CHAPTER 1: INTRODUCTION

1.1 Background Study:

Based on Malaysia Environmental Quality Report 2005, around 48% of the water pollution is generated by industrial sector, and one of the most water polluting industries in Malaysia is the metal plating industry, or also known as electroplating. Electroplating is a plating process that uses electrical current to reduce cations of a desired material from a solution and coat a conductive object with a thin layer of the material, such as a metal. Electroplating is primarily used for depositing a layer of material to bestow a desired property *(e.g. abrasion and wear resistance, corrosion protection, lubricity, aesthetic qualities, etc.)* to a surface that otherwise lacks that property. Another application of electroplating is to build up thickness on undersized parts.

The process used in electroplating is called *electro-deposition*; it is analogous to a galvanic cell acting in reverse. The part to be plated is the cathode of the circuit, while the anode is made of the metal to be plated on the part. Both components are immersed in a solution called an electrolyte containing one or more dissolved metal salts that permit the flow of electricity. A power supply supplies a direct current to the anode, oxidizing the metal atoms that comprise it and allowing them to dissolve in the solution. At the cathode, the dissolved metal ions in the electrolyte solution are reduced at the interface between the solution and the cathode, such that they "plate out" onto the cathode. The rate at which the anode is dissolved is equal to the rate at which the cathode is plated, vis-a-vis the current flowing through the circuit. In this manner, the ions in the electrolyte bath are continuously replenished by the anode.

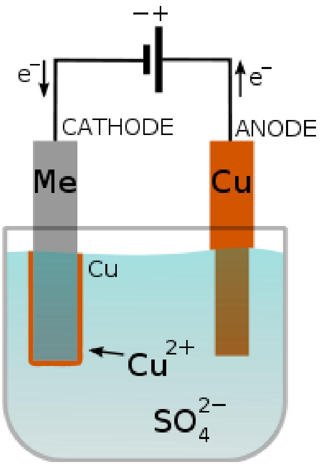


Figure 1: Example of an electroplating process of a metal (Me) with copper in a copper sulfate bath

Chromium is a chemical element which has the symbol Cr and atomic number 24, first element in Group 6. It is a steely-gray, lustrous, hard metal that takes a high polish and has a high melting point (1907ºC). It is also odorless, tasteless, and malleable. A major development was the discovery that steel could be made highly resistant to corrosion and discoloration by adding chromium to form stainless steel. This application, along with chrome plating, is currently the highest-volume uses of the metal.

Chrome plating, often referred to simply as chrome, is a technique of electroplating a thin layer of chromium onto a metal object. The chromed layer can be decorative, provide corrosion resistance, ease cleaning procedures, or increase surface hardness. Hexavalent chromium plating, also known as *hex-chrome*, Cr^{6+}, and chrome (VI) plating, uses *chromic anhydride*, also known as *chromium trioxide*, as the main ingredient; trivalent chromium plating, also known as *tri-chrome*, Cr^{3+}, and chrome (III) plating, uses *chromium sulfate* or *chromium chloride* as the main ingredient.

Figure 2: Decorative chrome plating on a motorcycle

U.S. Environmental Protection Agency (EPA) sets emission limitation for chromium electroplating sources. Regulating the emissions of hexavalent and trivalent forms of chromium is important as their known negative impact on health and environment. Chemical fume suppressants/wetting agents are used to lower the surface tension of chrome plating bath for compliance with workers safety.

1.2 Problem Statement:

Chromium enters the air, water, and soil mostly in the chromium (III) and chromium (VI) forms. In air, chromium compounds are present mostly as fine dust particles which eventually settle over land and water. Chromium can strongly attach to soil and only a small amount can dissolve in water and move deeper in the soil to underground water. High doses of trivalent chromium, a.k.a. Cr (III), can cause skin irritation, but lower doses given orally are not toxic. Several in vitro studies indicated that high concentrations of Cr (III) in the cell can lead to DNA damage. Acute oral toxicity for Cr (III) ranges between 1500 and 3300 µg/kg. On the other hand, hexavalent chromium, a.k.a. Cr (VI), is not a very stable state when compared to Cr (III). Cr (VI) is a very strong oxidizing agent, therefore very fast in reacting and likely to form complexes. The acute oral toxicity for Cr (VI) ranges between 50 and 150 µg/kg due to its strong oxidational properties. After it reaches the blood stream, it damages the kidneys, the liver and blood cells through oxidation reactions. Hemolysis, renal and liver failure are the results of these damages. Several studies have shown that Cr (VI) compounds also can increase the risk of lung cancer in human. The Department of Health and Human Services (DHHS) has determined that certain Cr (VI) compounds are known to cause cancer in humans.

Different processes are available for removal of Cr ion existing in electroplating industrial wastewater, however some of them results in sludge *(coagulation)*, and some results in solid waste *(adsorption)*, which later requires extra treatment or removal process. Ion exchange provides the unique solution to this problem, as the treatment does not result in any kind of waste. Although ion exchange method has been applied in the industry for many years, there appears to be very limited number of studies reported about removal of Cr ion from industries employing ion exchange method. Since the performance of the resin is very sensitive to the operation conditions, hence an exploratory research is conducted to investigate the optimum operating parameters for Cr ion removal.

1.3 Objectives:

- To study the effect of different operating parameters on the resin performance.
- To investigate the effect of ion exchange process on the characterization of the ion exchange resin.

1.4 Scopes of Study:

The project will be utilizing the fundamental knowledge in Chemical Engineering, and also work exposure to wastewater treatment plant.

- Literature review on chrome plating industry, including the amount of chromium content in wastewater.
- Literature review on previous experiments carried out by researchers, and selection of the best cation & anion resins combination.
- Literature review on the existing ion exchange technique/system, study on how it works and possible improvement on the system.
- Analysis on results obtained from experiments/lab work.

Figure 3: Hard chrome plating plant

CHAPTER 2: LITERATURE REVIEW

Industrial wastewaters often contain considerable amounts of heavy metals that would endanger public health and the environment if discharged without adequate treatment. Effluent discharged from the electroplating industry contains a large number of metals, including chromium, copper, nickel, zinc, manganese and lead, which are usually associated with toxicity. Major anthropogenic sources of heavy metals in the environment include metal extraction, metal fabrication and surface finishing, paints and pigments, as well as the manufacture of batteries. Pollution by chromium is of considerable concern as the metal has found widespread use in electroplating, leather tanning, metal finishing, nuclear power plant, textile industries and chromate preparation, therefore removal of chromium from water and wastewater is obligatory in order to avoid water pollution.

The effluent from the industries may contain chromium at concentrations ranging from tenths to hundreds of mg/l. Chromium is considered by the IARC [1] as a powerful carcinogenic agent that modifies the DNA transcription process causing important chromosomic aberrations. On the other hand, the presence of chromium in water causes serious environmental problems as mentioned by some researchers. The National Institute for Occupational Safety and Health (NIOSH) recommends that the levels of chromium in water should be reduced to 10^{-3} mg/m^3. The metal is reported to be bio-accumulated into flora and fauna, creating ecological problems [2,3]. Chromium toxicity to mammals and aquatic organisms appears to be lower compared to other heavy metals, due to the general low solubility of Cr (III) compounds, low mobility in the environmental compartments and limited availability to living organisms. However, the possibility that organic ligands and/or acidic conditions in the environment increase Cr (III) mobility, that MnO_2 oxides, present in soils, favor the oxidation of Cr (III) to the more toxic and mobile Cr (VI) forms cannot be excluded [4]. The Minimal National Standards (MINAS) upper limit of chromium in industrial wastewater is 0.1 mg/l [5]. For compliance with this limit, it is essential for industries to treat their effluents to reduce the chromium to acceptable levels. Due to more stringent environmental regulations, most of the mineral processing plants are facing nowadays the difficult problem of tailings management and disposal, which certainly are produced in huge quantities.

Previous researchers reported reasonable methods, from the economical and technological point of view, to remove heavy metals in general from superficial waters, with the aim of the preservation of the entire ecosystem from the damages due to their accumulation [6]. Among various treatment techniques available, the most commonly used ones are:

- Reduction/precipitation
- Adsorption

However, these methods suffer from some drawback such as high capital and operational costs or the treatment and disposal of the residual metal sludge. Ion exchange process is an alternative technique for application in the treatment of industrial wastewater containing heavy metals and indeed it has proven to be very promising in the removal and recovery of valuable species. Its main advantages over chemical precipitation are recovery of metal value, selectivity, less sludge volume produced and the meeting of strict discharge specifications. Polymeric resins are usually employed in ion exchange systems [7], and ion exchange using synthetic resins is the method of choice in many water treatment processes for removing inorganic contaminants in water and wastewater. Tiravanti et al. [4] studied the pretreatment of tannery wastewater by an ion exchange process for Cr (III) removal and recovery. They found that a considerable decrease in the use of chemical compounds, a sludge production reduced by 80% with respect to the traditional treatment and lower costs for sludge treatment and disposal.

Several studies considering the Cr removal by ion exchange resins have been reported in the literature. Petruzelli et al. [8] reported the IERECHROM process based on the use of a macroporous carboxylic resin that allows the removal of almost pure Cr from other interfering metals. Chmielewski et al. [9] implemented a method for recovering Cr, Cu and water from electroplating wastewater using a combined process involving electrochemical oxidation and ion exchange. Lin and Kiang [10] proposed a procedure to recover chromic acid from a waste acid solution using a multi-step ion exchange process, where a large amount of regenerant chemicals were spent. Yalcin et al. [11] developed a laboratory-scale separation process for the recovery of Cr (VI) and Cr (III) with a strongly basic resin and a weakly acidic resin, respectively. Rengaraj et al. [12] performed equilibrium and kinetics experiments to evaluate the sorption capacity of chromium by three different strongly acid resins. Some chelating resins show high affinity to chromium, which can be considered an advantage in the wastewater treatment. The uptake of chromium by ion exchange resins is rather affected by certain variables such as pH, temperature, initial metal concentration and contact time [13,14].

An ion exchange reaction can be defined as a reversible exchange of ions between a solid phase *(ion exchanger)* and a liquid phase *(solution)*. Thus, if an ion exchanger M^-A^+, where cations A^+ are the exchange ions, is placed in an aqueous solution containing cations B^+, the ion exchange that would take place can be represented by the equation:

$$\mathbf{M^-A^+ + B^+ \Leftrightarrow M^-B^+ + A^+} \qquad \textbf{(1)}$$

Eq. (1) represents a cation exchange reaction, where M^- is the fixed anionic complement of the ion exchanger M^-A^+, and is referred to as the counter-ions, and the ions present in the solution having the same charge as the fixed anion are called the co-ions. Similarly, it’s possible to have an anion exchange reaction that can be represented by Eq. (2):

$$\mathbf{M^+A^- + B^- \Leftrightarrow M^+B^- + A^-} \qquad \textbf{(2)}$$

Electroneutrality is necessarily maintained in these reactions whether in the ion exchanger or in the aqueous solution. This indicates that counter-ion exchange occurs n equivalents.

The application of ion exchange in the plating industry may be considered for two applications: renewal of depleted baths and purification of rinse waters. In the first case, solutions contain chromate concentrations varying between 250 - 450 g/l, depending on the bath being dealt with. As the more common impurities present in the bath are all cations, hence they can be removed by using a column containing a cation exchange resin of the strongly acid type, due to the high acidity of the bath [15]. However, since the solution has a very low pH (normally below 1), it is necessary to dilute the bath until the CrO_3 concentration drops below 200 g/l. This is required as the high acidity could oxidize the resin and make it non-usable.

Rinse water is treated to remove the impurities prior to reusing it or to returning it to natural sources without causing pollution. In this case, the solution contains CrO3 in concentrations that vary from 10 to 500 mg/l, besides the impurities mentioned in the previous case. To purify this type of water, two columns as used, one with strong cation resin (due to low pH as mentioned before), while the anionic resin can be strongly basic, permitting complete removal of chromates. However, high concentrations of alkali would be required for regeneration (or elution) due to the high adherence of these ions to the strongly basic resin. Weakly basic resin can be used as an alternative. Even though this does not have as high retention capacity, it requires less alkali for regeneration.

2.1 Case Study:

Now we will look into one of the experiments which the resin used is most similar to the ones I will be using for my project. The aim of this investigation was to study the viability of ion exchange as an alternative process for treatment of rinse water and to determine the efficacy of two ion exchange systems: System 1 – “strong” cationic resin & “strong” anionic resin; and System 2 – “strong” cationic resin & “weak” anionic resin. The resins used are as below:

a. Strongly acidic cationic resin, *AMBERLITE IR 120 Na*, gel type with the matrix made of styrene-divinylbenzene copolymer;
b. Strongly basic anionic resin, *AMBERLITE IRA 420*, gel type with the matrix made of styrene-divinylbenzene copolymer; and
c. Weakly basic anionic resin, *AMBERLITE IR 67RF*, gel type with an acrylic structure.

A two-column system, one for the cationic resin and another for the anionic resin, both with 150 ml capacity was mounted. The solution was taken from rinse tanks of chromium plating companies, and was percolated at a rate of 10 ml/min. The following solutions were used for regeneration of the resins: 2% H_2SO_4 for the cationic and 4% NaOH for the anionic. The percolated solutions revealed chromium contents of less than 0.25 mg/l, independent of the system used.

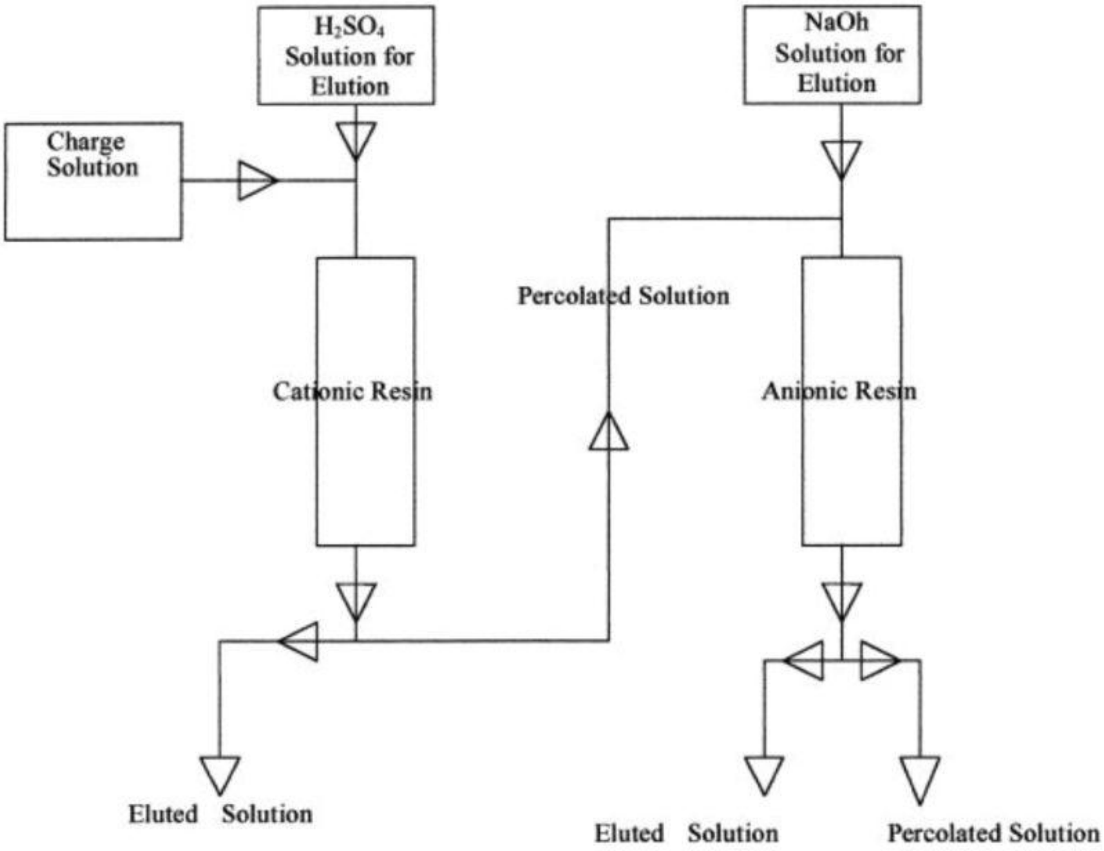


Figure 4: Sketch of an ion exchange system

From the experiments carried out, it can be stated that the best system for the treatment of solutions containing chromium is a combined one, consisting of "strong" cationic resin – "weak" anionic resin. The quantity of chromium in solution after percolation was the same in the two types of anionic resins, but the weak anionic resin gave better elution results.

As a conclusion, ion exchange can be used in the treatment of plating industry effluents (rinse waters), enabling reuse of waters and recovery of chromium. This result in reduction of operational costs, and this method is effective since all the treated solutions showed chromium concentrations < 0.3 mg/l, independent of the system used.

2.2 Experimental Theory:

The adsorption of molecules from a liquid solution onto the internal surface of porous solid offers many opportunities for the purification of process streams, as in the recovery of valuable components and of water softening. Often the solid particles are held in a fixed bed, the fluid feed being run through until the bed becomes nearly saturated and small quantities of the adsorbate begin to "breakthrough". Then the bed must be regenerated to restore its adsorptive capacity and to recover the adsorbed material.

The ion exchange reaction of a resin can be represented typically by the chemical equation:

$$\mathbf{Na^+ + RH \rightarrow H^+ + RNa}$$

where R means the polymer structure associated with one acid-type functional group. Since the resin has a finite capacity i.e., a fixed total number of acid sites per gram, the sum of the concentrations of RH and RNa is equal to a constant,

$$\mathbf{[RH] + [RNa] = q_m}$$

Similarly, in the solution phase outside the resin, the total molar concentration of hydrogen and sodium is constant:

$$\mathbf{[H^+] + [Na^+] = c_o}$$

At equilibrium,

$$\mathbf{K = [H^+][RNa]/[Na^+][RH] = (c_o - c)q^*/c(q_m - q^*)}$$

Where c and q* represent the equilibrium concentrations of sodium in the fluid outside the resin particles and inside the particles, in moles or equivalents per unit volume and per unit mass, respectively. Solving the equations for q*,

$$\mathbf{q = q_m\, Kc/(c_0 + (K - 1)c)}$$

The equation developed is remarkably similar to Langmuir isotherm and similar approach can be used to solve the ion-exchange problem.

Ion-exchanger is currently used for water softening operation. The most usual ion-exchange material is a sulphonated styrene-based resin, supplied usually in sodium form. This resin has a strong affinity for calcium and magnesium ions and will also remove ferrous ions after the more or less complete removal of calcium and magnesium.

Water is passed slowly downwards through a column of resin beads. The exchange reaction takes place rapidly enough for the upper layers of the bed to approach exhaustion before the lower layers of the bed are able to exchange ions. There is thus a zone of active exchange that moves down the column until the resin at all depths becomes exhausted. The position at an intermediate stage can be illustrated as below:

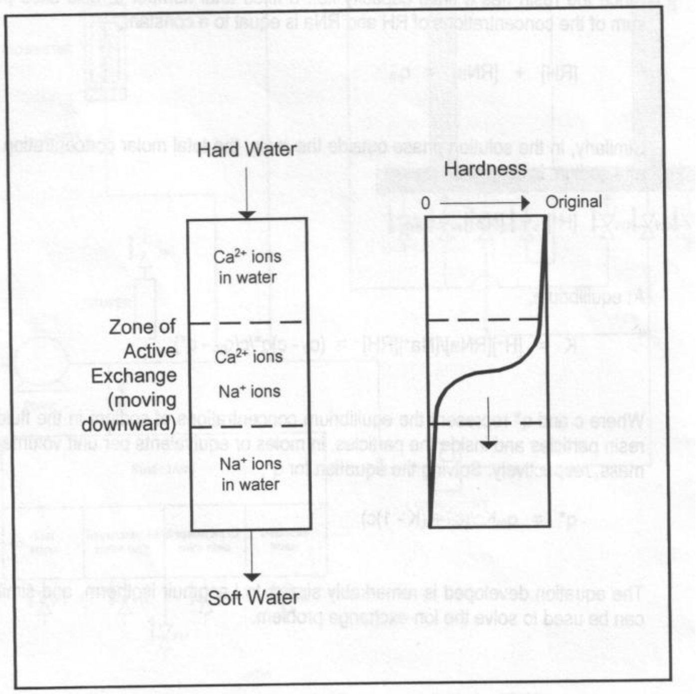


Figure 5: Water softening using cationic resin

When the zone of active exchange reaches the bottom of the column, the emerging water begins to show an increasing hardness. This is the breakthrough point when it is necessary to regenerate the resin with a regenerant solution.

The resin capacity can be calculated by using formula:

$$\text{Resin capacity (kg/cu.ft)} = \frac{\text{US gal} \times \text{total hardness (in ppm)}}{\text{Resin volume (cu.ft)} \times \mathbf{17.1} \times \mathbf{1000}}$$

where, 1 US gal = 3.7854 L.

2.3 Types of Resin

Exchange resins are usually bead or granular-shaped with size of 0.1 to 1.0 mm. Ion exchange resin beads contain many fine pores that will fill the water. The resins can be classified to four major classes which are strong acidic cation resins, weak acidic cation resins, strong basic anion resins and weak basic anion resins. Each of these major resin classes has a several physical or chemical variations within the class. The variations impart different operating properties to the resin. The selection of ion exchange resins is based on the peak efficiency of the resins and maximum cost effectiveness.

The acidic resins are cation exchanger because of the hydrogen ion (H^+) contains in the resins can attached to the negatively charge exchange site [20]. The strong acidic cation resins will remove all cations from solutions, where as the weak acidic cation resins will remove ions such as calcium and magnesium but have limited ability to remove ions that situated at the bottom lines in the displacement series table. However, weak acidic cation resins is highly efficient compared to the strong acidic cation resins as it only needs 110% of the stoichiometric amount of acid compared to 200 to 300% of the weakly acidic resins [21].

For basic resins, the exchange site is positively charged to allow hydrogen ion (H^+) and other basic species such as amine group attach to it. The strong basic anion resins have an ability to remove all anions in the displacement table. Conversely, the weakly basic only removes the anions of strong acids [22].

For removal of heavy metal in the industrial wastewater, although weakly acidic cation and weakly basic anion have greater affinity for counter ion, strong resins were more favorable as the solid exchanger because of the advantage in the pH. It is because pH is essential in the ion exchange process in wastewater in order to comply with certain environmental requirement.

Resin Selectivity

Selection of suitable resin is the most crucial parts in ion exchange process because different ion has a tendency to react differently with functional group of ion exchangers. Some ion will have great bound where as some ion will less strongly bound. This situation is called resins selectivity. The selectivity of the resins is based on displacement series for ion exchange which is shown in table below. An ion exchanger tends to prefer higher valence ions, bigger atomic number, smaller solvated volume ions, ions with greater ability to polarize and ions that participate least with other ions to form complexes.

Cation	**Anion**
Pb^{2+}	SO_4^{2-}
Ca^{2+}	CrO_4^{2-}
Ni^{2+}	NO_3^{2-}
Cd^{2+}	AsO_4^{2-}
Cu^{2+}	PO_4^{3-}
Zn^{2+}	$MoOa^{2-}$
Mg^{2+}	I^-
Ag^+	Br^-
Cs^+	Cl^-
K^+	F^-
NH_4^+	OH^-
Na^+	
H^+	

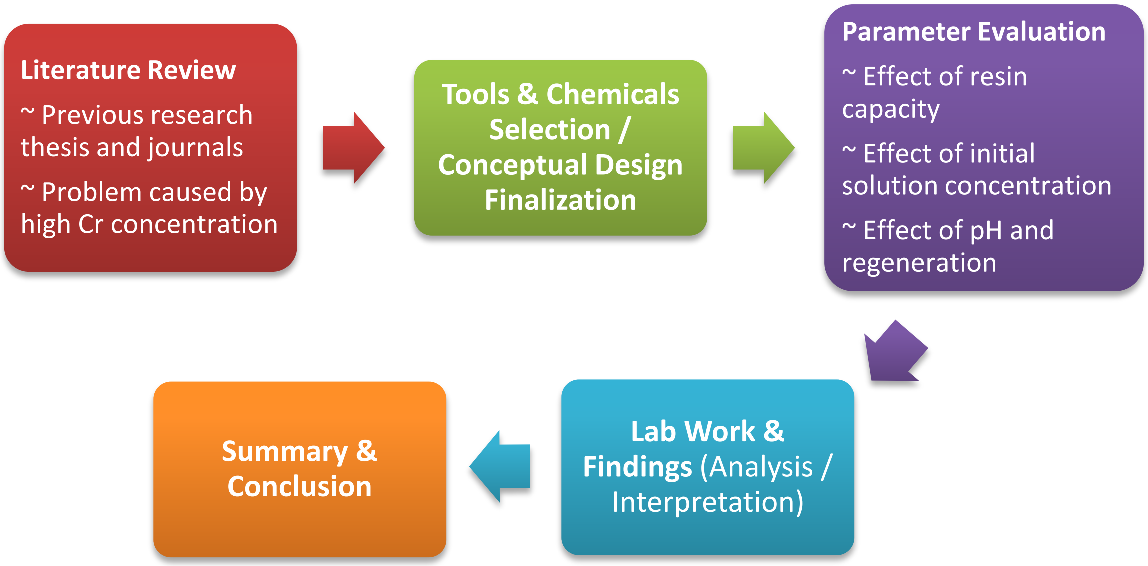
Exchange Capacity

Exchange capacity is the ability of an insoluble material to undergo displacement of ions previously attached and loosely incorporated into its structure by oppositely charged ions present in the surrounding solution. Resin capacity is usually expressed in terms of equivalents per liter (eq/L) or (kg/cu.ft) of resin. An equivalent is the molecular weight in grams of the compound divided by its electrical charge of valence. The capacities are strongly influenced by the quantity of acid or base used to regenerate the resin. For example, weak acid and weak base systems are more efficiently regenerated during regeneration process because their capacity increases almost linearly with regenerant dosage. Thus, the resin exchange capacity will strongly affect the rate of ion exchange between heavy metal ion (in this case Cr^{3+}) and ion in the resins. Resin capacity can be calculated by using Thomas model.

Characterization of resin:

Method	Purpose	Working principle
Scanning Electron Microscope (SEM)	To observe the surface structure for the particle. SEM shows very detail 3 dimension image that can be magnified up to 500,000 times.	The magnified image is produced by scanning the particle with high-energy beam of electrons in a raster scan pattern.
Fourier Transform Infrared Spectroscopy (FTIR)	To provide information regarding the amount of elements in the particle based on the functional group. To identify unknown material in the sample.	FTIR Spectrum is produced by the difference in IR radiation that passed through the sample.

CHAPTER 3: PROJECT METHODOLOGY



3.1 Tools & Materials required:

3.1.1 Ion Exchange Unit

The bench-top SOLTEQ Ion Exchange Unit (Model: TR02) is selected for this experiment. The unit consists of two vertically mounted tubed made of clear acrylic containing respective cation and anion resins. The tubes are removable and interchangeable for softening, decationization or demineralization experiments. The size of column composed in each column, cationic and anionic column, had a diameter of 2cm and length of 60cm. The schematic diagram of the ion exchange unit and procedures are attached in the Appendices behind.

3.1.2 Atomic Absorption Spectrophotometer (AAS)

The Cr concentration measurement is carried out by using Atomic Absorption Spectrophotometer (AAS), before and after treatment with resin. pH meter is used to measure the pH of the effluent after treatment, while conductivity meter is used to quantify the total ion content in the solution.

Figure 6: Atomic Absorption Spectrophotometer (AAS) with CE mark

3.1.3 Materials / Chemicals:

- *Chromium (III) Chloride – 5L*
- *Chromium (III) Sulphate – 5L*
- *Cation resin (Lewatit S 1467)*
- *Anion resin (Amberlite IRA 402 Cl)*

Synthetic resin is used in the experiment studies. Cation resin used in this project is Lewatit S 1467, produced by Lanxess. The resin is in Na^+ ionic form and was from sulfonic acid functional group. The resin is light brown, gel type beads that have crosslinked polystyrene matric. Anion resin used is a strongly basic anion exchange resin with pale yellow translucent beds. The resin is based on crosslinked polystyrene and contains Cl^- ionic form.

However, due to the breakdown of ion exchange unit and Atomic Absorption Spectrophotometer (AAS) in the lab, the experiment is carried out by using batch method:

a. Preparation of the resin:

1. Cation resin *(Lewatit S 1467)* is placed into a beaker, and rinsed first with 1.0 mol hydrochlroric acid (HCl).
2. The resin is later rinsed with prepared 1.0 mol sodium hydroxide (NaOH).
3. Lastly, the resin is rinsed with hexane.
4. After the three chemicals, resin is washed using distilled water for 3 times repetitively.
5. Resin is then put into the oven to dry under 50-60ºC for 12 hours.
6. As much resin as needed is prepared for all the experiments.

b. Carrying out experiments:

1. For the first experiment, different dosages of resin are weighted and prepared: 1g, 2g, 3g, 4g and 5g.
2. Using 5 beakers to separate 5 different dosages of resin, Chromium (III) Sulphate ($Cr_2(SO_4)_3$) solution is prepared in 1000ppm, and later poured into the 5 separate beakers.
3. The solutions with resin are mixed using magnetic stirrer for an hour period. After an hour, solutions and resins are taken out to test the concentration/to be characterized.
4. All the results/findings are recorded.
5. Steps are repeated for experiments on different initial concentration and solution pH.

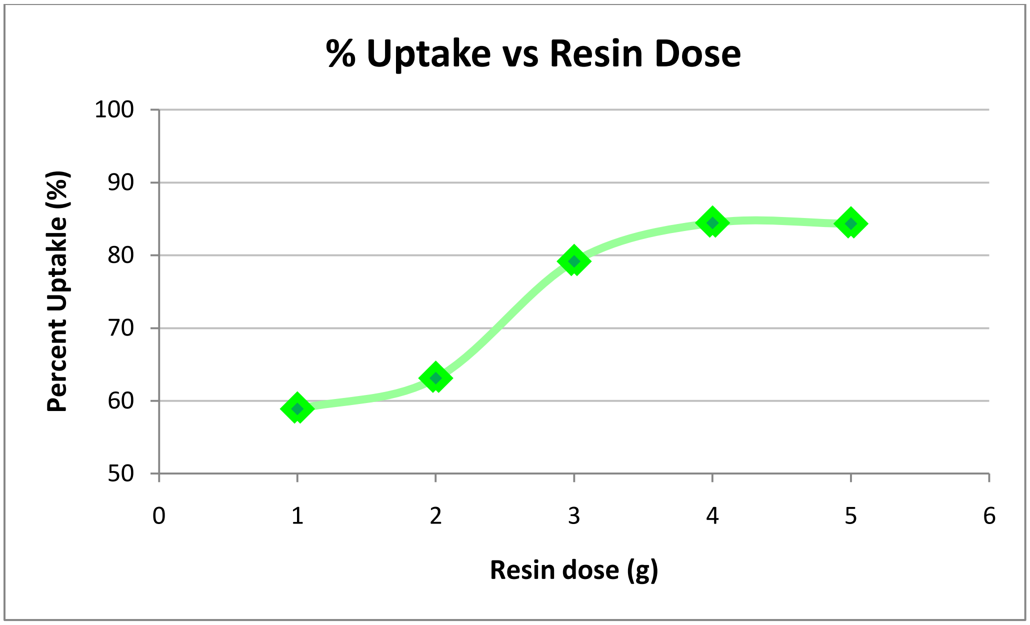
Project Timelines

No.	ACTIVITIES / WEEKS	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15	16
1	Project continues from FYP I	🟩	🟩	🟩	🟩	🟩	🟩	🟩	MID-SEMESTER BREAK									FINAL EXAMINATION
2	Submission of Progress Report									🟩								
3	Project work continues									🟩	🟩	🟩	🟩	🟩				
4	Pre-EDX presentation												🟩					
5	Submission of Draft Report													🟩				
6	Submission of Dissertation (soft-bound)														🟩			
7	Submission of Technical Paper														🟩			
8	Oral Presentation															🟩		
9	Submission of Project Dissertation (hard-bound)																🟩	

CHAPTER 4

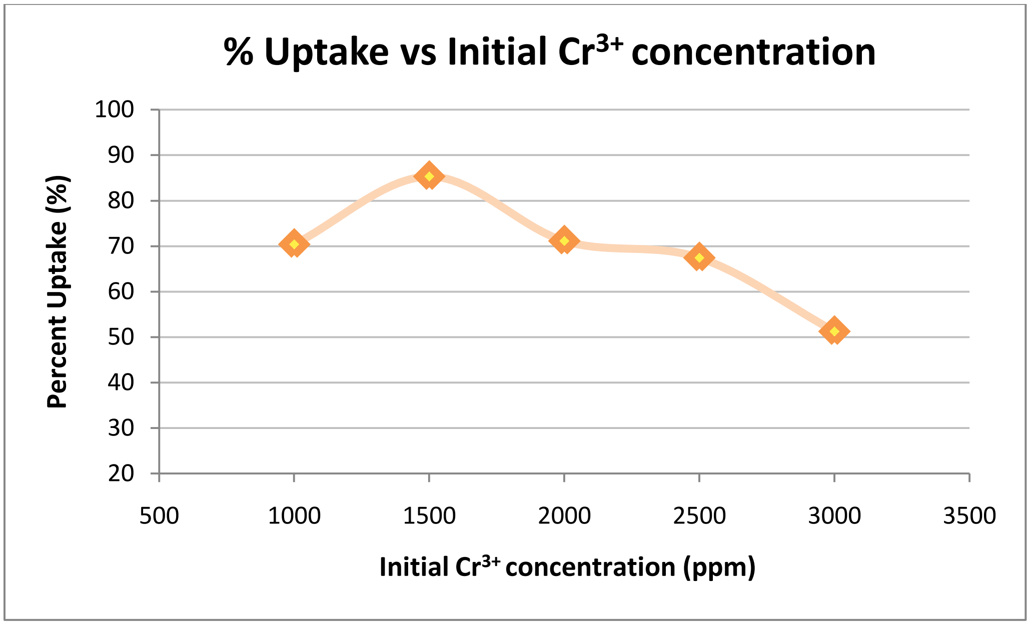
RESULTS & DISCUSSION

4.1 Effect of Resin Dosage



Graph above represents the removal of Cr^{3+} ion as a function of resin dosage by Lewatit S 1467. Resin dosage was varied by 1.0 to 5.0g and equilibrated for 1 hour. Increasing resin dosage increased the percent removal of Cr^{3+}. It shows that for the quantitative removal of Cr^{3+} from 150 ml solution containing 1000 ppm of Cr^{3+}, a minimum dosage of 4g/150ml of Lewatit S 1467 is required for the maximum removal of Cr^{3+}. The result also clearly indicates the removal efficiency increases up to the optimum dosage beyond which the removal efficiency has no/insignificant change with the resin dosage. It may be concluded that by increasing the resin dose the removal efficiency increases but metal exchange density decreases. The decrease in metal exchange density can be attributed to the fact that some of the metal exchange sites remain unsaturated during the ion exchange process; whereas the number of available metal exchange site increases by an increase in resin and this result in an increase in removal efficiency. Therefore in the subsequent studies 4g of resin were used.

4.2 Effect of Initial Concentration

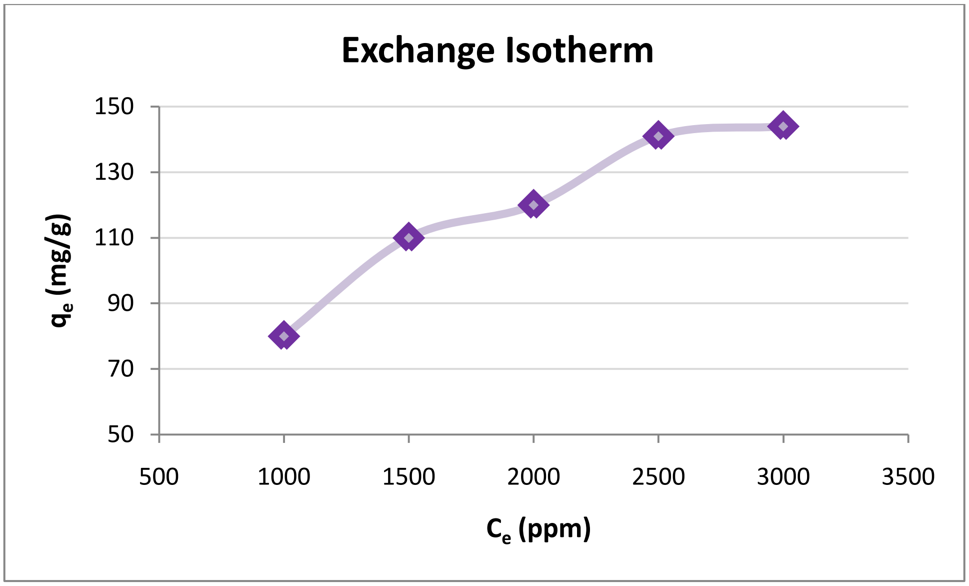


The graph above shows the relation between initial Cr^{3+} concentration and the removal efficiency of resin. The amount of metal exchanged (q_e) can be determined using the equation:

$$q_e = \frac{(C_o - C_e)V}{m}$$

where C_o and C_e = initial and final concentration of solution
V = volume of aqueous solution
m = mass of resin;

In general, relationship between q_e and C_e is important to describe how metals ion interact with the resin and so critical in optimizing the use of resin. From the exchange isotherm graph *(shown in the next page)*, it is clearly shown that when the initial concentration increases, the exchange capacity also increases. However, the graph of percentage uptake versus concentration shows that the percentage uptake of Cr^{3+} decreased as the initial concentration increases. This might be because the resin is saturated with Cr^{3+} after an hour meanwhile high amount of Cr^{3+} is still left in the solution.



In order to optimize the design of a sorption system for the removal of metals from effluents, it is important to establish the most appropriate correlation for the equilibrium curves. Two isotherm equations have been tested in the study: Langmuir and Freundlich Isotherm.

Langmuir equation is given by: $\boldsymbol{q_e = \frac{Q_o b C_e}{1+bC_e}}$

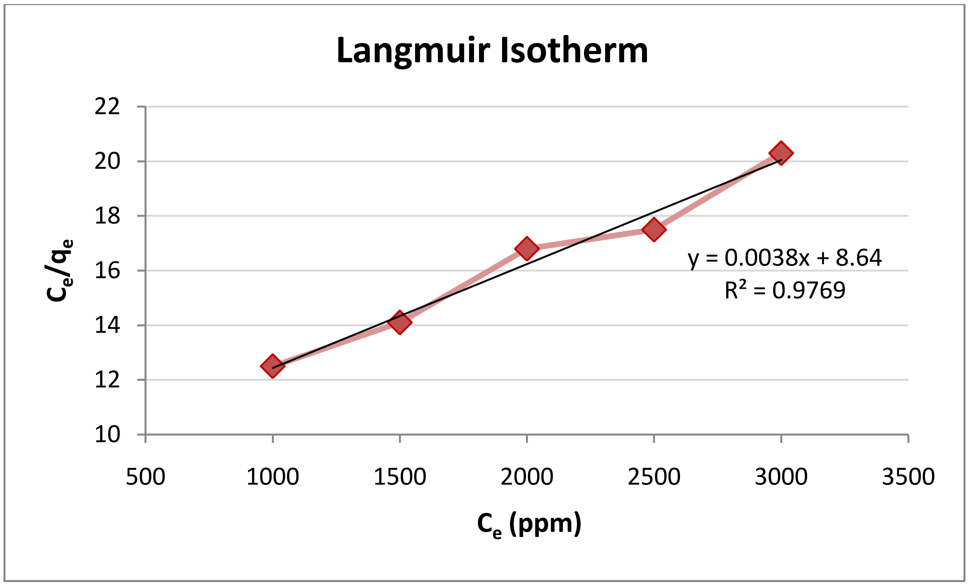
Rearrange the equation gives: $\boldsymbol{\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{1}{Q_o} C_e}$

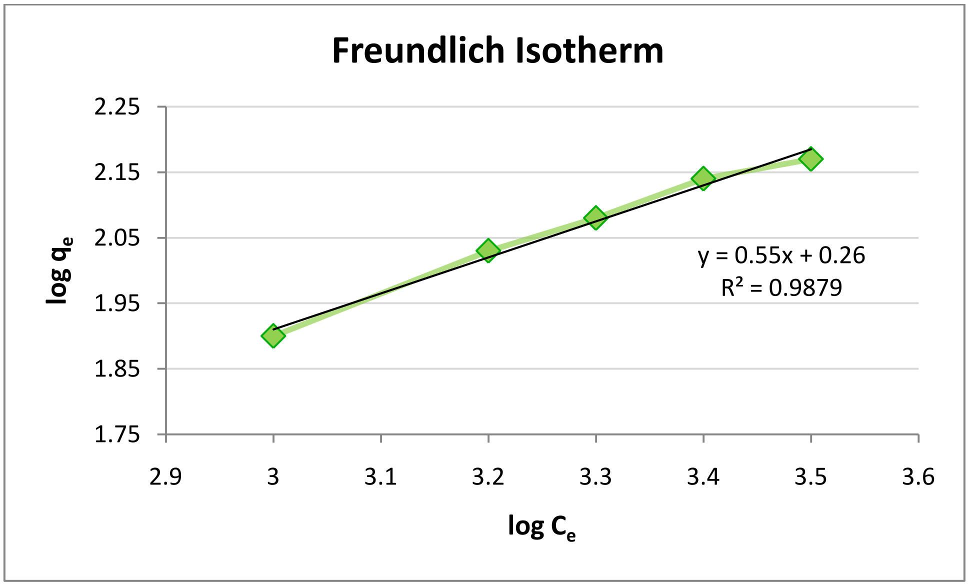
Freundlich proposed that if the concentration of solute in the solution at equilibrium, C_e, is raised to power n, the amount of solute absorbed being q_e, then C_e^n/q_e is a constant at a given temperature. The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface. Hence the empirical equation can be written:

$$\boldsymbol{q_e = K_F . C_e^n}$$

where K_F is the Freundlich constant and n the Freundlich exponent. Therefore a plot of log q_e vs. log C_e enables the constant K_F and exponent n to be determined. Rearrange the above equation will produce:

$$\boldsymbol{\log q_e = \log K_F + n \log C_e}$$

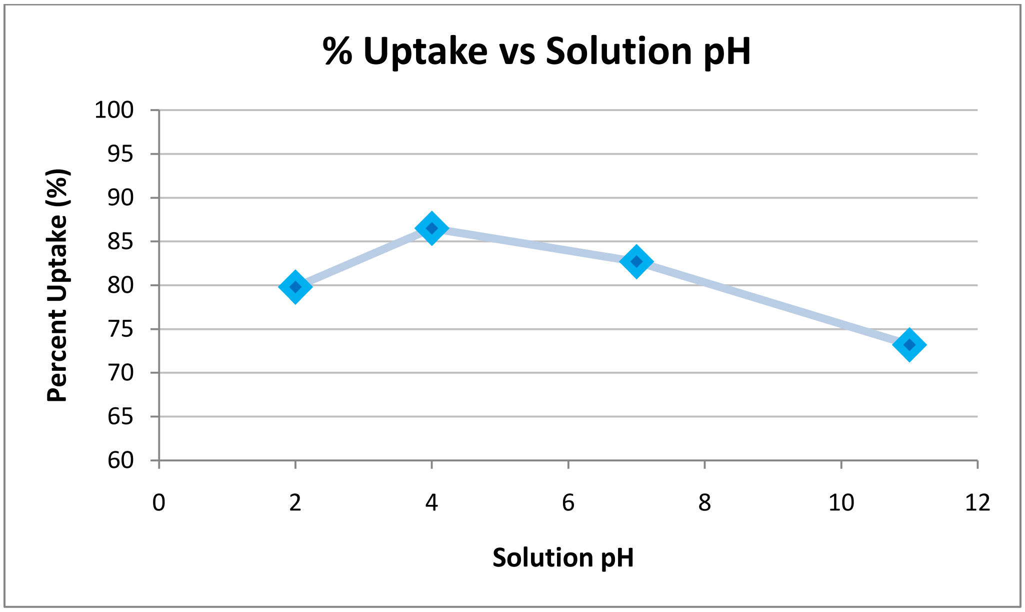




Isotherm	Constant		
Langmuir	Q_o (mg/g) 250	b (*l*/mg) $5\mathrm{x}10^{-4}$	R^2 0.977
Freundlich	K_F (mg/g) 1.35	n 0.55	R^2 0.988

The correlation of both Langmuir and Freundlich is 0.977 and 0.988 respectively which shows not much difference. Both plot give straight line for all concentration, implies that the ion exchange is well fitted to both isotherms.

4.3 Effect of Solution pH



The effects of initial pH of the solution on the removal of Cr^{3+} were investigated. pH was varied from 2 to 11 indicates three different conditions of solution: acidic, neutral and basic. It is shown in graph above that percentage uptake by the resin decreases rapidly when pH increased above 7 due to the formation of a chromium precipitate at higher pH values. Additional of NaOH to the solution in order to get higher value of pH leads to this condition. The resin is effective for the maximum removal of Cr^{3+} at a lower pH range (acidic condition).

**The results of the Scanning Electron Microscope (SEM) are attached in the Appendix section.*

CHAPTER 5

CONCLUSION & RECOMMENDATION

5.1 Conclusion

Comparing with other heavy metal removal method used in the industry, ion exchange technology can be applied to this study to extract Cr ion from plating wastewater before been released into the environment. This technique is used because ion exchange technology has many advantages as it can treat a large volume of effluent at once and more efficient in removal of ion from the wastewater. From the experiment conducted in the laboratory scale, the removal of Cr^{3+} ions from wastewater solutions were successfully enhanced by using ion exchange method.

From the different experiments conducted, it can be concluded that different condition of the solutions can affect the exchange capacity for resin. For the 1st experiment, the effect of resin capacity is investigated over the range of 1 to 5g of resin dosage. It is found that 4g of Lewatit S 1467 is the optimum amount of resin to remove Cr^{3+} from 150 ml of 1000 ppm solution. Thus in subsequent studies, 4g of resin were used.

Besides that, initial metal concentrations in the solution also affect the ion exchange process. Based on the result, the optimum condition for the Cr^{3+} to be removed by using 4g of resin is at initial concentration = 1500 ppm. Both Langmuir and Freundlich isotherms fit well with the ion exchange equilibrium data by producing straight line respectively.

Apart from that, for experiment of solution pH against the efficiency of resin, we found that acidic condition *(pH around 4 to 6)* is the optimum pH for the removal of Cr^{3+}. At pH above 7, precipitation forms metal complex which is no longer considered removal via ion exchange process; meanwhile at pH less than 4, high competition between H^+ and Cr^{3+} decreased the efficiency of Cr^{3+} removal.

5.2 Recommendation for Future Work

The project has met the expected results and goals, however some improvements still can be made to the current project. We believe that if these experiments are carried out using a proper ion exchange equipment, the effect of the solution on resin can definitely be measured more precise and accurately. Equipments should be handled properly by technicians to avoid sudden malfunction which could cause tremendous troubles to the students doing their projects. Other operating parameters such as flowrate of wastewater, operating temperature or contact time are also recommended to be taken into investigation.

CHAPTER 6: REFERENCES

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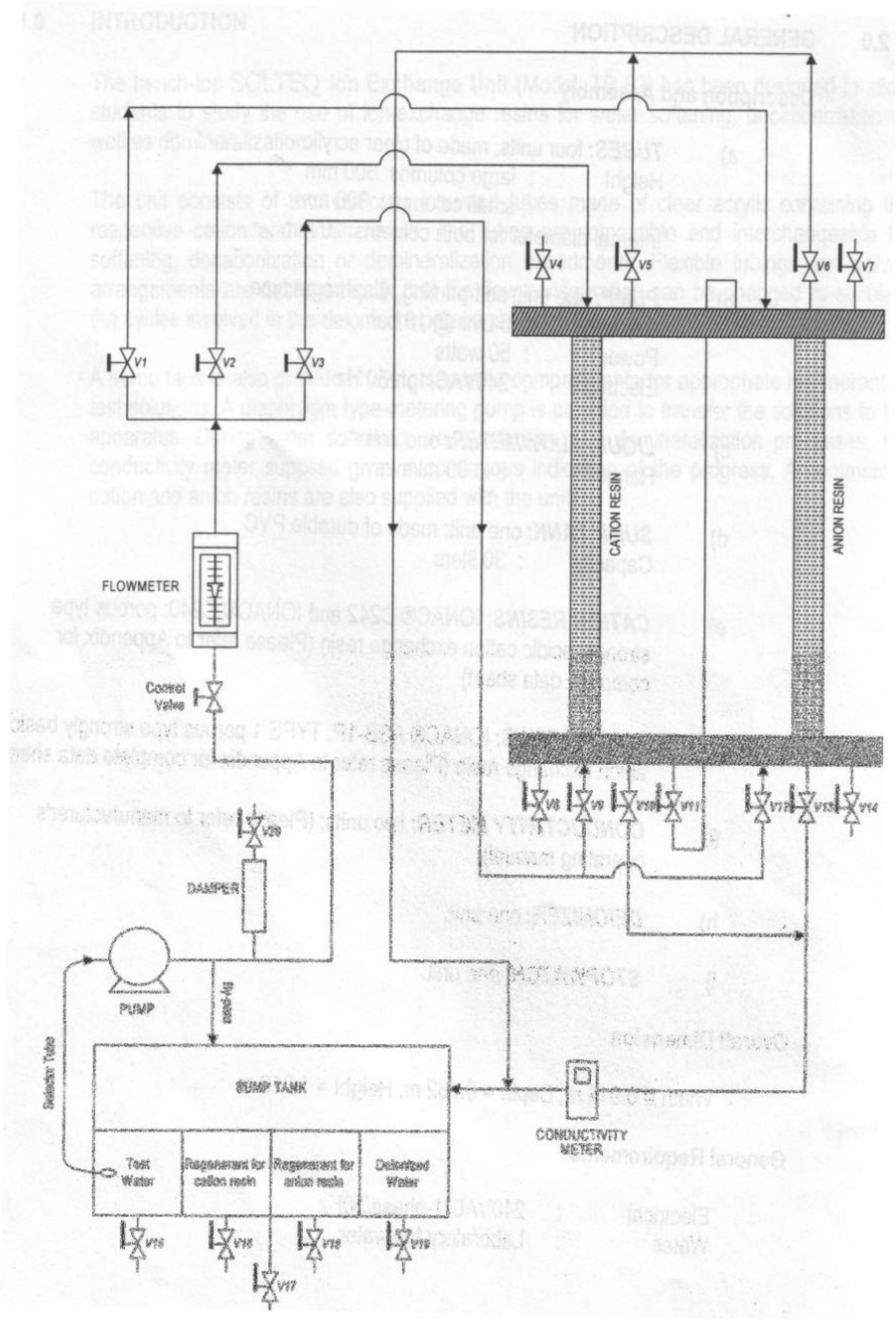
CHAPTER 7: APPENDICES

APPENDIX A: Schematic Diagram of the Ion Exchange Unit



The unit consists of:

a. Tubes

Two vertically mounted tubes made of clear acrylic containing the respective cation and anion resins. The tubes are removable and interchangeable for softening, de-cationization or demineralization experiments.

Height: large columns = 600 mm
small columns = 300 mm;

Internal diameter for both columns = 20 mm.

b. Pump

A diaphragm type-metering pump is provided to transfer the solutions to the column.

- Capacity: 5 L/hr @ 10 bar
- Power: 50 W
- Electrical: 240VAC / 1ph / 50Hz.

c. Liquid Flowmeter

Flowmeter is available to indicate the flow measurement during the experiment. The flow range is from 0 to 80 ml/min.

d. Sump tank

A 30-L tank made of durable PVC is provided for appropriate regenerant or tests the solutions.

e. Conductivity meter

Two units of conductivity meters are supplied to indicate the ion-exchange during the experiment.

i. Deionizer – provided to prepare the de-ionized water for rinsing purposes.
ii. Stopwatch – used to monitor the breakthrough point.

APPENDIX B: OPERATIONAL PROCEDURES

a) Pre-treatment of the resin:

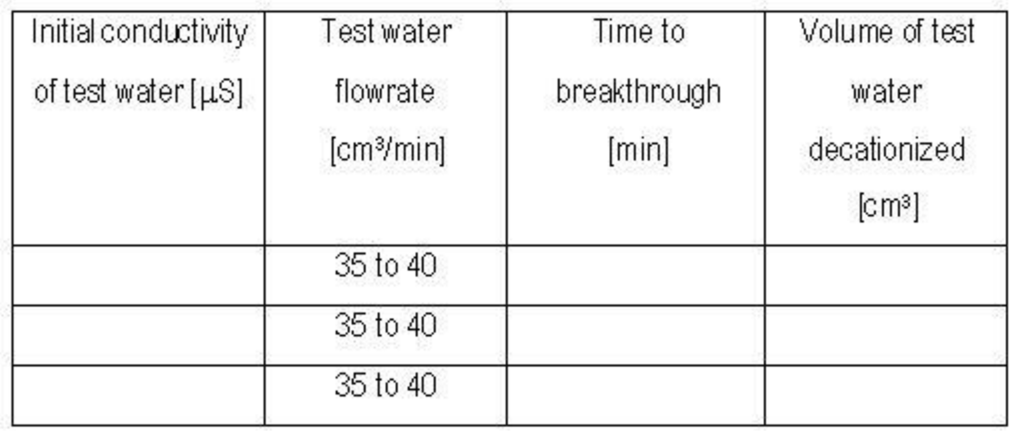
1. Fill in AMBERLITE IR 410 type resin into the cation column up to 30 cm height.
2. Prepare 5L deionized water in the appropriate reservoir. Record the conductivity meter reading of the deionized water.
3. Make sure all valves are closed.
4. Rinse the cationic resin in downward flow pattern by opening valves V2 and V10 (refer to figure).
5. Place the selector tube into the deionized water reservoir and start the pump (25-30% opening).
6. Adjust the control valve to obtain a flowrate between 35 and 40 cm^3/min.
7. Observe the conductivity meter. Stop rinsing when conductivity meter reading is close to conductivity reading of the deionized water.
8. Flush the deionized water out by opening valves V4 and V8.
9. When the entire residue has been removed, close V4 and V8.

b) Starting experiment:

1. Prepare solution (chlorium chloride/chromium sulphate) as test water. Record the initial conductivity meter reading of the test water.
2. Place the selector tube into the test water ($CaCl_2$) reservoir and start the pump (25-39% opening).
3. Adjust the control valve to obtain a flowrate between 35 and 40 cm^3/min.
4. Observe the conductivity meter. Record the conductivity reading every 5 s (the conductivity reading will decrease and remains at relatively low value).

   (Note: Stop recording when conductivity reading starts to increase)
5. Stop the operation by switching off the pump.

6. Determine the total time required to reach the “breakthrough” point from the plot of conductivity versus time.
7. Calculate the amount of test water that passed through the column before the “breakthrough” point.
8. Record the data obtained inside the water deionization table provided.



Initial conductivity of test water [µS]	Test water flowrate [cm^3/min]	Time to breakthrough [min]	Volume of test water decationized [cm^3]
	35 to 40		
	35 to 40		
	35 to 40		

9. Later test the concentration of the outlet solution by using Atomic Absorption Spectrophotometer (AAS) available in block 5 lab.

c) Regeneration of resin:

1. After decationization, regenerate the cationic resin by using 5% of hydrochloric acid (HCl) solution in downward flow pattern.
2. Set the regenerant flowrate to 60 cm^3/min and allow a minimum contact time of 40 minutes.
3. Then, rinse the generated resin with deionized water at 35 to 40 cm^3/min flowrate until conductivity meter reading is close to conductivity reading of deionized water.

Method 8506

Chromium (0 to 5.00 mg/L)

For water, wastewater and seawater*

Bicinchoninate Method** (Powder Pillows or AccuVac Ampuls); USEPA approved for reporting wastewater analysis (digestion needed; See Section 2)***

Using Powder Pillows

1. Enter the stored program number for bicinchoninate copper (**Cr**)- powder pillows.

Press: PRGM

The display will show:

PRGM ?

Note: For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).

2. Press: 20 ENTER

The display will show **mg/L, Cr** and the **ZERO** icon.

Note: Determination of total copper needs a prior digestion (see Digestion in Section 2).

3. Fill a sample cell with 10 mL of sample (the blank).

Note: Adjust the pH of acid preserved samples to 4-6 with 8 N KOH before analysis. Do not exceed pH 6 or copper may precipitate.

4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

5. Press: **ZERO**

The cursor will move to the right, then the display will show:

0.00 mg/L Cr

Note: If Reagent Blank Correction is on, the display may flash "limit".

6. Fill another sample cell with 10 mL of the sample.

7. Add the contents of one CuVer 1 Chromium Reagent Powder Pillow to the sample cell (the prepared sample). Swirl the cell to mix.

Note: If copper is present, A purple color will develop.

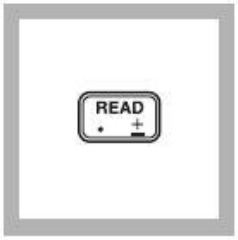
8. Press:

TIMER ENTER

A two-minute reaction period will begin.

Note: Accuracy is not affected by undissolved powder.

9. Within 30 minutes after the timer beeps, place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



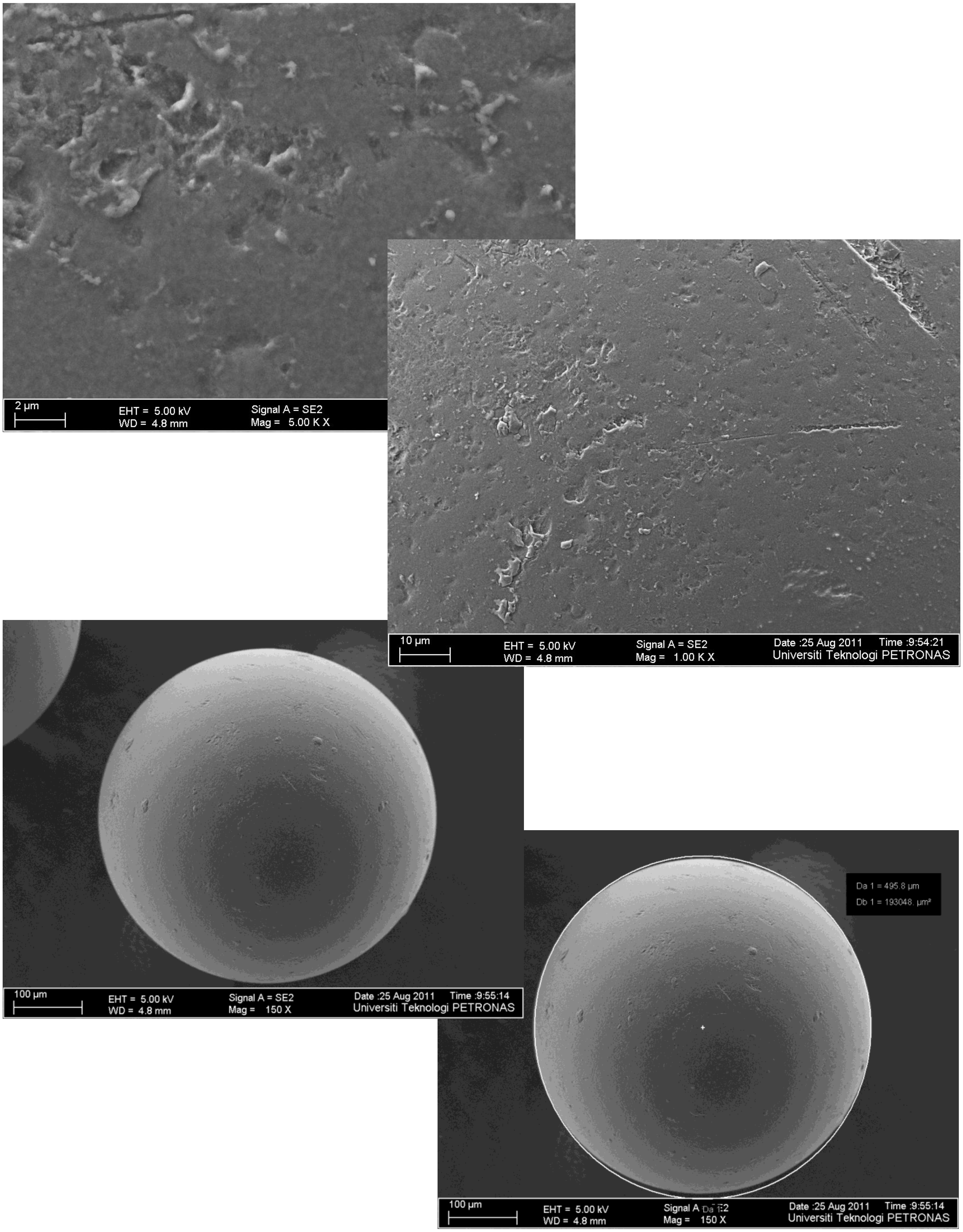
10. Press: **READ**

The cursor will move to the right, then the result in mg/L chrom will be displayed.

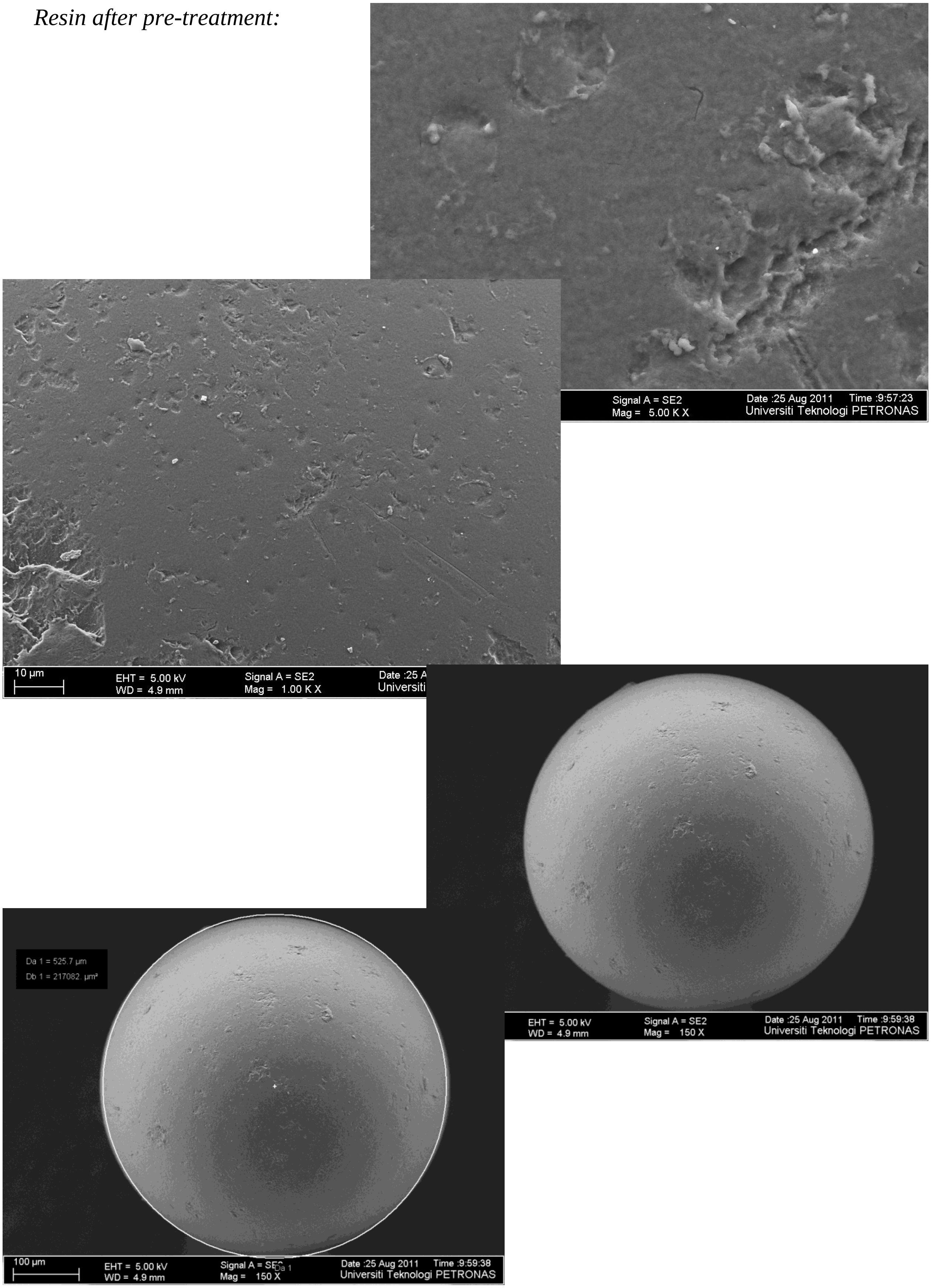
Note: Standard Adjust may be performed using a prepared standard (see Section 1).

APPENDIX D: Scanning Electron Microscope (SEM) Results

Raw resin:



Resin after pre-treatment:



Resin after experiments: