CATION EXCHANGER MIXED MATRIX MEMBRANE FOR COPPER REMOVAL

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SUPERVISOR'S DECLARATION

I hereby declare that I have read this thesis and in my opinion this thesis has fulfilled the qualities and requirements for the award of the Degree of Bachelor of Engineering (Chemical)

Signature :

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Date : 30 March 2012

STUDENT'S DECLARATION

I declare that this thesis entitled **"Cation Exchanger Mixed Matrix Membrane for Copper Removal"** is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any degree.

Signature :

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DEDICATION

Special dedication to my beloved family especially my father (Ismail) and my mother (Zaharah) for their love and encouragement.

And,

Thanks to my friends, my fellow course mates and all faculty members.

For all your care, support and best wishes.

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ABSTRACT

The pollution of heavy metals into environment has attracted a major concern around the world due to their toxicity and adverse effect to the environment. In the current study, cation exchanger mixed matrix membrane (MMM) was produced for the removal of copper in wastewater effluent. Several potential commercial cation resins was screened for maximum copper removal which are Dowex M-31, Dowex MAC-3, Dowex Marathon MSC, Amberlite IR 120, Amberlite IRC 86, Amberlite IRN 150, Lewatit SP 112, Lewatit CNP-105and Lewatit TP 214. The selected resin, Amberlite IR 120 was embedded into ethylene vinyl alcohol (EVAL) polymer and casted into membrane sheet at different cation loading which were 20 and 30 weight %. The effect of copper concentration was studied in batch adsorption experiment. At initial copper concentration of 300 ppm, 20% and 30% cation loading in MMM showed 44.78 and 54.02 mg Cu/g resin binding capacity respectively. The regeneration by using both HCl and H_2SO_4 give the high percent of copper recovery on MMM with 30% resin loading which were 99.13% and 99.03% respectively. By operating chromatography operation in a membrane format, the limitation of packed bed cation exchanger chromatography such as high-pressure drop, limited flow rate and flow channeling can be overcome.

ABSTRAK

Pencemaran logam berat terhadap persekitaran telah menarik perhatian utama di seluruh dunia akibat ketoksikan dan kesan buruk kepada alam sekitar. Dalam kajian semasa, membrane matriks campuran penukar kation (MMM) telah dihasilkan untuk penyingkiran kuprum di dalam sisa efluen. Beberapa potensi komersial kation resin telah dipilih untuk penyingkiran kuprum yang maksimum seperti Dowex M-31, Dowex MAC-3, Dowex Marathon MSC, Amberlite IR 120, Amberlite IRC 86, Amberlite IRN 150, Lewatit SP 112, Lewatit CNP-105dan Lewatit TP 214. Resin yang terpilih iaitu Amberlite IR 120 telah dienapkan ke dalam etilena vinil alcohol (EVAL) polimer dan dibentukkan kepada helaian membrane pada muatan kation yang berbeza iaitu 20 dan 30% berat. Kesan kepekatan kuprum telah dikaji dalam eksperimen serapan secara kumpulan. Pada kepekatan awal kuprum 300 ppm, 20% dan 30% muatan kation dalam MMM masing-masing menunjukkan 44.78 dan 54.02 mg kuprum / g resin kapasiti pengikat. Regenerasi dengan menggunakan kedua-dua HCl dan H_2SO_4 memberikan peratus pemulihan kuprum yang tinggi pada MMM dengan muatan resin 30% iaitu 99.13% dan 99.03%. Dengan menggunakan kromatografi operasi dalam format membrane, limitasi kromatografi *packed bed* penukar kation seperti tinggi kadar penurunan tekanan, kadar aliran yang terhad dan masalah menyalurkan aliran boleh diatasi.

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AAS	-	Atomic Absorption Spectroscopy
CMP	-	Chemical and mechanical polishing
DMSO	-	Dimethyl sulfoxide
EVAL	-	Ethylene vinyl alcohol
MMM	-	Mixed Matrix Membrane
PEI	-	Polyethylene imine
PVA	-	Polyvinyl alcohol

CHAPTER 1

INTRODUCTION

1.1 Background

Nowadays, heavy metal toxic waste has turn into one of the most serious environmental problems. The treatment of heavy metals is very concern due to their uprising level in the environment. Heavy metals are very toxic and can cause some diseases to humans and animals if the effluent from the industry is not properly control and manage.

Copper is widely used in electronics industry as a major interconnecting material due to its good electrical and thermal conductivity properties. The processing and manufacture of electronic parts involve a variety of steps such as electroplating, etching, rinsing, and chemical and mechanical polishing (CMP). Electroplating of metal on wafer substrates has recently been identified as a promising technique for depositing conductive layers on substrates in the manufacture of metal interconnect lines in integrated circuits and flat panel displays (Chou and Lee, 2004).

Wastewater from this process contains relatively large amounts of dissolved copper at low concentrations generally contains ≤1000 ppm (Campbell *et. al,* 2001).

Copper is one of the heavy metals that are very toxic and hazardous to human although copper does essential work for animal metabolism. Excessive ingestion of copper brings about serious toxicological concerns such as vomiting, cramps, convulsions or even death (Nguyen *et. al,* 2009).

Various methods have been studied for the removal of heavy metal from wastewater. These method include chemical precipitation, ion-exchange chromatography, adsorption, membrane filtration, coagulation, flocculation, flotation and electrochemical.

In the current study, ion exchange membrane was used for copper removal from simulated wastewater. The preparation concept of mixed matrix membrane (MMM), that extensively used for making a membrane for gas separation and protein separation application was adopted in this study to prepare cation exchange membrane for copper removal. Selected cation resin was incorporated at specific percentage in membrane polymer solution before the membrane casting process. Based on the author knowledge, this type of cation exchanger mixed matrix membrane was firstly introduced for the copper removal in the literature.

1.2 Problem Statement

Copper removal from wastewater normally achieved through packed bed ion exchange chromatography. However by operating as packed bed configuration, several limitations have been identified such as high pressure drop, limited flow rate and flow channeling. The increase demand of copper removal from wastewater encourage to the improvement of the current techniques.

The preparation of ion exchange membrane using MMM concept is quite simple and only involve a physical modification. Various types of ion exchange resin can be incorporate into a membrane polymer solution to prepare ion exchange membrane.

The application of MMM for heavy metal removal is still new and so far it has been tested for silver removal (Ladhe *et. al.,* 2009). Therefore, in the current research the feasibility of MMM for copper removal was studied.

1.3 Objective

The main objective of this research is to prepare cation exchanger membrane using the preparation concept of MMM for the application of copper removal.

1.4 Scope

In order to fulfill the research objective, the following scopes were outlined:

i. To screen several commercial cation exchange resin that give high binding capacity to copper.
ii. To characterize the binding properties of cation exchanger MMM prepared from ethylene vinyl alcohol (EVAL) based membrane for copper removal.
iii. To study the regeneration technique of MMM after binding to the copper.

CHAPTER 2

LITERATURE REVIEW

2.1 Source of Copper Effluent

Copper is extensively used in electronics industry for the manufacturer of resistors, capacitors, inductors, semiconductor components, printed circuit boards and printed wiring assemblies. Such industries generate a large amount of copper waste streams during different steps which are electroplating, etching, rinsing, chemical and mechanical polishing and some more (Chou and Lee, 2004). Electroplating has been used to deposit copper or other metal layers with a smooth, level or uniform top surface.

Electronic process waste is one of the major contributors to heavy metal toxic waste in surface water (Rengaraj *et. al,* 2007). CMP is a process used by semiconductor industry to produce very smooth surfaces on each layer of a microchip by polishing the microchip with water slurry of silica or alumina. In making microchips for computers, pagers, phones and other electronic equipment, a large volume of purified water is used for the dilution and rinsing steps of CMP process (Campbell *et. al,* 2001).

2.2 Principles of Ion Exchange

Industrially produced ion exchange resins consist of small, porous beads that are insoluble in water and organic solvents. The most commonly used base materials are polystyrene and polyacrylate. The diameter of the beads is in a range of 0.3 to 1.3 mm. The beads contain around 50% of water, which is dispersed in the gel-structured compartments of the material as showed in Figure 2.1 (Neumann and Fatula, 2009).

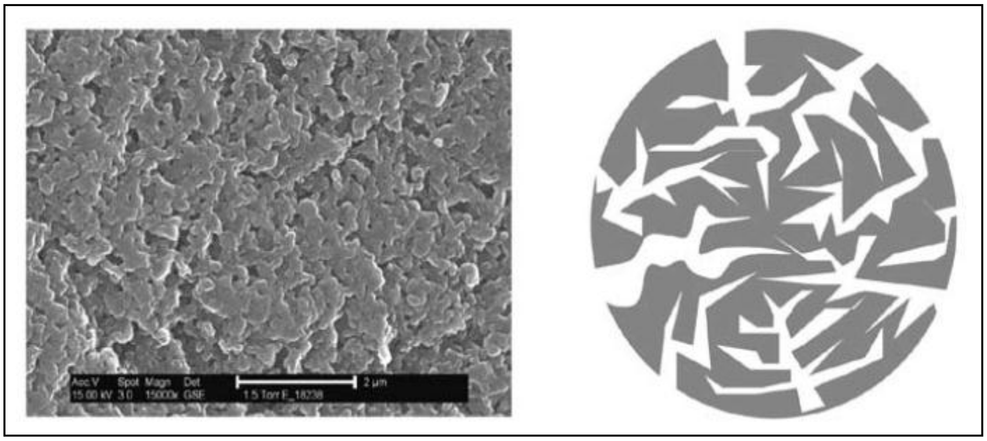


Figure 2.1: Ion exchange resin beads contain many fine pores that fill with water.

Water soluble materials can move freely, in and out since water is dispersed homogenously through the bead. In each of the monomer units of the polymer they are specific functional groups. These functional groups can interact with water soluble species, mainly with ions either positively (cations) or negatively (anions) charged.

The interaction between ions and functional groups is demonstrated by electrostatic forces since the functional groups had a charged group as showed in Figure 2.2. Positively charged functional groups interact with anions and negatively charged functional group will interact with cations.

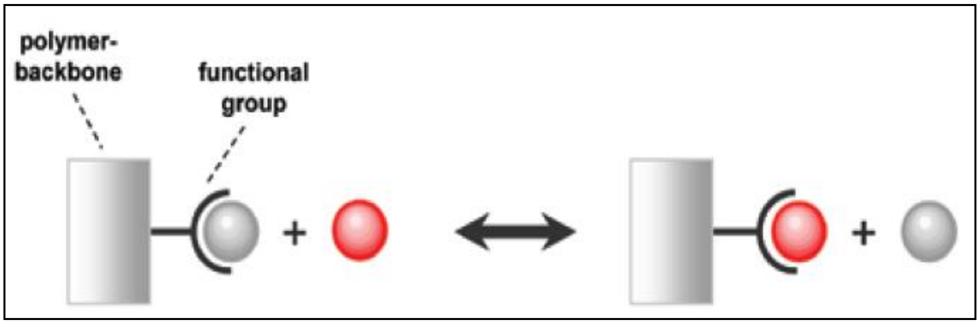


Figure 2.2: A fixed and a mobile ion are changing places in a so-called ion exchange reaction

The binding force between the attached ion and the functional group is relatively loose. The exchange can be reversed by another ion passing across the functional group. Then another exchange reaction can take place and so on.

2.3 Cation Resin

Adsorption of metals using solid resin is a proven technique for the purification and separation of metals from different aqueous solutions. Previous study has reported the adsorption of copper using various types of ion exchange resins such as Amberlite IR-120 (Hsien et al., 2006, 2007; Kocaoba, 2007; Jha *et. al*, 2009), Dowex 50 W (Pehlivan and Altun, 2006), Dowex G-26 (Winterton *et al.,* 2005), Chelex 100 and Amberlite IRC 748 (Lin and Juang, 2007). Gode and Pehlivan (2006) mentioned that the main advantages of ion exchange over other techniques are the improvement of the metals value, high selectivity, lower sludge volume and the ability to meet strict discharge specifications. Other than that, ion exchange is also widely applied in the purification of aqueous solution, extraction of acid from pickle solution, and the extraction and separation of metals. Table 2.1 below showed the characteristics of commercial cation exchange resin.

Table 2.1: Characteristics of commercial cation exchange resin (Hubicki and Wolowicz, 2008)

Resin	Ionic form	Matrix	Density, g/mL	pH	Particle size	Regenerant
Amberlite IRC 86	H^+	Gel polyacrylic copolymer	1.17 – 1.195	0-14	0.58 – 0.78 mm	2-5% HCl, 0.5-0.7% H_2SO_4,
Amberlite IR 120	H^+	Styrene divinylbenzene copolymer	>1 (vs air)	0-14	16-50 mesh	5-8% HCl, 0.7-6% H_2SO_4
Amberlite IRN 150	H^+	Styrene divinylbenzene copolymer	1.0 – 1.3	5 - 8	0.6-0.7 mm	NA
Dowex M-31	H^+	Styrene divinylbenzene (macroporous)	0.76	0-14	16-40 mesh	1-8% H_2SO_4, 4-8% HCl, 8-12% NaCl
Dowex MAC-3	H^+	Polyacrylic (macroporous)	1.18	5-14	300-1200μm (50-16 mesh)	1-5% HCL, 0.5-0.8% H_2SO_4
Dowex Marathon MSC	H^+, Na^+	Styrene divinylbenzene (macroporous)	1.20, 1.28	0-14	520-50μm, 500-50μm	1-10% H_2SO_4, 4-8% HCl, 8-12% NaCl
Lewatit Monoplus SP 112	Na^+	Cross linked polystyrene	1.24	0-14	0.65 mm	HCl, H_2SO_4, NaCl
Lewatit Monoplus TP 214	Na^+	Cross linked polystyrene	1.1	0-10	400 – 1250 μm	NA

2.4 Mixed Matrix Membrane

Mixed matrix membranes (MMM) are generally defined as the incorporation of a solid dispersed phase into a continuous polymer matrix. Theses solids can be porous (zeolites, MOFs, etc.), solid nano particles or catalysts.

This concept of mixed matrix membrane had been applied successfully for gas separation and protein separation. It is physical modification process involve the mixing of solid/resin into polymer solution by retaining the chemical properties of both materials. Mixed matrix membrane is not a new concept of membrane. In facts, early researchers have done it by filling rubbery polymer with fillers and it is used for liquid separation such as reverse osmosis (Solenberger and Withers, 1982), pervaporation, and the separation of submicro particles such as enzymes (Goldberg et al., 1979). The preparation of membrane through mixed matrix concept has several advantages as follows:

i. Variety of commercial resin available in market that can be mixed in membrane.
ii. MMM involve only physical modification
iii. The efficiency of MMM retained as in packed chromatography
iv. The membrane form is easy to scale up and making a module

The MMM combine the advantages of each medium with high separation capabilities, desirable mechanical properties and economical processing capabilities of the polymers.

2.5 Adsorption of Copper Ion

A typical method for recovering metal ions from wastewater is by using ion exchange resins. The advantages of ion exchange are high regeneration of material and very high metal selectivity.

Conventional methods such as precipitation technique are unfavorable in particular when dealing with large volumes of substance which contains heavy metal ions in low concentration. In general these ions are precipitated as hydrated metal oxides or hydroxides, sulfides or xanthiogenates using calcium oxide. Precipitation is accompanied by other processes which are flocculation or coagulation, and one major problem is the formation of large amounts of sediments containing heavy metal ions. For example, industrial wastewaters containing 0.1 g/dm^3 of Cu (II), Cd(II) or Hg(II) compounds give 10-, 9- and 5-times larger amounts of sediments, respectively; and 6 kg of sediments are obtained from one kilogram of chromates (Fabiani, 1992). Table 2.2 showed a comparison of technologies used for heavy metal removal from wastewater.

Table 2.2: Comparison of technologies used for heavy metal removal from wastewater (Farooq *et. al.*, 2010)

Method	Advantage	Disadvantage
Chemical precipitation	• Simple • Inexpensive • Most of metals can be removed	• Large amount of sludge produced • Disposal problem
Chemical coagulation	• Sludge settling • Dewatering	• High cost • Large consumption of chemicals
Ion-exchange	• High regeneration of materials • Metal selective	• High cost • Less number of metal ions removed
Electrochemical method	• Metal selective • No consumption of chemicals • Pure metals can be achieved	• High capital cost • High running cost • Initial solution pH and current density
Adsorption using activated carbon	• Most of metals can be removed • High efficiency (99%)	• Cost of activated carbon • No regeneration • Performance depends upon adsorbent
Using natural zeolite	• Most of metals can be removed • Relatively less costly materials	• Low efficiency
Membrane process and ultra filtration	• Less solid waste produced • Less chemical consumption • High efficiency (>95% for single metal)	• High initial and running cost • Low flow rates • Removal (%) decrease with the presence of other metals

Membrane based process also used for the removal of heavy metal. Thiol functionalized silica-polysulfone MMMs were successfully applied for silver ion removal from aqueous solutions. The specific nature of the thiol-silver interaction permits selective silver capture from aqueous solution containing other metal ions such as calcium and copper. This property is significant towards useful application of the MMMs, as the feed stream often contains other metal ions in high concentrations (Ladhe *et. al*, 2009).

In other work, the removal efficiency of heavy metals is about 80% to 99% by using polyethylene imine (PEI) and polyvinyl alcohol (PVA) as a based membrane (Bessbousse *et. al,* 2007). Kagaya *et. al,* (2009) used polythioamide to remove mercury and it achieved 100% of mercury removal.

2.6 Adsorption Isotherm

An adsorption isotherm is a plot of the concentration of a species on a surface as a function of its concentration to characterize an adsorption process. The quantity adsorbed is normalized by the mass of the adsorbent to allow comparison of different materials. There are two types of adsorption isotherm which are Langmuir and Freundlich isotherm.

Irving Langmuir published a new model isotherm in 1961 for gases adsorbed to solids, which retained his name. It is a semi empirical isotherm derived from a proposed kinetic mechanism. This isotherm was based on different assumptions one of which is that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules. Example of adsorption process that follows the Langmuir isotherm is illustrated in Figure 2.3. The equation of Langmuir isotherm as showed in Equation 2.1.

The Langmuir isotherm is based on four assumptions:

1. All the adsorption sites are equivalent where the surface of the adsorbent is uniform.
2. There are not interactions of adsorbed molecules.
3. All adsorption occurs through the same mechanism.
4. At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

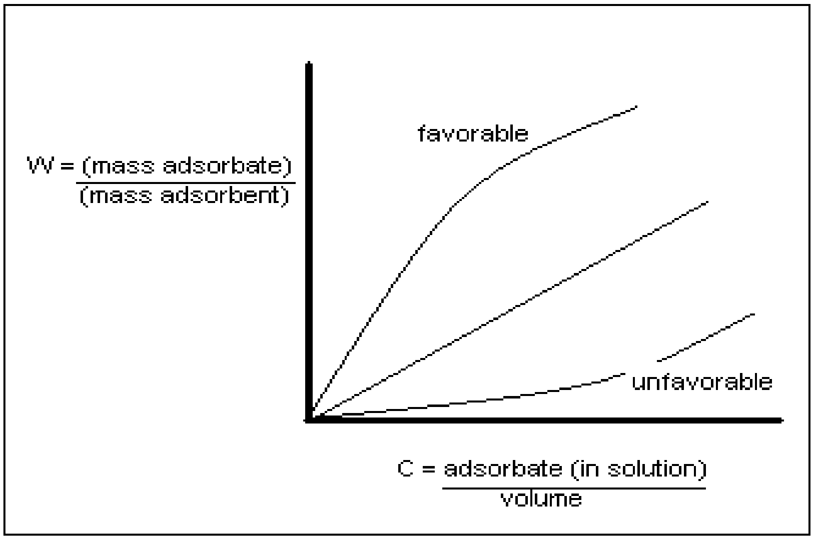


Figure 2.3: Langmuir adsorption isotherm

$$W = W_{max} \left(\frac{kC}{1+kC}\right)$$ **Equation 2.1**

Where,

W = (mass adsorbate) kg /(mass adsorbent) kg

C = adsorbate kg (in solution) / m^3 volume

k = empirical constant

While in 1909, Freundlich expressed an empirical equation for representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure. This equation is known as Freundlich Adsorption Isotherm or Freundlich Adsorption equation or simply Freundlich Isotherm as showed in Equation 2.2.

$$\frac{x}{m} = kP^{1/n}$$ **Equation 2.2**

Where,

x/m = adsorption per gram of adsorbent which is obtained be dividing the amount of adsorbate (x) by the weight of the adsorbent (m).

P= Pressure

k and n are constants whose values depend upon adsorbent and gas at particular temperature . This constant can be calculated by plotting Log x/m versus Log P as in graph showed in Figure 2.4.

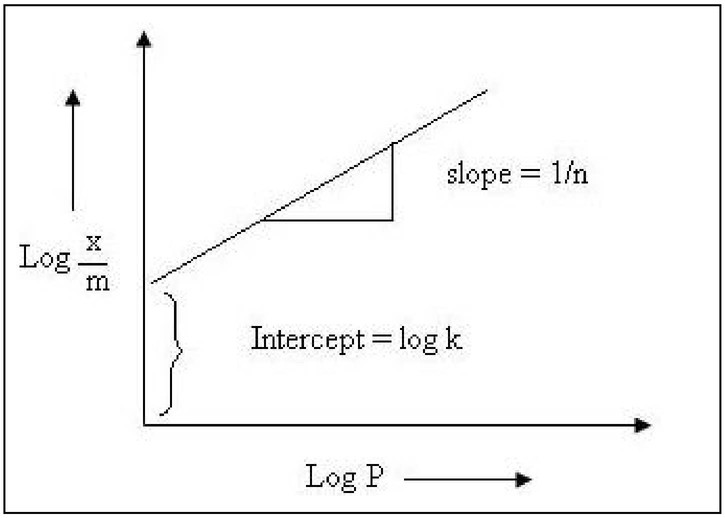


Figure 2.4: Freundlich adsorption isotherm

CHAPTER 3

METHODOLOGY

3.1 Materials

Ethylene vinyl alcohol (EVAL), 1-octanol, dimethyl sulfoxide (DMSO), and several types of commercial cation resin were purchased from Sigma Aldrich and Fluka. The resins used were Lewatit Monoplus TP 214, Lewatit Monoplus SP112, Dowex M-31, Dowex MAC-3, Dowex Marathon MSC, Amberlite IRC 86, Amberlite IRN 150 and Amberlite IR 120. Copper ion solution used in binding experiment was prepared by diluting $CuSO_4.5H_2O$ from Merck. Hydrochloride acid (HCl) and sulfuric acid (H_2SO_4) acid used for regeneration of the membrane were purchased from Fisher Chemicals.

3.2 Cation Resin Screening

The purpose of screening experiment is to select the best cation resin from the list of commercial cation resin. Cation resins were firstly washed by ultra pure water and then dried using freeze drying. Dried resin was ground using ultra centrifugal grinding machine and was passed through a series sieve tray to get resin particles less than 45 μm.

0.1 g cation resin, in centrifuge tube was equilibrated with 10 mL of phosphate buffer pH 7 for 3 hours. After equilibrium step, the solution was removed by centrifugation at 10 000 rpm for 10 minutes. 30 mL of $CuSO_4.5H_2O$ solution with 500 ppm concentration was added to tube and was left overnight for binding in rotator machine. The remaining copper concentration after binding was measured by Atomic Absorption Spectroscopy (AAS).

3.3 Preparation of Mixed Matrix Membrane

Based on the screening result, Amberlite IR 120 was further selected for preparation of mixed matrix membrane. A based polymer solution consisting of 15 wt% of EVAL polymer and 15 wt% of 1-octanol in DMSO was prepared (Saufi and Fee, 2009). All the component mixture was continuously stirred at about 60°C for more than 8 hours until all EVAL pellets were completely dissolved. Then, cation resin was mixed into the polymer solution until the mixture was become homogeneous. Figure 3.1 shows the homogenous casting slurry of the membrane.

Figure 3.1: Homogenous casting slurry of the MMM

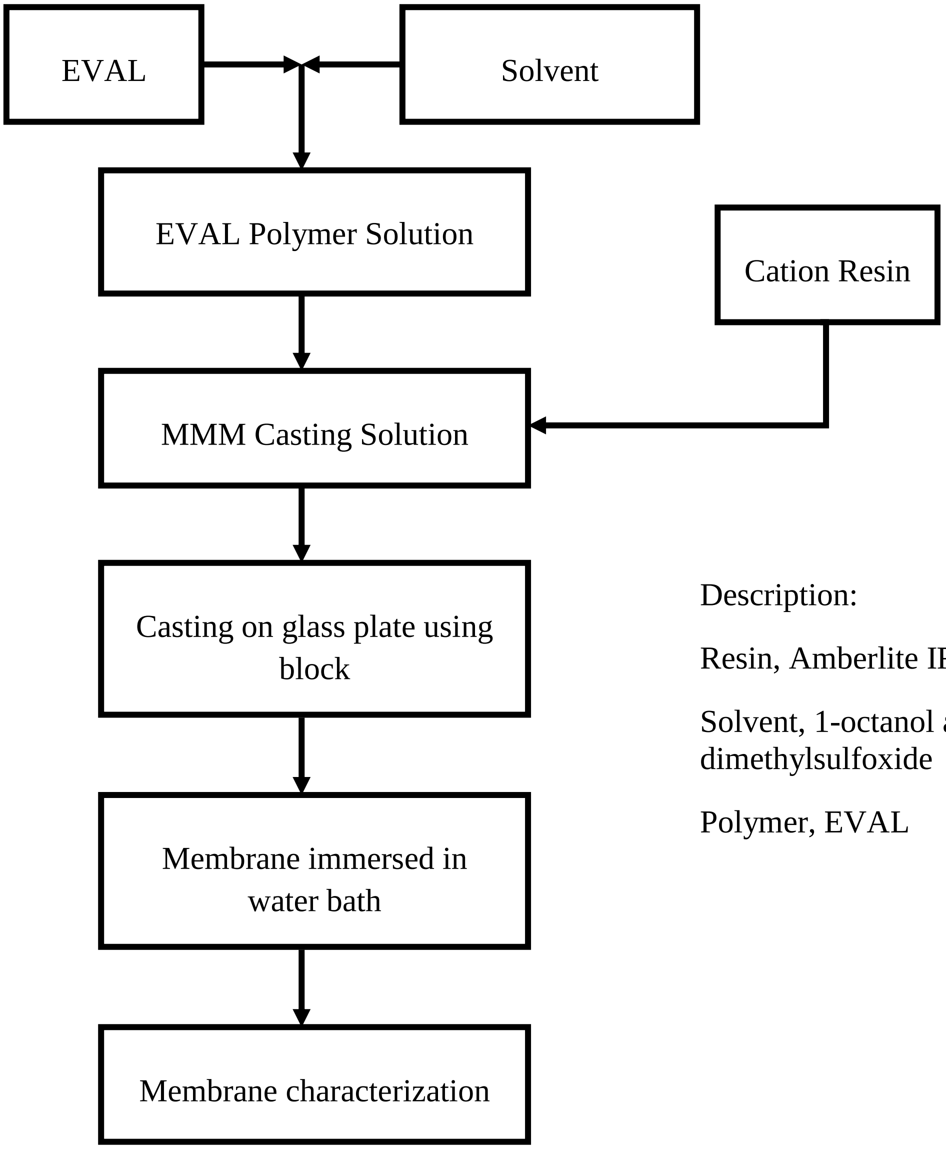
Casting solution with 20% and 30% of resin loading was prepared. The amount of cation resin loading to be mixed with EVAL polymer solution was calculated by using the equation below (Saiful *et. al*, 2006),

$$R\ loading = \frac{Wr}{Wp + Wr} \times 100 \qquad \textbf{Equation 3.1}$$

Where,
R = Percentage of resin loading
W_r = amount of cation resins (g)
W_p = amount of EVAL polymer in casting solution (g)

Prepared casting solution was treated in ultrasonic bath to remove the bubbles. Conventional casting method was used to prepare flat sheet membrane. The casting solution was pour into a glass plate then spread it to make it thin film using a casting block. The plate was immersed into a coagulation water bath until the membrane become solidified and detached from the glass plate. Figure 3.2 showed the formed flat sheet membrane and Figure 3.3 summarized the steps in making the membrane.

Figure 3.2: Flat sheet membrane formed after immersing in coagulation water bath



Description:

Resin, Amberlite IR 120

Solvent, 1-octanol and dimethylsulfoxide

Polymer, EVAL

Figure 3.3: Flow diagram for mixed matrix membrane preparation procedure (Ladhe *et. al*, 2009).

3.4 Binding Experiment

Membrane with a dimension of 2cm x 4cm was used in binding experiment. 40 ml of copper ion solution with different concentration was added to the membrane in centrifuge tube during binding. The initial copper ion solution concentration was varied from 100, 200, 300 and 400 ppm. The binding was done on rotator for overnight. Figure 3.4 shows the rotator used to make sure that the copper ion was well bind to the ground resin and membrane.

Figure 3.4: Rotate the tubes for copper ion binding

The remaining concentration of copper after binding was measured by AAS. The binding experiment also done for ground resin with similar method as above. Figure 3.5 shoes the concentration of copper ion solutions were measured after binding experiment.

Figure 3.5: Measuring the final concentration of copper ion solution after binding experiment

The binding capacity for cation resins or MMM was calculated using Equation 3.2.

$$\boldsymbol{q = \frac{V \times (C - Ce)}{m}}$$ **Equation 3.2**

Where,

$q = dynamic\ binding\ capacity, mg\ Cu/g\ resin$

$V = volume\ of\ Cu\ solution, mL$

$C = initial\ Cu\ concentration, mg/L$

$Ce = equilibrium\ Cu\ concentration, mg/L$

$m = mass\ of\ resin, g$

3.5 Regeneration of Adsorbent

Cation resin and MMM were bound with 500 ppm copper ion solution overnight. The remaining copper ion solution was measured to determine the amount of copper bound. The regeneration of bound copper on resin or MMM was tested using 6% of HCl and 3% of H_2SO_4 with a contact time about 20 minutes at room temperature. The concentration of copper ion in regeneration solution was measured by AAS to calculate the percentage of recovery.

3.6 Atomic Absorption Spectroscopy

To measure the remaining concentration of the copper ion, Atomic Adsorption Spectroscopy (AAS) were used. The standard curve for copper ion solution had been prepared for 1.5675, 3.125, 6.25, 12.5 and 25 ppm.

Figure 3.6: Polarized Zeeman Atomic Absorption Spectrophotometer (Model Z-5000 Series)

A Polarized Zeeman Atomic Absorption Spectrophotometer in Figure 3.6 is operating for water and wastewater analysis. The main unit consists of a lamp chamber, burner, graphite atomizer furnace, monochromator, detector, mechanisms and electrical circuits. In addition, it is provided with a gas controller used to control various gases in flame analysis, power supply for graphite furnace automization and auto sampler (Operation Manual: Flame, 2001).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Cation Resin Screening

Resin screening experiment were done for 8 different types of cation resins. The equilibrium concentration was measured by using AAS to calculate the copper binding capacity using equation reported in Chapter 3. The copper binding for different types of cation resins was summarized in Table 4.1.

Table 4.1: Binding capacity of cation resin to copper

Cation resin	**Copper bound, mg Cu bound/ g resin**
Lewatit Monoplus TP 214	134.96
Lewatit Monoplus SP 112	145.22
Dowex M-31	144.10
Dowex MAC-3	126.56
Dowex Marathon MSC	146.89
Amberlite IRC 86	124.74
Amberlite IRN 150	141.63
Amberlite IR 120	148.34

From the calculated result in Table 4.1, bar chart was constructed in Figure 4.1 to show the differences of copper binding clearly. Four cation resins, which showed high binding capacity to copper, was shortlisted to be used in MMM which are Lewatit Monoplus SP 112, Dowex M-31, Dowex Marathon MSC and Amberlite IR 120. Another properties for these resins were also compared in Table 4.2 such as total exchange capacity and price.

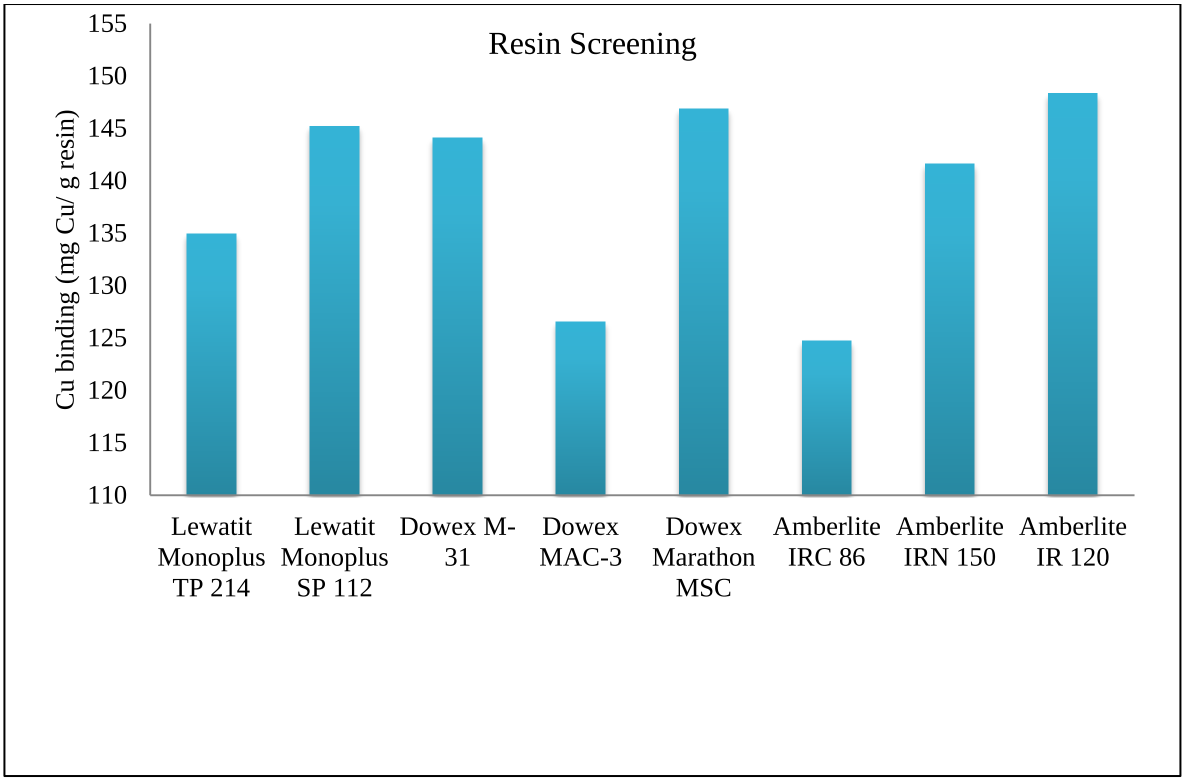


Figure 4.1: Comparison of Copper bound by each type of cation resin

Table 4.2: Criteria of cation resin selection

Cation Resin	Average mg Cu bound/g resin	Total exchange capacity,min (eq/L)	Regenerant	Price, MYR/kg
Lewatit Monoplus SP 112	145.22	1.7	HCl , H_2SO_4 or NaCl	541.96
Dowex M-31	144.10	NA	1-8% H_2SO_4 4-8% HCl 8-12% NaCl	203.49
Dowex Marathon MSC	146.89	1.6/1.7	1-10 % H_2SO_4 , 4-8% HCl or 8-12% NaCl	1580.00
Amberlite IR 120	148.34	≥ 1.8	5-8% HCl or 0.7-6% H_2SO_4	295.98

In term of resin price, Dowex M-31 was the cheapest price among all but it gives lowest binding capacity. Dowex Marathon MSC was rejected because it has very high price. The price for Lewatit Monoplus SP 112 is nearly double compare to Amberlite IR 120 plus it show low capacity to copper binding. Therefore in further experiment, Amberlite IR 120 was used to prepare MMM. In addition, Amberlite IR 120 also has good total exchange capacity more than 1.8 compare with all the three above resin. Based on Kocaoba (2007), Amberlite IR 120 was strong cation exchange resin that has been performed well for the removal of heavy metals.

4.2 Effect of Resin Loading In EVAL Polymer Solution

Preliminary experiment using 50% of resin loading was done. However, at this high loading percentage the casting solution is too viscous and difficult to form the MMM. Therefore, MMM with a resin loading of 20% and 30% was produced.

MMM with 20% and 30% of resin loading were analyzed by comparing the copper bound in the MMM. The result obtained was tabulated in Table 4.3. The effect of resin loading on copper adsorption from the copper ion solution at concentration of 100 to 400 ppm was investigated. The results in Figure 4.2 indicate that copper adsorption increased with increasing resin loading. It is obvious that the amount of metal ions adsorbed per unit mass increases with increasing resin loading and the sorption density.

With an increase in resin loading of 20% to 30%, the copper binding capacity increased from 18.51, 30.77, 44.78 and 61.53 mg Cu/ g MMM to 18.44, 36.45, 54.02 and 60.19 mg Cu/ g MMM for initial copper ion concentration 400, 300, 200 and 100 ppm respectively. As expected, increasing adsorbent loading provides a greater surface area or ion exchange sites for a fixed initial solute concentration (Gode and Pehlivan, 2006).

The result obtained were tabulated in Table 4.3 and illustrated in Figure 4.2 as follows.

Table 4.3: Result of copper binding for MMM 20%, MMM 30% resin loading and ground resin

Contact medium	**Initial concentration (ppm)**	**Equilibrium concentration (ppm)**	**Copper binding (mg Cu/ g resin)**
MMM 20%	400	70.81	61.53
	300	61.33	44.78
	200	38.14	30.77
	100	1.371	18.51
MMM 30%	400	68.95	60.19
	300	10.43	54.02
	200	3.51	36.45
	100	1.01	18.44
Ground resin Amberlite IR 120	400	92.37	122.81
	300	8.23	116.36
	200	0.44	79.27
	100	0.27	39.77

4.3 Adsorption Isotherm of Cation Resin and MMM

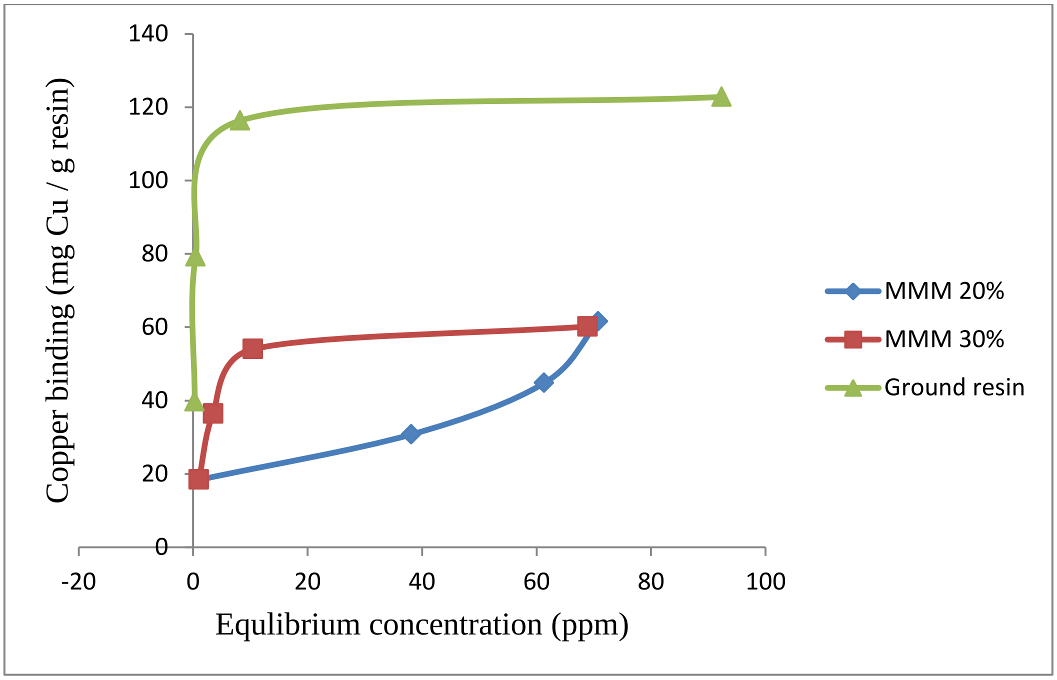


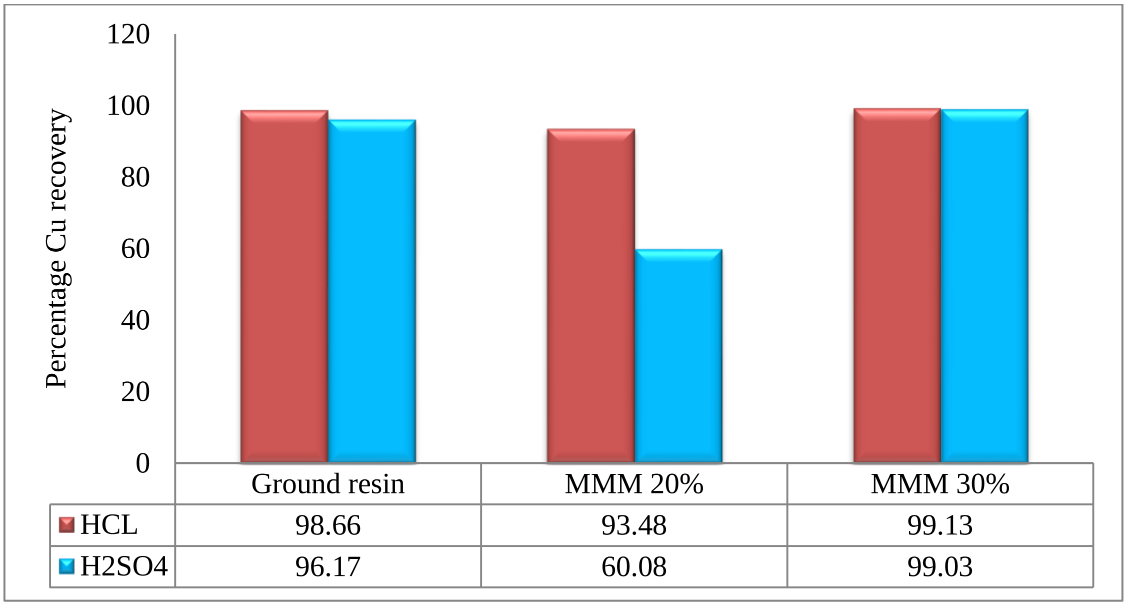
Figure 4.2: Graph of Copper binding (mg Cu/ g resin) versus Equilibrium concentration (ppm)

Equilibrium experiments were done and adsorption isotherms were obtained and presented in Figure 4.2. Sorption data have been fitted and it shows that it follows Langmuir isotherm for ground resin and MMM with 30% resin loading and Freundlich isotherm for MMM with 20% resin loading. To obtain this kind of isotherm, the initial concentration of copper ion solution were kept constant for all contact medium which were 100, 200, 300 and 400 ppm.

The Figure 4.2 shows that ground resin give the highest binding capacity of copper among others. While the copper binding capacity of MMM with 30% resin loading was higher than MMM with 20% resin loading. The difference of copper biding capacity between both MMM was discussed in part 4.2.

4.4 Regeneration

Copper desorption was performed by contact of loaded cation resin and membranes with HCl (6%) and H_2SO_4 (3%) solution as eluant. Desorption was carried out in order to recover and separate the copper ions that were simultaneously loaded on cation resin and membranes. Based on result, the percentages of copper recovery after regeneration by using HCl was higher compared to regeneration using H_2SO_4. By using HCl, the percentage of copper recovery from the cation resin and MMM with resin loading 20% and 30% were 98.66%, 93.48% and 99.13% respectively but the percents were decreased by using H_2SO_4 which were 96.17%, 60.08% and 99.03% for cation resin and MMM with 20% and 30% resin loading respectively. The result of this recovery was showed in Figure 4.3.



	Ground resin	MMM 20%	MMM 30%
🟥 HCL	98.66	93.48	99.13
🟦 H2SO4	96.17	60.08	99.03

Figure 4.3: comparison of copper recovery by using HCl and H_2SO_4

The percent of copper recovery by using HCl was higher than H_2SO_4 due to its concentration used where the concentration of HCl used was 6% while H_2SO_4 was 3%. There were a large amount of hydrogen ions provided by HCl due to the higher concentration. These hydrogen ions were able to uptake the copper ions that attached at either cation resin or MMM. Based on research that has been done by Van Nguyen *et. al*, (2009), the percentage elution increased with increasing acid concentration. Therefore, the concentration of regenerant influenced on the copper recovery.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATION

5.1 Conclusions

The concept of mixed matrix membrane which normally applied for gas separation and protein separation was successfully extended for heavy metal removal. By incorporating Amberlite IR 120 on the membrane matrix, cation exchanger MMM was developed which is capable to absorb more than 98% copper from the copper ion solution.

By increasing the resin loading in MMM, the copper binding capacity also increased accordingly. At initial copper concentration of 300 ppm, 20% and 30% cation loading in MMM showed 44.78 and 54.02 mg Cu/g resin binding capacity respectively. In this study, the copper bound was found higher by incorporating 30% of Amberlite IR 120 cation resin in membrane. A membrane with higher resin loading will provide more binding capacity but it is limited to the viscosity of casting solution to produce the MMM. For the regeneration of ground resin and MMM, it is found that found by using HCl with 6% concentration, high percentage of copper recovery up to 99.13% can be obtained.

5.2 Recommendation

There were several recommendations that can be taken for further study in order to improve the efficiency of MMM in heavy metals removal.

i. Prepared and characterized MMM using another type of polymer such as polysulfone, polyethylene mine, polyvinyl alcohol. Based on previous research, removal efficiency of heavy metals are about 80% to 99% by using polyethylene imine (PEI) and polyvinyl alcohol (PVA) as a based membrane (Bessbousse *et. al,* 2007). Kagaya *et. al,* (2009) used polythioamide to remove mercury and it achieved 100% of mercury removal.
ii. Optimizing the pH in order to get the ideal pH for operation of heavy metals removal. Copper are more selective in acidic condition as showed by Nguyen *et. al,* (2009) which used pH 2.5 for copper removal and achieved 99.6% of copper removal.
iii. Mixed more than one cation resin into membrane to extend the adsorption for other metals.

REFERENCES

A.R. Ladhe, P. Frailie, D. Hua, M. Darsillo, D. Bhattacharyya, (2009). *Thiol Functionalized Silica-Mixed Matrix Membranes for Silver Capture from Aqueous Solutions: Experimental Results and Modeling*. NIH Public Access Author Manuscript.

Bessbousse, H., Rhlalou,T., Verch`ere, J.F. and Lebrun, L., (2007). *Removal of heavy metal ions from aqueous solutions by filtration with a novel complexing membrane containing poly(ethyleneimine) in a poly(vinyl alcohol) matrix.* Journal of Membrane Science 307 (2008) 249–259.

Campbell, D.E., Nguyen, T. and James, D.K., (2001). *Process for treating wastewater containing copper.* US Patent 6,203,705.

Chou, Y.H. and Lee, L.L., (2004). *Reverse tone mask method for post-CMP elimination of copper overburden.* US Patent 7,125,803 B2.

Fabiani, C., (1992). *Metal removal from aqueous wastes by means of membrane hybrid processes.* In: Aimar, P., Apt'el P. (Eds.), Recents Progress and Genie des Procedes, Membrane Processes Water Treatment Pervaporation. Lavoisier Press, Paris 6, 211.

Farooq,U., Kozinski,J.A., Khan, M.A. and Athar, M., (2010). *Biosorption of heavy metal ions using wheat based biosorbents – A review of the recent literature*. Bioresource Technology 101 5043–5053

Geankoplis, C.J., (1993).*Transport Processes and Unit Operations* (3rd Edition). Prentice-Hall, pp. 697-704.

Gode,F. and 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 (2006) 330–337.

Goldberg, B.S., Hausser, A.G., Gilman, K.R and Chen, R.Y, (1979). *Evaluation of a Novel Microporous PVC-silica Support for Immobilized Enzymes – It's Use in a Flow-through Reactor System for Production of Fructose.* ACS Symposium.Ser.173-86.

Hsien, I.L., Kuan, Y.C., and Chern, M.J., (2006). *Factorial experimental design for recovering heavy metals from sludge with ion exchange resin.* Journal of Hazardous Materials 138, 549–559.

Hsien, I.L., Kuan, Y.C., and Chern, M.J., (2007). *Equilibrium and kinetics of heavy metal ion exchange.* Journal of the Chinese Institute of Chemical Engineers 38, 71–84.

Hubicki, Z. and Wolowicz, A., (2008). *A comparative study of chelating and cationic ion exchange resins for the removal of palladium(II) complexes from acidic chloride media.* Journal of Hazardous Materials 164 (2009) 1414–1419

Jha,M.K., Nghiem, V.N., Lee,J.C., Jeong,J. and 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, 948–953.

Kagaya, S., Miyazaki, H., Ito, M., Tohda, K. and Kanbara, T., (2009). *Selective removal of mercury(II) from wastewater using polythioamides.* Journal of Hazardous Materials 175 (2010) 1113–1115.

Kocaoba, S., (2007). *Comparison of Amberlite IR 120 and dolomite's performance for removal of heavy metals.* Journal of Hazardous Materials 147, 488–496.

Lin, L.C., and Juang, R.S., (2007). *Ion-exchange kinetics of Cu (II) and Zn (II) from aqueous solutions with two chelating resins*. Chemical Engineering Journal 132, 205–213.

Neumann, S. and Fatula, P., (2009). *Principles of Ion Exchange in Wastewater Treatment*. Magazine of Techno Focus 14-19.

Nguyen, V., Lee,N., Jha,J.K., Yoo,M. and Jeong, K., (2009). *Copper recovery from low concentration waste solution using Dowex G-26 resin* . Hydrometallurgy 97 (2009) 237–242.

Operation Manual: Flame, (2001)

Pehlivan, E., and Altun,T., (2006). *The study of various parameters affecting the ion exchange of Cu2+, Zn2+, Ni2+, Cd2+, and Pb2+ from aqueous solution on Dowex 50 W synthetic resin.* Journal of Hazardous Materials B134, 149–156.

Rengaraj, S., Yeon, J.W., Kim, Y.H., Jung, Y.J., Ha, Y.K., Kim and W.H., (2007). *Adsorption characteristics of Cu (II) onto ion exchange resins 252H and 1500H: kinetics, isotherms and error analysis*. Journal of Hazardous Materials 143, 469–477.

Saiful, Z., Borneman, M., and Wessling, (2006). *Enzyme capturing and concentration with mixed matrix membrane adsorbers*. Journal of Membrane Science 280 (2006) 406–417.

S.M. Saufi, and C.J. Fee, (2009). *Fractionation of b-Lactoglobulin From Whey by Mixed Matrix Membrane Ion Exchange Chromatography*. Article of Bioetechnology and Bioengineering.

Solenberger, J.C. and Withers, M. S., (1982). *Cation permeable Membrane Containing a Reinforcing Fabric*. FR Patent 2,498,116.

Winterton, J.D., Darmawan, F., and Doyle, F.M., (2005). *Investigation of ion exchange resins for use in treatment of semiconductor processing waste streams.* Proceedings of the EPD Conference 2005. The Mineral, Metal & Materials Society, Warrendale, USA, pp. 885–894.

APPENDIX A

EQUIPMENT USED FOR EXPERIMENT

A.1 Atomic Absorption Spectrophotometer

Figure A.1: Equipment used for heavy metal concentration analysis

A.2 Ultra centrifugal grinder

Figure A.2: Equipment used to grind the resins

A.3 Freezer Dryer

Figure A.3: Equipment used to dry the resins

Figure A.4: Equipment used to dry the membranes

A.4 Centrifuge 5810 R

Figure A.5: Equipment used to separate the ground resin from the copper ion solution

A.5 Stirrer

Figure A.6: Equipment used to mixed the resin with membrane polymer to form homogeneous slurry

APPENDIX B

AAS ANALYSIS RESULTS

B.1 Resin screening analysis

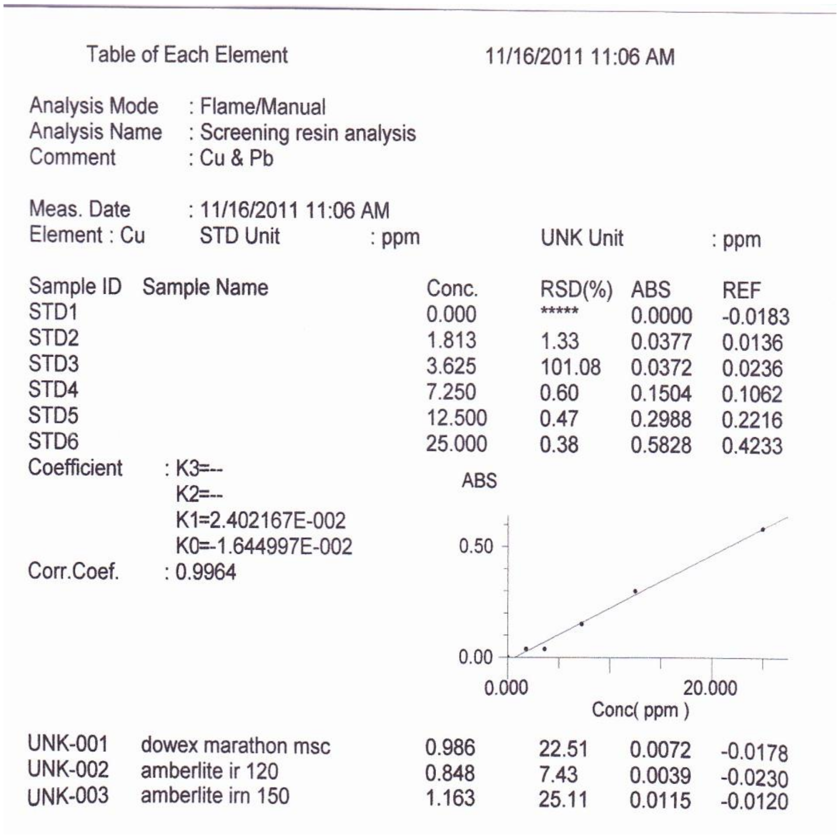


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      Table of Each Element                         11/16/2011 11:06 AM

Analysis Mode    : Flame/Manual
Analysis Name    : Screening resin analysis
Comment          : Cu & Pb

Meas. Date       : 11/16/2011 11:06 AM
Element : Cu      STD Unit         : ppm        UNK Unit         : ppm

Sample ID  Sample Name                Conc.     RSD(%)   ABS      REF
STD1                                  0.000     *****    0.0000   -0.0183
STD2                                  1.813     1.33     0.0377   0.0136
STD3                                  3.625     101.08   0.0372   0.0236
STD4                                  7.250     0.60     0.1504   0.1062
STD5                                  12.500    0.47     0.2988   0.2216
STD6                                  25.000    0.38     0.5828   0.4233
Coefficient    : K3=--
                 K2=--
                 K1=2.402167E-002
                 K0=-1.644997E-002
Corr.Coef.     : 0.9964

UNK-001    dowex marathon msc         0.986     22.51    0.0072   -0.0178
UNK-002    amberlite ir 120           0.848     7.43     0.0039   -0.0230
UNK-003    amberlite irn 150          1.163     25.11    0.0115   -0.0120
```

Figure B.1: Resin screening analysis part I

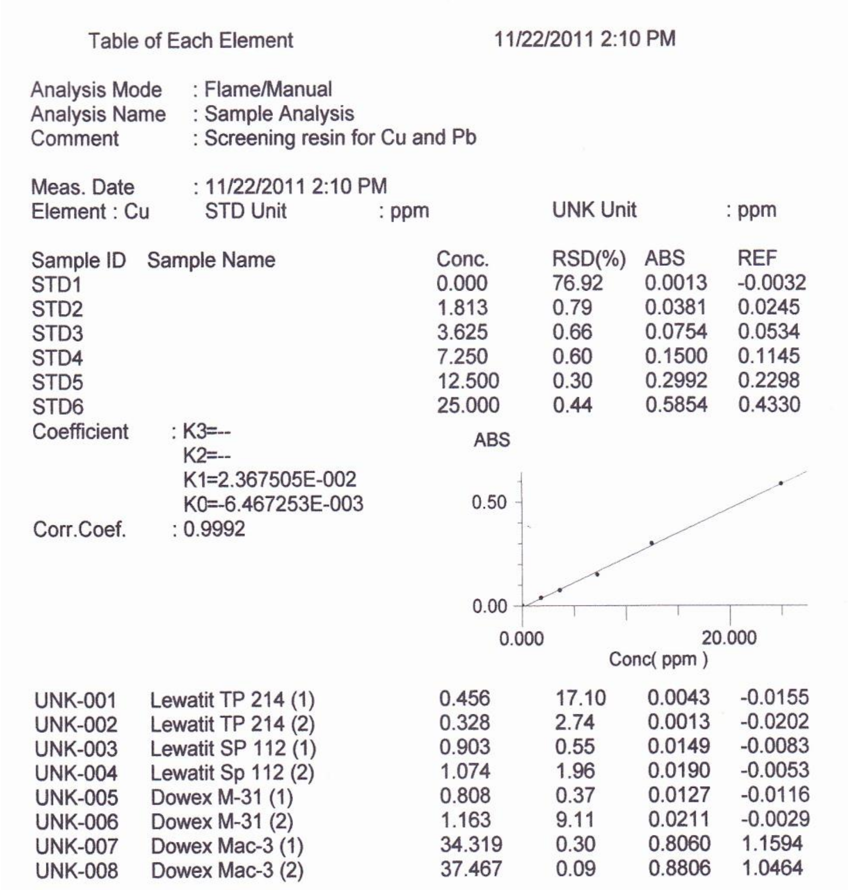

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Table of Each Element                    11/22/2011 2:10 PM

Analysis Mode    : Flame/Manual
Analysis Name    : Sample Analysis
Comment          : Screening resin for Cu and Pb

Meas. Date       : 11/22/2011 2:10 PM
Element : Cu       STD Unit        : ppm           UNK Unit         : ppm

Sample ID   Sample Name                  Conc.       RSD(%)   ABS      REF
STD1                                     0.000       76.92    0.0013   -0.0032
STD2                                     1.813       0.79     0.0381   0.0245
STD3                                     3.625       0.66     0.0754   0.0534
STD4                                     7.250       0.60     0.1500   0.1145
STD5                                     12.500      0.30     0.2992   0.2298
STD6                                     25.000      0.44     0.5854   0.4330
Coefficient     : K3=--
                  K2=--
                  K1=2.367505E-002
                  K0=-6.467253E-003
Corr.Coef.      : 0.9992

UNK-001     Lewatit TP 214 (1)           0.456       17.10    0.0043   -0.0155
UNK-002     Lewatit TP 214 (2)           0.328       2.74     0.0013   -0.0202
UNK-003     Lewatit SP 112 (1)           0.903       0.55     0.0149   -0.0083
UNK-004     Lewatit Sp 112 (2)           1.074       1.96     0.0190   -0.0053
UNK-005     Dowex M-31 (1)               0.808       0.37     0.0127   -0.0116
UNK-006     Dowex M-31 (2)               1.163       9.11     0.0211   -0.0029
UNK-007     Dowex Mac-3 (1)              34.319      0.30     0.8060   1.1594
UNK-008     Dowex Mac-3 (2)              37.467      0.09     0.8806   1.0464
```
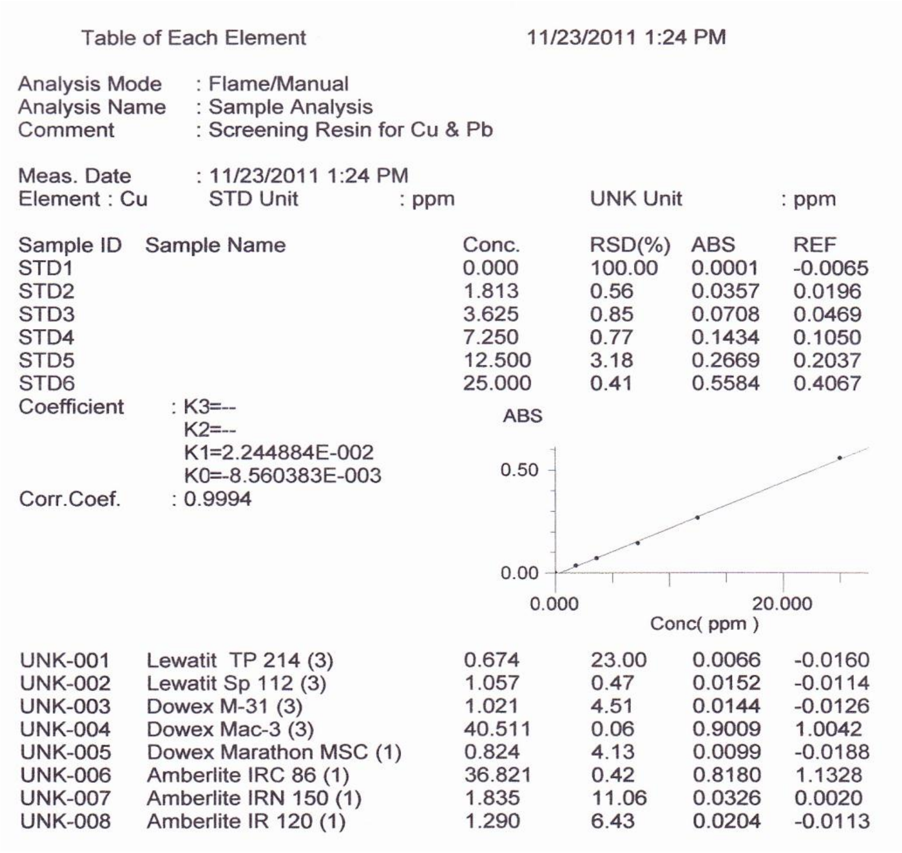

Figure B.2: Resin screening analysis part II



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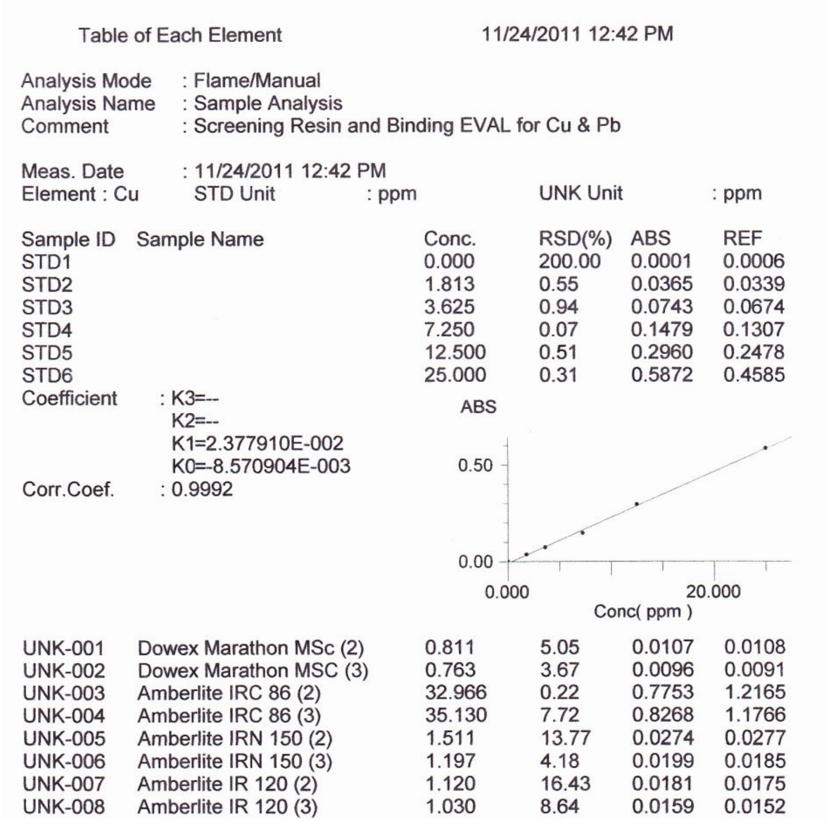
Analysis Mode    : Flame/Manual
Analysis Name    : Sample Analysis
Comment          : Screening Resin for Cu & Pb

Meas. Date       : 11/23/2011 1:24 PM
Element : Cu       STD Unit          : ppm          UNK Unit          : ppm

Sample ID   Sample Name                      Conc.       RSD(%)   ABS       REF
STD1                                         0.000       100.00   0.0001    -0.0065
STD2                                         1.813       0.56     0.0357    0.0196
STD3                                         3.625       0.85     0.0708    0.0469
STD4                                         7.250       0.77     0.1434    0.1050
STD5                                         12.500      3.18     0.2669    0.2037
STD6                                         25.000      0.41     0.5584    0.4067
Coefficient     : K3=--
                  K2=--
                  K1=2.244884E-002
                  K0=-8.560383E-003
Corr.Coef.      : 0.9994

UNK-001     Lewatit  TP 214 (3)              0.674       23.00    0.0066    -0.0160
UNK-002     Lewatit Sp 112 (3)               1.057       0.47     0.0152    -0.0114
UNK-003     Dowex M-31 (3)                   1.021       4.51     0.0144    -0.0126
UNK-004     Dowex Mac-3 (3)                  40.511      0.06     0.9009    1.0042
UNK-005     Dowex Marathon MSC (1)           0.824       4.13     0.0099    -0.0188
UNK-006     Amberlite IRC 86 (1)             36.821      0.42     0.8180    1.1328
UNK-007     Amberlite IRN 150 (1)            1.835       11.06    0.0326    0.0020
UNK-008     Amberlite IR 120 (1)             1.290       6.43     0.0204    -0.0113
```

Figure B.3: Resin screening analysis part III



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Analysis Name     : Sample Analysis
Comment           : Screening Resin and Binding EVAL for Cu & Pb

Meas. Date        : 11/24/2011 12:42 PM
Element : Cu        STD Unit          : ppm              UNK Unit          : ppm

Sample ID   Sample Name                   Conc.       RSD(%)    ABS       REF
STD1                                      0.000       200.00    0.0001    0.0006
STD2                                      1.813       0.55      0.0365    0.0339
STD3                                      3.625       0.94      0.0743    0.0674
STD4                                      7.250       0.07      0.1479    0.1307
STD5                                      12.500      0.51      0.2960    0.2478
STD6                                      25.000      0.31      0.5872    0.4585
Coefficient      : K3=--
                   K2=--
                   K1=2.377910E-002
                   K0=-8.570904E-003
Corr.Coef.       : 0.9992

UNK-001     Dowex Marathon MSc (2)        0.811       5.05      0.0107    0.0108
UNK-002     Dowex Marathon MSC (3)        0.763       3.67      0.0096    0.0091
UNK-003     Amberlite IRC 86 (2)          32.966      0.22      0.7753    1.2165
UNK-004     Amberlite IRC 86 (3)          35.130      7.72      0.8268    1.1766
UNK-005     Amberlite IRN 150 (2)         1.511       13.77     0.0274    0.0277
UNK-006     Amberlite IRN 150 (3)         1.197       4.18      0.0199    0.0185
UNK-007     Amberlite IR 120 (2)          1.120       16.43     0.0181    0.0175
UNK-008     Amberlite IR 120 (3)          1.030       8.64      0.0159    0.0152
```

Figure B.4: Resin screening analysis part IV

B.2 Binding and regeneration analysis

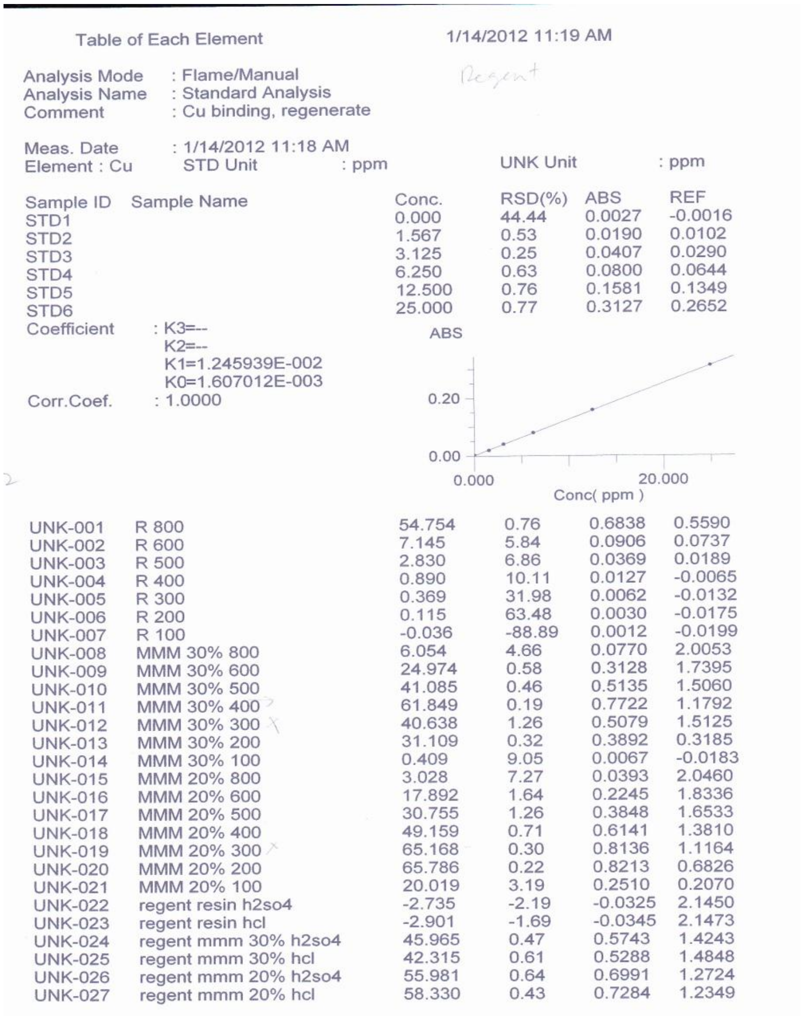

Table of Each Element 1/14/2012 11:19 AM

Regent

Analysis Mode : Flame/Manual
Analysis Name : Standard Analysis
Comment : Cu binding, regenerate

Meas. Date : 1/14/2012 11:18 AM
Element : Cu STD Unit : ppm UNK Unit : ppm

Sample ID	Sample Name	Conc.	RSD(%)	ABS	REF
STD1		0.000	44.44	0.0027	-0.0016
STD2		1.567	0.53	0.0190	0.0102
STD3		3.125	0.25	0.0407	0.0290
STD4		6.250	0.63	0.0800	0.0644
STD5		12.500	0.76	0.1581	0.1349
STD6		25.000	0.77	0.3127	0.2652

Coefficient : K3=--
K2=--
K1=1.245939E-002
K0=1.607012E-003

Corr.Coef. : 1.0000

2

UNK-001	R 800	54.754	0.76	0.6838	0.5590
UNK-002	R 600	7.145	5.84	0.0906	0.0737
UNK-003	R 500	2.830	6.86	0.0369	0.0189
UNK-004	R 400	0.890	10.11	0.0127	-0.0065
UNK-005	R 300	0.369	31.98	0.0062	-0.0132
UNK-006	R 200	0.115	63.48	0.0030	-0.0175
UNK-007	R 100	-0.036	-88.89	0.0012	-0.0199
UNK-008	MMM 30% 800	6.054	4.66	0.0770	2.0053
UNK-009	MMM 30% 600	24.974	0.58	0.3128	1.7395
UNK-010	MMM 30% 500	41.085	0.46	0.5135	1.5060
UNK-011	MMM 30% 400	61.849	0.19	0.7722	1.1792
UNK-012	MMM 30% 300	40.638	1.26	0.5079	1.5125
UNK-013	MMM 30% 200	31.109	0.32	0.3892	0.3185
UNK-014	MMM 30% 100	0.409	9.05	0.0067	-0.0183
UNK-015	MMM 20% 800	3.028	7.27	0.0393	2.0460
UNK-016	MMM 20% 600	17.892	1.64	0.2245	1.8336
UNK-017	MMM 20% 500	30.755	1.26	0.3848	1.6533
UNK-018	MMM 20% 400	49.159	0.71	0.6141	1.3810
UNK-019	MMM 20% 300	65.168	0.30	0.8136	1.1164
UNK-020	MMM 20% 200	65.786	0.22	0.8213	0.6826
UNK-021	MMM 20% 100	20.019	3.19	0.2510	0.2070
UNK-022	regent resin h2so4	-2.735	-2.19	-0.0325	2.1450
UNK-023	regent resin hcl	-2.901	-1.69	-0.0345	2.1473
UNK-024	regent mmm 30% h2so4	45.965	0.47	0.5743	1.4243
UNK-025	regent mmm 30% hcl	42.315	0.61	0.5288	1.4848
UNK-026	regent mmm 20% h2so4	55.981	0.64	0.6991	1.2724
UNK-027	regent mmm 20% hcl	58.330	0.43	0.7284	1.2349

Figure B.5: Binding and regeneration analysis

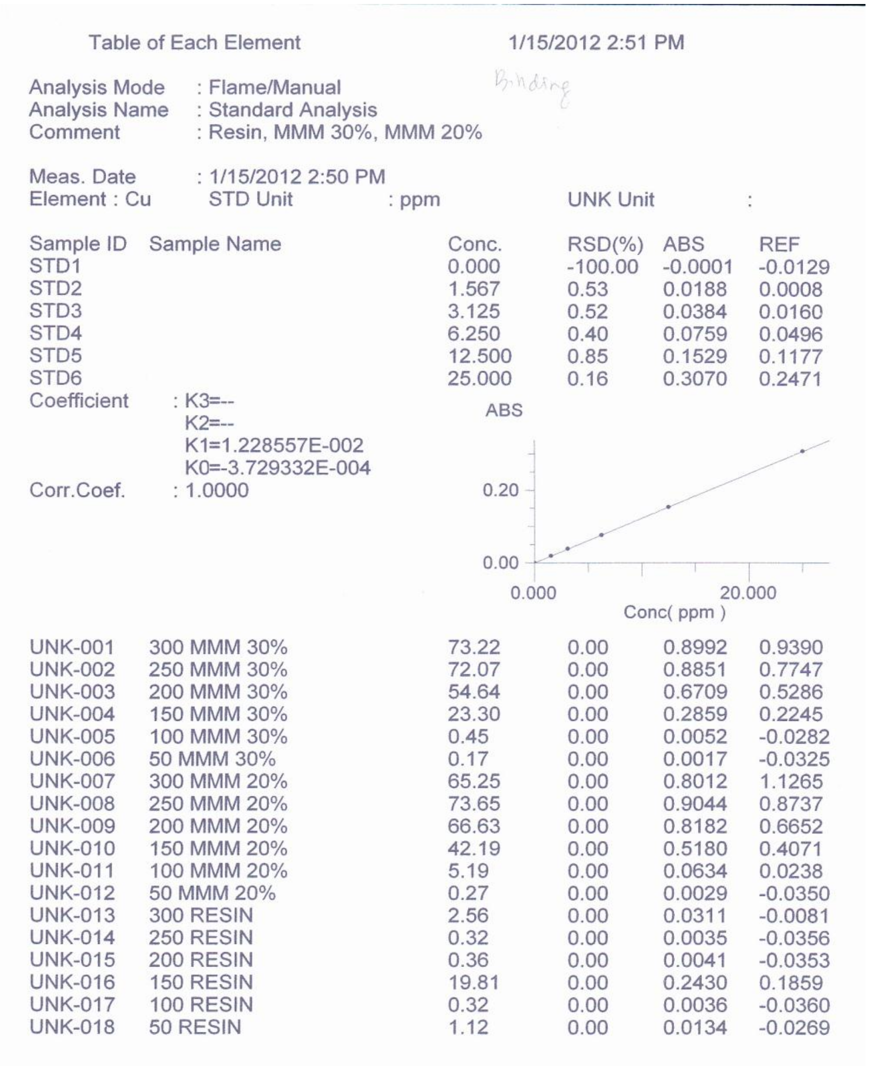

Table of Each Element 1/15/2012 2:51 PM

Binding

Analysis Mode : Flame/Manual
Analysis Name : Standard Analysis
Comment : Resin, MMM 30%, MMM 20%

Meas. Date : 1/15/2012 2:50 PM
Element : Cu STD Unit : ppm UNK Unit :

Sample ID	Sample Name	Conc.	RSD(%)	ABS	REF
STD1		0.000	-100.00	-0.0001	-0.0129
STD2		1.567	0.53	0.0188	0.0008
STD3		3.125	0.52	0.0384	0.0160
STD4		6.250	0.40	0.0759	0.0496
STD5		12.500	0.85	0.1529	0.1177
STD6		25.000	0.16	0.3070	0.2471

Coefficient : K3=--
K2=--
K1=1.228557E-002
K0=-3.729332E-004
Corr.Coef. : 1.0000

Sample ID	Sample Name	Conc.	RSD(%)	ABS	REF
UNK-001	300 MMM 30%	73.22	0.00	0.8992	0.9390
UNK-002	250 MMM 30%	72.07	0.00	0.8851	0.7747
UNK-003	200 MMM 30%	54.64	0.00	0.6709	0.5286
UNK-004	150 MMM 30%	23.30	0.00	0.2859	0.2245
UNK-005	100 MMM 30%	0.45	0.00	0.0052	-0.0282
UNK-006	50 MMM 30%	0.17	0.00	0.0017	-0.0325
UNK-007	300 MMM 20%	65.25	0.00	0.8012	1.1265
UNK-008	250 MMM 20%	73.65	0.00	0.9044	0.8737
UNK-009	200 MMM 20%	66.63	0.00	0.8182	0.6652
UNK-010	150 MMM 20%	42.19	0.00	0.5180	0.4071
UNK-011	100 MMM 20%	5.19	0.00	0.0634	0.0238
UNK-012	50 MMM 20%	0.27	0.00	0.0029	-0.0350
UNK-013	300 RESIN	2.56	0.00	0.0311	-0.0081
UNK-014	250 RESIN	0.32	0.00	0.0035	-0.0356
UNK-015	200 RESIN	0.36	0.00	0.0041	-0.0353
UNK-016	150 RESIN	19.81	0.00	0.2430	0.1859
UNK-017	100 RESIN	0.32	0.00	0.0036	-0.0360
UNK-018	50 RESIN	1.12	0.00	0.0134	-0.0269

Figure B.6: Binding analysis