amount of resin loading was calculated using Equation (3.1) (Saiful *et al.*, 2006):

$$R = \frac{W_r}{W_p + W_r} \times 100\% \quad (3.1)$$

where R is the percentage of resin loading, W_r is the amount of resin (g) and W_p is amount of EVAL (g).

3.3 Flat Sheet Membrane Casting Process

Homogeneous casting solution was treated in ultrasonic bath for overnight to remove any bubbles inside the solution. Conventional flat sheet casting was used to cast the MMM. The casting solution was poured into a glass plate support and then spread to form a thin film using a stainless steel block. The glass plate with the film on the surface was carefully immersed for coagulation into a water bath at temperature of 40°C. The membrane was kept in the water bath until it was fully solidified and detached from the glass. The MMM was washed with water for several times and left in the water bath overnight to make sure the traces of the solvent was completely remove from the membrane structure. Freeze dried method was used to dry the MMM without affecting the structure of the membrane. Figure 3.2 show the flat sheet membrane after freezes dried method.



Figure 3.2 Flat sheet membrane after freeze dried.

3.4 Synthetic wastewater preparation

Synthetic wastewater solution was prepared by dissolving analytical grade $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in distilled water to obtain 10 000 mg /L stock solution. The solution was dilute to the required concentration range from 1000 mg/L to 8500 mg/L for binding experiments.

3.5 Binding Experiment

The ground resin of 0.1 g and membrane with dimension of 1 cm x 2 cm were used for binding experiment. The adsorbent were added to 15 ml of copper solution in centrifuge tube at different concentration range 1000 mg/L to 8500 mg/L. The binding was performed on the rotator at 40 rpm for 24 hours as shown in Figure 3.3.

The remaining copper concentration after binding was measured using Atomic Absorption Spectrometry (AAS) method.

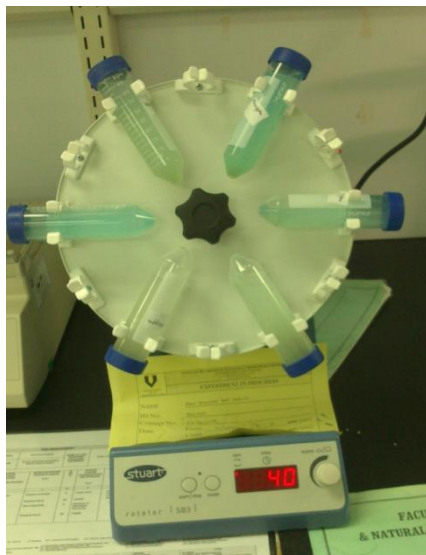


Figure 3.3 Rotate the centrifuge tube for copper binding.

The binding capacity for ground resin and membrane was calculated using Equation (3.2):

$$q = \frac{V \times (C_o - C_f)}{m} \quad (3.2)$$

where, q is dynamic binding capacity (mg Cu/g adsorbent), V is the volume of Cu solution (L), C_o is initial Cu concentration (mg/L), C_f is Equilibrium Cu concentration (mg/L) and m is the mass of adsorbent (g)

3.6 Regeneration of Adsorbent

In order to recover metal ions and for a possible re-use of the membrane, membrane regeneration were investigated. EVAL membrane and cation exchanger MMM were selected for the regeneration experiments. The membranes were put on the rotator in 15 ml centrifuge tube of copper ion solutions with 1000 ppm and 5000 ppm for 24 hours. After calculating the amount of copper ion adsorbed, the membranes were washed with deionized water and then immersed in 50 ml of 0.1M HCl solution about 6 hours. The concentration of copper ion in regeneration solution was measured by AAS to calculate the percentage of the recovery.

3.7 Atomic Absorption Spectrophotometry (AAS) Analysis

Atomic absorption spectrophotometry (AAS) model Z-500 Series with an air-acetylene flame and hollow cathode lamp for Cu was used to measure the concentration of the copper ion in solution. The standard curve was prepared from the copper concentration of 10 ppm, 30 ppm, 80 ppm and 100 ppm to determine the concentration in unknown samples. The absorbance for each sample was read in triplicate.

3.8 Pure Water Flux Test

Pure water flux was measured using Amicon stirred cell Model 8200. The MMM was placed into the permeation cell and filled with distilled water. Then, the nitrogen gas was supplied at 0.5 bar to push the water flow through the membrane.

The time taken to reach 10 mL permeate was recorded to calculate the water flux.

The water flux was calculated using Equation (3.3):

$$J = \frac{V}{At} \quad (3.3)$$

Where V is the total volume of pure permeates (L), A is the membrane area (m²) and t is the operation time (s)

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Introduction

In this chapter, the results of copper binding for the ground resin, EVAL membrane and MMM was discussed.

4.2 Copper Binding for Ground Resin, EVAL Membrane and Cation Exchanger MMM

MMM with 30% cation loading, ground cation resin and EVAL membrane were analyzed using AAS to compare the amount of copper bound to the adsorbent. Cooper ion solutions were prepared at 1000 ppm, 2000 ppm, 3000 ppm, 5000 ppm, 7000 ppm and 8500 ppm in 15 ml centrifuge tube. The amount of copper binding was calculated using Equation (3.2) with the detail calculation showed in Appendix

B. Table 4.1 show the copper binding capacity for ground resin, EVAL membrane and cation exchanger MMM.

Table 4.1 Copper binding capacity for ground resin, EVAL membrane and cation exchanger MMM.

Contact Medium	Initial Concentration (ppm)	Equilibrium Concentration (ppm)	Copper Binding (mg Cu/g adsorbent)
Ground Resin	1000	5.71	149.14
	2000	17.69	297.35
	3000	27.24	445.91
	5000	53.11	742.03
	7000	71.00	1039.35
	8500	86.09	1262.09
	EVAL Membrane	1000	12.30
2000		21.84	4363.59
3000		33.86	6094.81
5000		52.59	9276.39
7000		73.39	15057.85
8500		89.68	15968.96
Cation Exchanger MMM		1000	13.62
	2000	24.00	1127.00
	3000	35.87	1544.34
	5000	56.15	2787.89
	7000	78.38	3734.69
	8500	92.65	4723.23

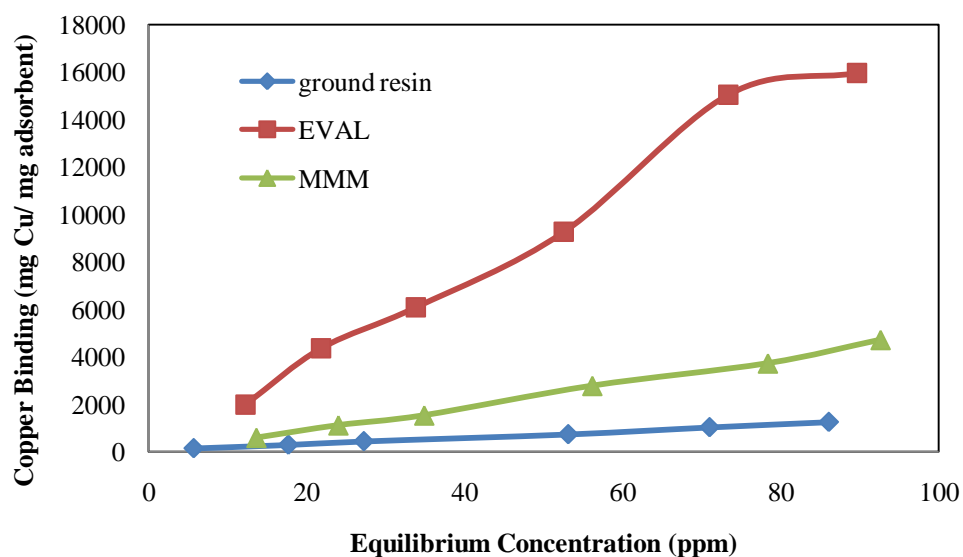


Figure 4.1 Graph of copper binding versus equilibrium concentration for ground resin, EVAL membrane and cation exchanger MMM.

Figure 4.1 shows that EVAL membrane was adsorbed high number of copper compare to cation exchanger MMM and ground resin. It is observed that all adsorbent show positive response towards copper binding. The maximum copper binding for EVAL membrane was 15968.96 mg Cu/g adsorbent at 8500 ppm. Meanwhile the copper binding for cation exchanger MMM was 4723.23 mg Cu/g adsorbent and for ground resin was 1262.09 mg Cu/g adsorbent at 8500 ppm. The binding order achieved in this study is quite strange because EVAL membrane itself had high copper binding compare to the cation resin based adsorbent. No detail explanation is possible to justify this result.

4.3 Effect of EVAL Composition on Copper Binding in MMM

The copper binding to the MMM was measured using cation exchanger MMM prepared from different EVAL content of 15% (called as MMM15) and 20%

(called as MMM20). The cation resin for both MMM15 and MMM20 was fixed at 30% cation loading relative to EVAL content. Table 4.2 and Figure 4.2 show the copper binding capacity for MMM15 and MMM20. At initial copper concentration of 8500 ppm, it show that MMM15 gave higher copper binding of 5688.190 mg Cu/g adsorbent compare to MMM20 that had a binding capacity of 4723.23 mg Cu/g adsorbent. However, the binding capacity trend was not differs too much for both MMM. Both membrane show increase copper removal efficiency as the equilibrium concentration increase similar trend achieve by Gode et al. (2006).

Table 4.2 Copper binding for MMM prepared using different EVAL content

Contact Medium	Initial Concentration (ppm)	Equilibrium Concentration (ppm)	Copper Binding (mg Cu/g adsorbent)
MMM 15	1000	12.79	611.907
	2000	23.56	1294.611
	3000	36.13	1916.295
	5000	55.34	3103.34
	7000	104.9	4458.04
	8500	119.4	5688.190
MMM 20	1000	13.62	601.45
	2000	24.00	1127.00
	3000	35.87	1544.34
	5000	56.15	2787.89
	7000	78.38	3734.69
	8500	92.65	4723.23

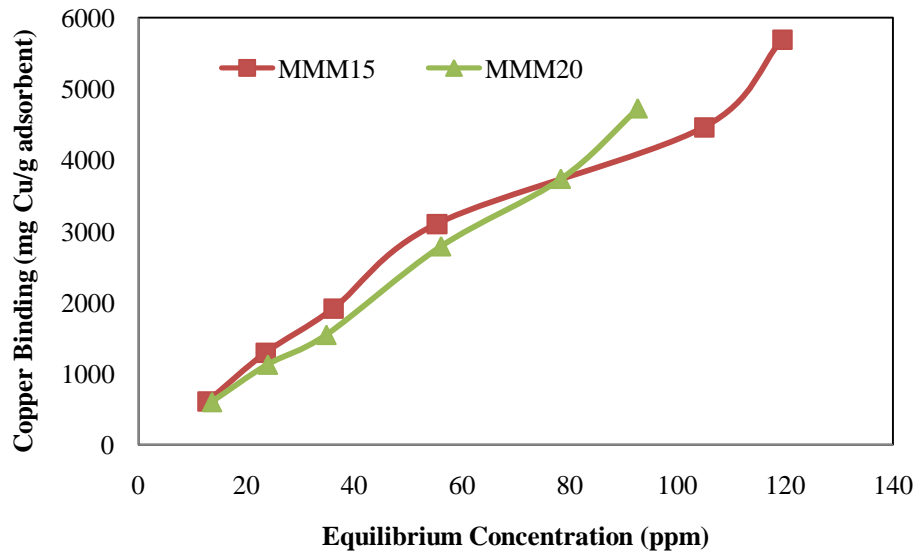


Figure 4.2 Copper binding versus equilibrium concentration for MMM15 and MMM20.

4.4 Regeneration of Adsorbent

Bound membrane after copper adsorption was regenerated by firstly washing with deionized water about 1 hour and followed by incubation in 0.1M HCl for about 6 hours at room temperature. The regeneration percentage MMM20 was compared with EVAL membrane as shown in Figure 4.3. Obviously, more effective regeneration was obtained in MMM20 compared to EVAL membrane. MMM20 shows the percentage Cu recovery about 99.86% compared to 98.86% showed by EVAL membrane.

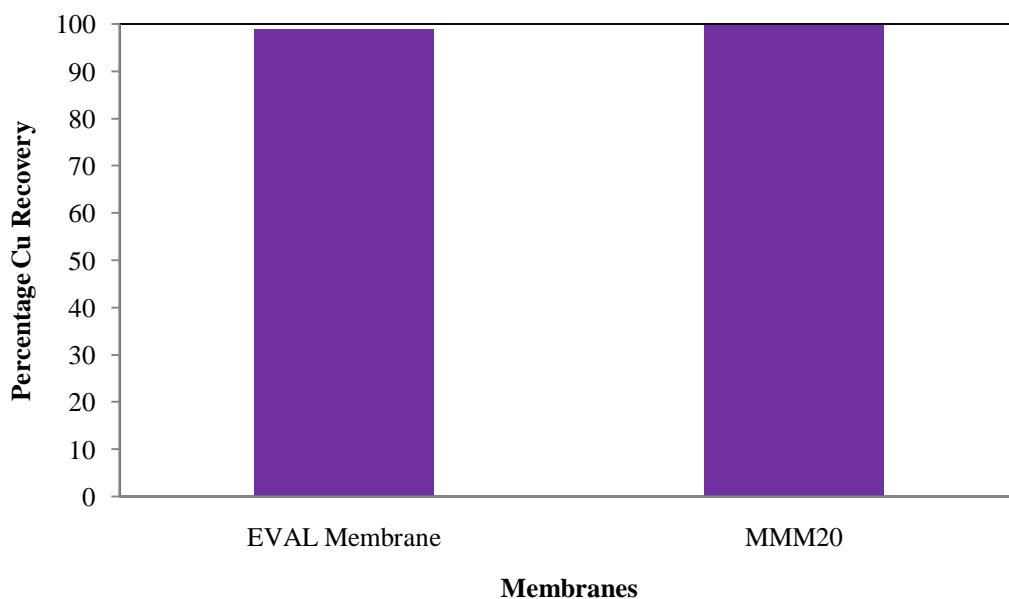


Figure 4.3 Comparison of copper recovery between EVAL membrane and MMM20

4.5 Pure Water Flux

Flux is the amount of water passed through the membrane per unit time per unit surface area. Figure 4.4 shows the comparison of water flux for MMM15 and MMM20 prepared at different of EVAL composition (15% EVAL and 20% EVAL). From figure above it shows that at 15% EVAL gave the higher flux with 0.5512 L/m².s compare to 20% EVAL with 0.1731 L/m².s. According to Baker (2004), flux is inversely proportional to thickness of the membrane where the more thickness of the membrane will give a lower flux. In this study, 20% EVAL MMM has more polymer content compare to 15% EVAL MMM. So the flux for 20% EVAL MMM is less than 15% EVAL MMM.

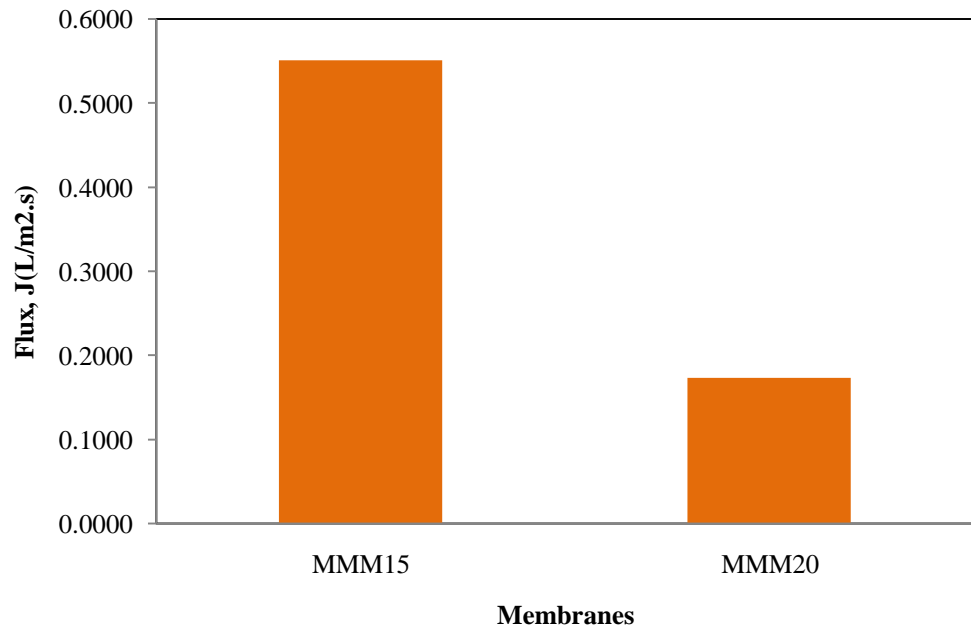


Figure 4.4 Graph of water flux with MMM15 and MMM20.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this study, mixed matrix membrane (MMM) was developed and investigated for adsorption of copper ions from aqueous solutions. Amberlite IR-120 was used as active cation resin in MMM.

MMM15 prepared from 15% EVAL content had a binding capacity of 5688.190 mg Cu/g MMM at 8000 ppm. For MMM20 membrane, the binding capacity of copper was 4723.23 mg Cu/g MMM at 8000 ppm. The regeneration of EVAL membrane and MMM20 using 0.1M HCl give the higher regeneration of MMM20 than pure EVAL membrane, the regeneration was higher for 20% EVAL compare to EVAL membrane. 99.86% of Cu recovery was obtained from MMM20 and 98.89% Cu recovery for EVAL membrane. MMM15 gave higher flux compare to MMM20. The value of water flux MMM15 and MMM20 was 0.5512 L/m².s and 0.1731 L/m².s respectively.

5.2 Recommendations

Removal of heavy metal using mixed matrix membrane (MMM) can be improved by prepared MMM using another type of polymer such as polyethelene mine, polyvinyl alcohol and polysulfone. Kagaya *et. al.*, (2009) state that polythioamide can achieved until 100% removal of mercury. This study can be further improved by optimize the pH used for the copper removal. Copper are more selective in acidic condition and copper removal can be achieved until 99.6% with pH 2.5 (Nguyen *et al.*, 2009). In addition, removal heavy metal using MMM can be improved by mixed more than one type of cation resin to extend the adsorption for other metal. This can be done for another future research to compare the effects of MMM for removal heavy metal.

REFERENCES

- Abdel Seman, O.E., Reiad, N.A., & ElShafei, M.M. (2011). A study of the removal characteristics of heavy metals from wastewater by low cost adsorbents. *Journal of Advanced Research*, 2, pp. 297-303.
- Ahalya, N., Ramachandra, T.V., & Kanamadi, R.D. (2003). Biosorption of Heavy Metals. *Research Journal Of Chemistry And Environment*, Vol.7(4).
- Alguacil, F.J., (2003). The removal of toxic metals from liquid effluents by ion exchange resins. Part III: Copper(II)/Sulphate/Amberlite 200W. *Rev. Metal Madrid* 39, pp 205-209
- Ahluwalia, S.S, & Goyal, D. (2007). Microbial and plant derived biomass for removal of heavy metals from wastewater. *Bioresource Technology* 98, pp. 2243–2257.
- Amarasinghe, B.M.W.P.K., & Williams, R.A. (2007). Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater, *Chemical Engineering Journal*, Vol. 132, pp. 299-309.
- Anson, M., Marchese, J., Garis, E., Ochoa, N., & Pagliero, C. (2004) ABS copolymer-activated carbon mixed matrix membranes for CO₂/CH₄ separation. *J. Membr. Sci.* 243, pp. 19–28.
- Argun, M.E, Dursun S. (2008) A new approach to modification of natural adsorbent for heavy metal adsorption. *Bioresource Technol*;99(7):2516–27.
- Aroona, M.A., Ismail, A.F., Matsuura, T., & Montazer-Rahmati, M.M. (2010). Performance studies of mixed matrix membranes for gas separation: A review. *Separation and Purification Technology* 75, pp. 229–242.
- Baker, R. W. (2004). *Membrane technology and applications*. New York: John Wiley and Sons.
- Chen, T.X., Nie, H.L., Li, S.B., & Branford-White, C. (2009). Comparison: adsorption of papain using immobilized dye ligands on affinity membranes, *Colloid Surf. B* 72, pp. 25-31.
- Chung, T.S., Jian, L.Y., Lia, Y., & Kulprathipanja, S. (2007). Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation, *Prog. Polym. Sci.* 32, pp. 483–507.

- Cong, H., Radosz, M., Towler, B.F., & Shen, Y. (2007). Polymer–inorganic nanocomposite membranes for gas separation, *Sep. Purif. Technol.* 55, pp. 281–291.
- Coppen, J. (2004). *Advanced Wastewater Treatment Systems*.
- Dabrowski, A., Hubicki, Z., Podkoscielny, P., & Robens, E. (2004). Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method. *Chemosphere* 56, pp. 91–106.
- Dave, R.S., Dave, G.B., & Mishra, V.P. (2011). Removal of Nickel from electroplating wastewater by weakly basic chelating anion exchange resins: Dowex 50x4, Dowex 50x2 and Dowex M4195. *Journal of applied science in environmental sanitation*, vol. 6, no.1, pp. 39-44.
- Demirbas, A., Pehlivan, E., Gode, F., Altun T., & Arslan, G. (2005). Adsorption of Cu(II), Zn(II), Ni(II), Pb(II), and Cd(II) from aqueous solution on Amberlite IR-120 synthetic resin. *Journal of Colloid and Interface Science* 282, pp. 20–25.
- Denizli, A., Say, R., & Arica, Y. (2000). Removal of heavy metal ions from aquatic solutions by membrane chromatography. *Separation and Purification Technology* 21, pp. 181–190.
- Drioli, E., & Giorno, L. (2009). *Membrane Operations, Innovative separations and transformations*. Wiley-Vch.
- Fabiani, C. (1992). Metal removal from aqueous wastes by means of membrane hybrid processes. In: Aimar, P., Apt'el P. (Eds.), *Recent Progress in Genie des Procédés, Membrane Processes Water Treatment—Pervaporation*. Lavoisier Press, Paris 6, 211.
- Futalan, C.M., Kan C.C., Dalida, M.L., Hsien, K.J., Pascua, C., & Wan, M.W. (2011). Comparative and competitive adsorption of copper, lead, and nickel using chitosan immobilized on bentonite, *Carbohydr. Polym.* 83, pp. 528-536.
- Geankoplis, C.J. (2003). *Transport Processes and separation process principle (includes unit operation)*. New Jersey: Pearson Education, Inc.
- Ghaee, A., Shariaty-Niassar, M., Barzin, J., and Matsuura, T. (2010). Effect of chitosan membrane morphology on copper ion adsorption, *Chem. Eng. J.* 165, 46-55.

- Ghassabzadeh, H., Mohadespour, A., Torab-Mostaedi, M., Zaheri, P., Maragheh, M.G., and Taheri, H. (2010). Adsorption of Ag, Cu and Hg from aqueous solutions using expanded perlite, *J.Hazard. Mater.* Vol. 177, pp. 950-955.
- Godea, F., & Pehlivan, E., (2006). Removal of chromium(III) from aqueous solutions using Lewatit S 100: The effect of pH, time, metal concentration and temperature. *Journal of Hazardous Materials B136*, pp330-337.
- Gray, N.F., 1999. *Water Technology*. John Wiley & Sons, New York, pp. 473-474.
- Hellferich, F., (1962). *Ion-Exchange*, McGraw-Hill Book Company Inc, San Francisco.
- Jha, M.K., Nguyen, N.V., Lee, J.C., Jeong, J., & Yoo, J.M., (2009). Adsorption of copper from the sulphate solution of low copper contents using the cationic resin Amberlite IR 120. *Journal of Hazardous Materials* 164, pp 948-953.
- Jorgensen, T. C., (2002). *Removal Of Ammonia From Wastewater By Ion Exchange In The Presence Of Organic Compounds*. A Thesis Presented For The Degree Of Master Of Engineering In Chemical & Process Engineering, Department of Chemical & Process Engineering University of Canterbury Christchurch, New Zealand.
- Kagaya, S., Miyazaki, H., Ito, M., Tohda, K., & Kanbara, T., (2010). Selective removal of mercury (II) from wastewater using polythioamides. *Journal of Hazardous Materials* 175, pp 1113-1115.
- Kang, S.Y., Lee, J.U., Moon, S.H., & Kim, K.W. (2004). Competitive adsorption characteristics of Co^{2+} , Ni^{2+} , and Cr^{3+} by IRN-77 cation exchange resin in synthesized wastewater. *Chemosphere* 56, pp. 141-147.
- Kam, S.K., Hong, J.Y., Hyun, S.S, (2002). Removal of copper ion by Na-PI synthesized from Jeju scoria [J]. *J of Kor Environ Sci*, Vol. 11, pp. 75-83.
- Kim, D.S. (2002). A study on the removal of mixed heavy metal ion using crab shell *J of Kor Environ Sci*, Vol. 11, pp. 729-735.
- Li, X., Li, Y., Zhang, S., & Ye, Z. (2012). Preparation and characterization of new foam adsorbents of poly(vinyl alcohol)/chitosan composites and their removal for dye and heavy metal from aqueous solution. *Chemical Engineering Journal*, 183, pp. 88-97.

- Lim, K.H., Kim, S.J., Joo, K.H., Lee, M.J., Kil, S.G., & Cho, S.Y. (2002). Removal of Heavy Metal-Cyanide Complexes by Ion Exchange. *Korean J. Chem. Eng.*, 19(6), 1078-1084.
- Liu, C., Bai, R., & Hong, L. (2006). Diethylenetriamine-grafted poly(glycidyl methacrylate) adsorbent for effective copper ion adsorption. *Journal of Colloid and Interface Science* 303, pp. 99–108.
- Lokhande, R. S., Singare, P. U., & Pimple, D.S., (2011). Toxicity Study of Heavy Metals Pollutants in Waste Water Effluent Samples Collected from Taloja Industrial Estate of Mumbai, India. *Resources and Environment*. 1(1): pp.13-19.
- Mahajan, R., & Koros, W.J. (2000). Factors controlling successful formation of mixed matrix gas separation materials, *Ind. Eng. Chem. Res.* 39, pp. 2692–2696.
- Mahajan, R., & Koros, W.J. (2002) Mixed matrix membrane materials with glassy polymers. Part 2, *Polym. Eng. Sci.* 42, pp. 1432–1441.
- Markovska, L.T., Meshko, V.D., & Marinkovski, M.S. (2006). Modelling of the adsorption kinetics of zinc onto granular activated carbon and natural zeolite. *J. Serbian Chem. Soc.* 71 (8–9), 957–967.
- Mathur, J.N., & Khopkar, P.K. (1985). *Solvent Extr. Ion Exch.* 3, 653.
- Matsuura, T. (1994). *Synthetic membrane and membrane separation process*, CRC Press, Boca Rotan.
- Meena, A.K, Kadirvelu, K, Mishra, G.K. Rajagopal C, Nagar, P.N. (2008). Adsorptive removal of heavy metals from aqueous solution by treated sawdust (*Acacia arabica*). *J Hazard Mater*;150(3):604–11.
- Mohanty, K., Das, D., & Biswas, M.N. (2005). Adsorption of phenol from aqueous solutions using activated carbons prepared from *Tectonagrandis* sawdust by ZnCl₂ activation. *Chemical Engineering Journal* 115, pp. 121–131.
- Moslehi, P., Shayegan, J., & Bahrpayma, S. (2008). Performance of Membrane Bioreactor in Removal of Heavy Metals from Industrial Wastewater. *Iranian Journal of Chemical Engineering*, Vol.5, No.4.
- Mulder, M. (2003). *Basic principles of membrane technology*. Amsterdam: Kluwer Academic Publishers.
- Munir, A. (2006). *Dead End Membrane Filtration*.

- Muraviev, D., Gorshkov, V., & Warshawsky, A. (2000). *Ion Exchange*, Dekker, New York.
- Nguyen, V., Lee, N., Jha, J.K., Yoo, M., & Jeong, K., (2009). Copper recovery from low concentration waste solution using Dowex G-26 resin. *Hydrometallurgy* 97, pp 237-242.
- Neumann, S. and Fatula, P., (2009). *Principles of Ion Exchange in Wastewater Treatment*. Techno Focus.
- Panayotova M., & Velikov B. (2003). Influence of zeolite transformation in a homoionic form on the removal of some heavy metal ions from wastewater. *J Environ Sci Health A Toxic Hazard Subst Environ Eng*; 38(3):545–54.
- Ramakrishna, S., Ma, Z., & Matsuura, T. (2011). *Polymer membrane biotechnology. Preparation, Functionalization and application*. Imperial College Press.
- Rauf, N., & Tahir, S.S. (2000) *J. Chem. Thermodynam.* 32, 651.
- Reed, R.A., Lin, W., Matsumoto, M.R., & Jensen, J.N. (1997). *Water Environment Res.* 69, 444.
- Rengaraj, S., Yeon, K.H., & Moon, S.H. (2001). Removal of chromium from water and wastewater by ion exchange resins. *Journal of Hazardous Materials*, B87, pp. 273–287.
- Saiful, Z., Borneman, M., & Wessling. (2006). Enzyme capturing and concentration with mixed matrix membrane adsorbers. *Journal of Membrane Science* 280, pp. 406-417.
- Salehi, E., Madaeni, S.S., Rajabi, L., Vatanpour, V., Derakhshan, A.A., Zinadini, S., Ghorabi, Sh., & Ahmadi Monfared. H., (2012). Novel chitosan/poly(vinyl) alcohol thin adsorptive membrane modified with amino functional multi-walled carbon nanotubes for Cu(II) removal from water: Preparation, characterization, adsorption kinetics and thermodynamics. *Separation and Purification Technology*, 89, pp 309-319.
- Sang, Y., Li, F., Gu, Q., Liang, C., & Chen, J. (2008). Heavy metal-contaminated groundwater treatment by a novel nanofiber membrane. *Desalination* 223, pp. 349–360
- Sarkar, B. (2002). *Heavy Metals in the Environment*. New York: Marcel Dekker, Inc.

- Saufi, S.M. & Fee, C.J. (2009). Fractionation of b-Lactoglobulin From Whey by Mixed Matrix Membrane Ion Exchange Chromatography. *Biotechnology and Bioengineering*, Vol. 103, No. 1.
- Scholl, D.S. & Johnson, J.K. (2006). *Science*, 312, 1003-1004.
- Shaha, B., Iglesias, M., Cumming, I.W., & Streat, M. (2000) *Solvent Extr. Ion Exch.* 18, 133.
- Sengupta, A.K. (2002). *Environmental Separation of Heavy Metals, Engineering Processes*, Lewis Publisher.
- Volesky, B. (1990). Biosorption and biosorbents [M]. In: *Biosorption of heavy metals*. Boston: CRC Press.
- Weltrowski, M., Martel, B. and Morcellet, M., (1996). Chitosan N-benzyl Sulfonate Derivatives as Sorbents for Removal of Metal Ions in an Acidic Medium. *J. Appl. Polym. Sci.*, 59, 647.
- Xingcun, H., & Yimin J., (1997). *Guijinshu* 18, 35.

APPENDIX A Equipments used in this research.



Figure A.1 Freeze dryer used to dry the resins.



Figure A.2 Ultra centrifugal grinder used to grind the resins.

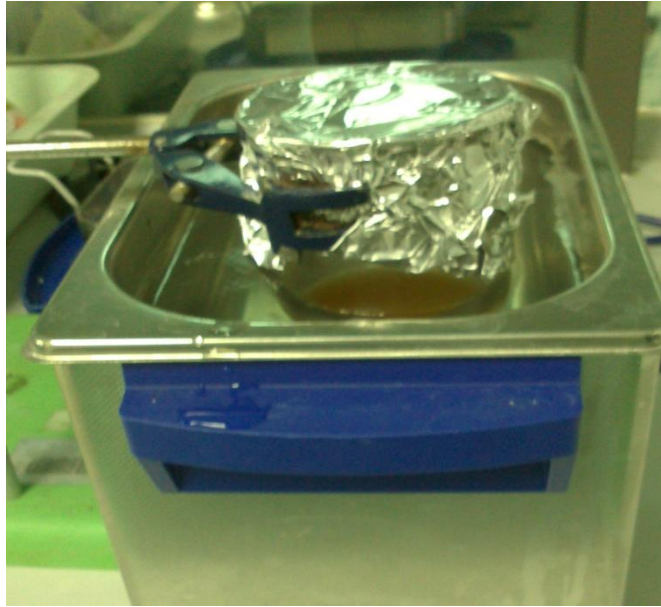


Figure A.3 Ultrasonic used to immersed homogenous casting slurry of MMM



Figure A.4 freeze dryer used to dry the flat sheet MMM.



Figure A.5 Centrifuge 5810 R used to separate the ground resin from the copper ion solution.



Figure A.6 Atomic Absorption Spectrophotometer used to measure heavy metal concentration.



Figure A.7 Amicon stirred cell used in water flux experiment.

APPENDIX B Calculation for standard curve, calculation for preparation of $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ solution and calculation for copper binding.

B.1 Calculation for standard curve.

$$M_1 = 1000 \text{ ppm} \qquad M_2 = 100 \text{ ppm}$$

$$V_1 = ? \text{ mL} \qquad V_2 = 100 \text{ mL}$$

$$M_1 V_1 = M_2 V_2$$

$$V_1 = \frac{(100 \text{ ppm})(100 \text{ mL})}{1000 \text{ ppm}}$$

$$= 10 \text{ mL}$$

➤ 10 mL of copper stock solution + 90 mL of ultra pure water.

From 100 ppm of copper standard solution, 3 samples for calibration curve were prepared (10 ppm, 30 ppm, and 80 ppm).

Table B.1 Standard copper solution for calibration curve.

Concentration (ppm)	Volume Copper Standard solution (mL)	Volume of ultra pure water (mL)
10	5	45
30	15	35
80	40	10
100	10	90

Table B.2 Absorbance for each concentration.

Concentration (ppm)	Absorbance
10	0.0061
30	0.0180
80	0.0474
100	0.0594

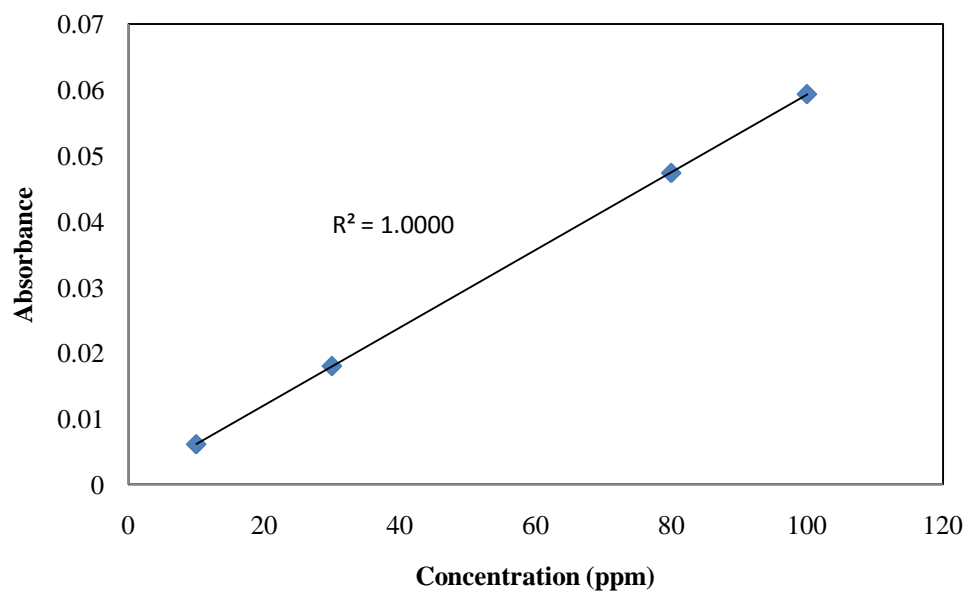


Figure B.1 Graph of standard curve.

B.2 Calculation for preparation of $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ solution.

Molecular Mass for $\text{CuSO}_4 \cdot \text{H}_2\text{O} = 249.68 \text{ g/mol}$

Molecular Mass for $\text{Cu} = 63.54 \text{ g/mol}$

$$\frac{249.68 \text{ g/mol}}{63.54 \text{ g/mol}} \\ = 3.92912 \text{ gCuSO}_4 \cdot \text{H}_2\text{O}$$

$$\frac{63.54 \text{ g/mol}}{63.54 \text{ g/mol}} \\ = 1 \text{ g Cu}$$

➤ In 3.92912 g of $\text{CuSO}_4 \cdot \text{H}_2\text{O}$, there is 1 g of Cu.

Prepare 10 000 ppm stock solution in 200 mL Volumetric flask.

$$\frac{10\,000 \text{ mg}}{\text{L}} \times 0.2 \text{ L} \\ = 2000 \text{ mg of Copper}$$

$$= 2 \text{ g} \times 3.92912 \text{ gCuSO}_4 \cdot \text{H}_2\text{O} \\ = 7.858 \text{ gCuSO}_4 \cdot \text{H}_2\text{O}$$

Preparation of $CuSO_4 \cdot H_2O$ solution,

$$M_1 = 10\,000 \text{ ppm} \quad M_2 = 1000 \text{ ppm}$$

$$V_1 = ? \text{ mL} \quad V_2 = 15 \text{ mL}$$

$$M_1 V_1 = M_2 V_2$$

$$V_1 = \frac{(10\,000 \text{ ppm})(15 \text{ mL})}{1000 \text{ ppm}} = 1.5 \text{ mL}$$

➤ 1.5 mL of $CuSO_4 \cdot H_2O$ solution + 13.5 mL of ultra pure water.

Table B.3 Preparation of $CuSO_4 \cdot H_2O$ solution.

Concentration (ppm)	Total volume (mL)	Volume $CuSO_4 \cdot H_2O$ (mL)	Volume ultra pure water (mL)
1000	15	1.5	13.5
2000	15	3	12
3000	15	4.5	10.5
5000	15	7.5	7.5
7000	15	10.5	4.5
8500	15	12.75	2.25

B.3 Calculation for copper binding

From Equation (3.2), the binding capacity for ground resin and membrane was calculated .

$$\begin{aligned} q &= \frac{V \times (C_o - C_f)}{m} \\ &= \frac{0.015 L \times (1000 - 5.71) ppm}{0.1 g} \\ &= 149.14 \frac{mg Cu}{g adsorbent} \end{aligned}$$

Table B.4: Copper Binding for Ground Resin.

Initial Concentration, C_o (ppm)	Equilibrium Concentration, C_f (ppm)	Weight, m (g)	Volume, V (L)	Copper binding (mg Cu/ g adsorbent)
1000	5.71	0.1	0.015	149.14
2000	17.69	0.1	0.015	297.35
3000	27.24	0.1	0.015	445.91
5000	53.11	0.1	0.015	742.03
7000	71.00	0.1	0.015	1039.35
8500	86.09	0.1	0.015	1262.09

Table B.5 Copper Binding for EVAL membrane.

Initial Concentration, C_o (ppm)	Equilibrium Concentration, C_f (ppm)	Weight, m (g)	Volume, V (L)	Copper binding (mg Cu/ g adsorbent)
1000	12.30	0.0074	0.015	2002.09
2000	21.84	0.0068	0.015	4363.59
3000	33.86	0.0073	0.015	6094.81
5000	52.59	0.0080	0.015	9276.39
7000	73.39	0.0069	0.015	15057.85
8500	89.68	0.0079	0.015	15968.96

Table B.6 Copper Binding for 15% EVAL MMM.

Initial Concentration, C_o (ppm)	Equilibrium Concentration, C_f (ppm)	Weight, m (g)	Volume, V (L)	Copper binding (mg Cu/ g adsorbent)
1000	12.79	0.0242	0.015	611.91
2000	23.56	0.0229	0.015	1294.61
3000	36.13	0.0232	0.015	1961.30
5000	55.34	0.0239	0.015	3103.34
7000	104.9	0.0232	0.015	4458.04
8500	119.4	0.0221	0.015	5688.19

Table B.7 Copper Binding for 20% EVAL MMM.

Initial Concentration, C_o (ppm)	Equilibrium Concentration, C_f (ppm)	Weight, m (g)	Volume, V (L)	Copper binding (mg Cu/ g adsorbent)
1000	13.62	0.0246	0.015	601.45
2000	24.00	0.0263	0.015	1127.00
3000	34.87	0.0288	0.015	1544.34
5000	56.15	0.0288	0.015	2787.69
7000	78.38	0.0278	0.015	3734.69
8500	92.65	0.0267	0.015	4723.23