UNIVERSITI
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Zinc ion removal from aqueous solution using ion exchange process

by

Mohd Shamsul Amri bin Mohd Jailani

10780

Dissertation submitted in partial fulfillment of

the requirements for

Bachelor of Engineering (Hons)

(Chemical Engineering)

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Universiti Teknologi PETRONAS
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CERTIFICATION OF APPROVAL

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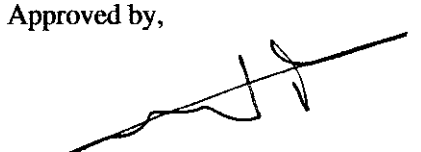
Approved by,



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(Dr. Usama Mohamed Nour Eldemerdash)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

SEPTEMBER 2011

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgement, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

(Mohd Shamsul Amri bin Mohd Jailani)

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ABSTRACT

Industries such as electroplating, dyes manufacturing, metal plating facilities and other similar industries produce heavy metal which are highly toxic for human and the environment. Zinc is one of the heavy metals discharge from above mentioned industries and need to be treated according to the regulation limit imposed by Malaysian government. There are several methods for removing heaving metals from wastewater. Ion exchange process using resin have many advantages compared to other methods hence will be used in this study. The extent of the project work are conducting experiment to determine the influence of different operating parameters on the zinc ion removal process specifically effect of initial concentration (50ppm, 100ppm & 150ppm) and effect of pH (3, 5 & 7), determine the effect of regeneration on the resin's performance and analyze the experimental data using Thomas model. Results from this project work will be useful in designing wastewater treatment system in the industry.

ACKNOWLEDGEMENT

I am very grateful and very thankful to ALLAH, the Most Gracious, the Most Merciful that give me the strength and His bless until I managed to finish this Final Year Project.

During this period of time, I am in debt to many people in order to finish this project successfully. My deepest gratitude goes to my supervisor, Dr. Usama Mohamed Nour Eldemerdash, who helps me a lot, giving me full support with enlightening supervision, and providing me with valuable guidance throughout the project.

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Finally, my thanks also go to all my friends who have directly or indirectly lent a helping hand for me in order to finish my final year project. Last but not least, to all my family members that continuously keeping me motivated throughout the year.

Thank you very much.

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Heavy metals can be found in many industries such as electroplating, dyes manufacturing, metal plating facilities and other similar industries. Nickel, cobalt, zinc, copper, lead and boron are examples of heavy metal ions discharged from different mentioned industries. The heavy metals can give serious impact to the environment and human because they are highly toxic, non biodegradable and can be accumulated in nature.

Zinc is a lustrous bluish-white metal. As one of the components of a certain protein inside human body it is an essential element for human life. However, overdose of zinc intake can cause various diseases to human such as stomach cramps, skin irritations, vomiting, nausea and anaemia. Free zinc ion in solution is also highly toxic to plants and animals. More information on zinc can be summarized on table 1.

Table 1.1: Zinc Properties

Atomic number	30
Atomic mass	65.37 $g.mol^{-1}$
Density	7.11 $g.cm^{-3}$ at 20°C
Melting point	420 °C
Boiling point	907 °C

(source: http://www.lenntech.com/periodic/elements/zn.htm)

Malaysian Government imposed strict environmental standards regarding the discharge limit of these heavy metal pollutants to protect the environment. The limit for zinc discharge in the wastewater is 2 mg/L (Environmental Quality [Industrial Effluent] Regulations, 2009). In order to meet these requirements, a lot of researches are made on industrial wastewater treatment methods.

1.2 Problem Statement

It is crucial to remove heavy metals specifically zinc ions because it is highly toxic to living organism and also can cause huge damage to the environment. Zinc is also among the most significant pollutants for surface and ground water. There are several methods for removal of zinc ions from industrial waste water such as chemical precipitation, ion exchange, and adsorption.

The main advantages of ion exchange compared to the conventional method which is chemical precipitation are recovery of metal value, less sludge volume produce and can meet the strict discharge requirement. Ion exchange process using resin also has many advantages over the other methods such as high efficiency, low cost and easy to operate. So, the present work will focus on the removal ability of an ion exchange resin in detail. The main concern in this work is to focus on the optimum operating parameters for column technique. It's important to have further experimental work as the data will be useful in designing effluent treatment plant.

1.3 Objectives and Scope of Study

Objectives:

- To determine the influence of different operating parameters namely initial metal concentration and pH on the zinc ion removal process.
- To investigate the effects of regeneration on the resin's performance.
- To calculate and identify the exchange kinetics of the ion exchange process.

Scope of Study:

- Conducting experiments to determine the influence of different operating parameters on the zinc ion removal process and the effects of regeneration on the resin's performance.
- Conducting research on the applicable model related to this study.

CHAPTER 2

LITERATURE REVIEW

2.1 Ion Exchange

Ion exchange is a reversible chemical reaction where ions from the solution interchange with the similarly charged ion in the solid phase which is the ion exchanger (Harland, 1994). The ion exchanger is insoluble in the medium which the exchange is carried out. Ion exchange resins are one of the typical ion exchangers that are used in chemical industry. The resins are made from synthetic organic materials that contain ionic functional groups to which exchangeable ions are attached. They also may be inorganic and natural polymeric materials. These resins can be regenerated for re-use after its capacity has been exhausted.

Two types of ion exchangers are anion exchangers that exchange negatively charged ions and cation exchangers that exchange positively charged ions. Both anion and cation resins are produced from the same basic organic polymers. The difference is in the ionizable group attached to the hydrocarbon network. It is this functional group that determines the chemical behavior of the resin. Resins can be generally classified as strong or weak acid cation exchangers or strong or weak base anion exchangers. The table below summarizes the resin types and its functional group.

Table 2.1: Resin Types

Resin Type	Functional Group	Structure	Remark
Strong Acid Cation	Sulphonic acid	$—SO_3^- H^+$	Independent of solution pH
Weak Acid Cation	Carboxylic acid	—COOH	Strongly influenced by the solution pH
Strong Base Anion	Quaternary ammonium	$—N(CH_3)_3^+ OH^-$	Independent of solution pH
Weak Base Anion	Amines	$—N(CH_3)_2$	Strongly influenced by the solution pH

2.2 Thomas Model

The experimental data will be analyzed using Thomas model. This model is accurate in predicting the breakthrough curve under various operating condition and its simplicity makes it convenient for practical use. Assumption made while using this model is that at a constant flow rate and no axial dispersion, the behavior matches with the Langmuir isotherm and the second order reversible reaction kinetics.

The model can be represented by

$$\frac{C}{C_O} = \frac{1}{1+\exp\left(\frac{k_{Th}}{u}\left(q_O W - C_O V_{eff}\right)\right)}$$

Where k_{Th} is the Thomas rate constant (m^3/mol min)), q_O is the maximum amount of exchange equivalent to an equilibrium aqueous-phase concentration of C_O (mol/kg), u is the volumetric flow rate (m^3/min), W is the amount of resin in the bed (kg) and V_{eff} is the effluent volume.

The linearized form of Thomas model is as follows:

$$\ln\left(\frac{C_O}{C} - 1\right) = \frac{K_{Th} q_O m}{Q} - \frac{K_T C_O}{Q} V$$

At a constant flow rate, a grap plot of ln $[C_o/C)-1]$ vs. t can be drawn. Then, the kinetic parameter k_{Th} and fixed-bed exchange q_o in the model can be calculated from the obtained slope and intercept, and parameter t can be obtained at $C = C_o/2$.

2.3 Operating Parameters

From literature, it has been reported that ion exchange technique using resin can be optimized through the analysis of several operating parameters such as pH value, initial metal concentration, temperature, resin dose, volumetric flow rates, and effect of regeneration. The table below summarizes previous works of Zn(II) ion removal employing ion exchange technique using resins.

Table 2.2: Previous Works

Variables	Metal Removed	Resin Type	Reference
1. initial concentration 2. resin dose 3. resin particle size	• Zn(II)	Chelating	Shek, Ma, Lee & Mckay (2008)
1. initial concentration 2. pH 3. temperature	• Zn(II) • Cu(II)	Chelating	Lin & Juang (2005)
1. pH 2. resin dose 3. contact time	• Zn(II) • Ni(II)	Strong Acid Cation	Alyuz & Veli (2009)
1. resin dose 2. pH 3. initial concentration 4. temperature 5. contact time	• Zn(II) • Cu(II) • Pb(II) • Cd(II)	Strong Base Anion	Koloynska (2011)
1. pH 2. contact time 3. resin dose 4. initial concentration	• Zn(II)	Chelating	Zhang et al. (2010)

2.3.1 pH

The pH of the solution is an important parameter in ion exchange process because it influences the ionization of resin's surface functional groups. Alyuz & Veli (2009) reported that the optimal uptake of Zn(II) occurred at pH 6. This is due to at higher pH values, the formation of $Zn(OH)_2$ during reaction of Zn^{2+} ions with OH^- lead to decrease in removal efficiency achieved by the resins. The figure below shows the result of their research.

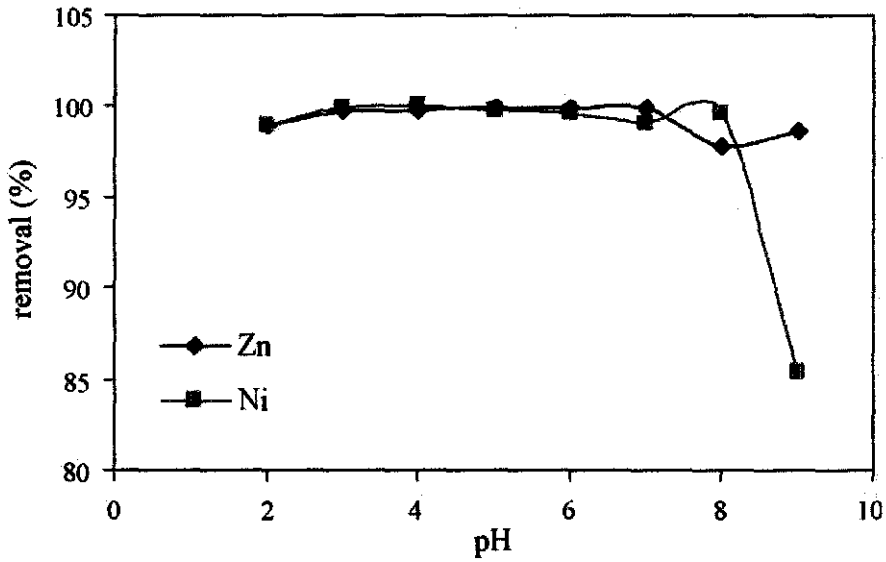


Figure 2.1: Effect of pH on removal of nickel and zinc by Dowex HCR S/S cation exchange resin.

2.3.2 Initial metal concentration

Zhang et al. (2010) studied the effect of initial Zn(II) concentration where it was adjusted in the ranges of 10-100 mg L^{-1}. The results showed that the removal percentage of Zn(II) by the resin increased rapidly with increase in the Zn(II) concentration in the ranges of 10-40 mg L^{-1}, while increased slowly as the ion concentration was higher than 40 mg L^{-1} as shown in figure 2. The increase in metal ion concentration will lead to an increase in metal ion adsorbed because there is an increase in the driving force of the metal ions towards the active sites on the adsorbents. However, the decrease in the active sites on the sorbents lead to the decrease of metal ion adsorbed as the Zn(II) concentration approaches 100 mg L^{-1}.

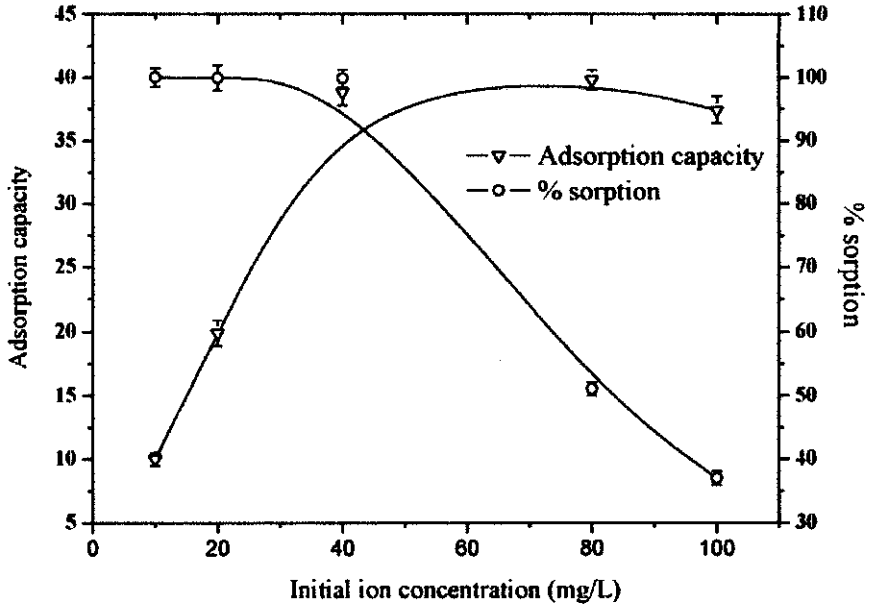


Figure 2.2: Effect of initial ion concentration of Zn(II) sorption under pH 6 at 30°C.

2.3.3 Temperature

Rao, Chaudhury & Mishra (2010) found out that the uptake capacity of the resin (Duolite ES 467, a cation exchange resin) increased with the increase of temperature. The experiment was carried out at four different temperatures 30, 40, 50 and 60°C. Figure 3 shows the result.

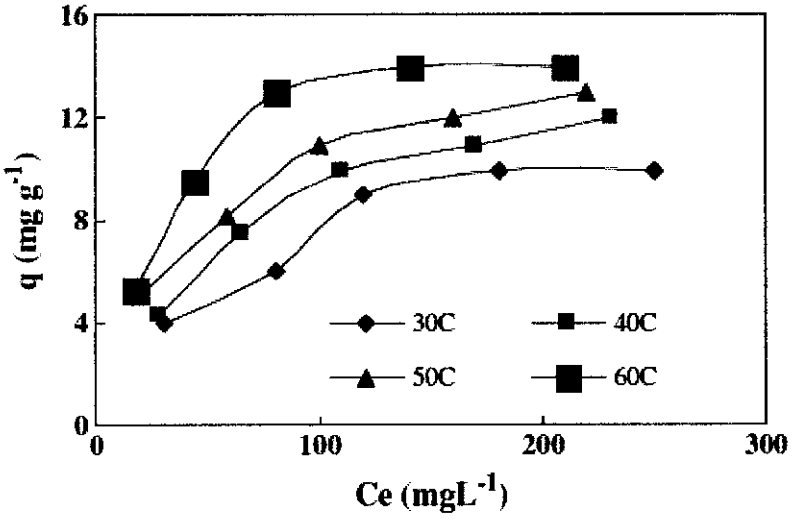


Figure 2.3: Equilibrium isotherms of cadmium sorption at different temperatures.

2.3.4 Resin Dose

The effect of the exchanger amount is an important variable in metal ion sorption. Alyuz & Velu (2009) studied the effect of resin dosage by varying the amount of Dowex HCR S/S (0.05-0.7 g) while the other operating are kept constant. The results showed that the percentage of metal adsorbed increased with higher resin dose due to formation of greater adsorption sites. Pehlivan & Cetin (2008) and Edebali & Pehlivan (2010) conclude that the removal efficiency increases but ion exchange density decreases by increasing the amount of the resin dose.

2.3.5 Volumetric flow rates

Haghsheno, Mohebbi, Hashemipour & Sarrafi (2008) reported when the flow rate increased from 30 to 70 ml/min, the breakthrough curve become steeper and the breakpoint time decreased. The figure below shows the result of the research.

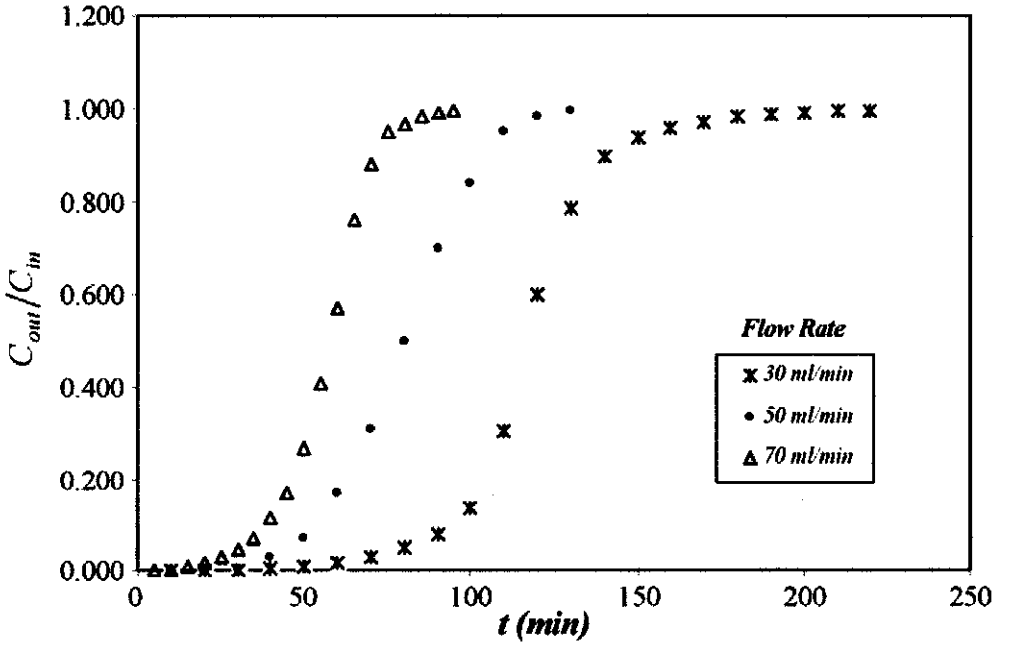


Figure 2.4: the effect of feed flow rate on the breakthrough curve

2.3.6 Regeneration

Regeneration purpose is to recover the metal adsorbed in concentrated form and also to reuse the resin for more usage thus lowering the operational cost. Donia, Atia & Mabrouk (2011) showed that the regeneration efficiency of the resin using 1M HCl is 99%. Kose & Ozturk (2007) carried out 3 consecutive cycles of regeneration using an anion exchange resin. The results showed that the capacity did not noticeably change after 2^{nd} and 3^{rd} cycles which conclude the resin could be repeated used. Cavaco, Fernandes, Quina & Ferreira (2007) also conclude that it is possible to regenerate the resins in their study.

CHAPTER 3

METHODOLOGY

3.1 Research Methodology

The first step taken for this project is to make decisions on the desired findings. In this study it is to find the optimum operating parameter for the resin, the effects of regeneration and study about related isotherm and kinetic model. After that, the next step is to find the literature review of articles, books or journals related to this project. Literature review is an important part in this research as it helps to improve the methodology while widen the knowledge related to this project. From all the information gathered, the flow chart of this project has been created and can be referred to in Figure 3.1.

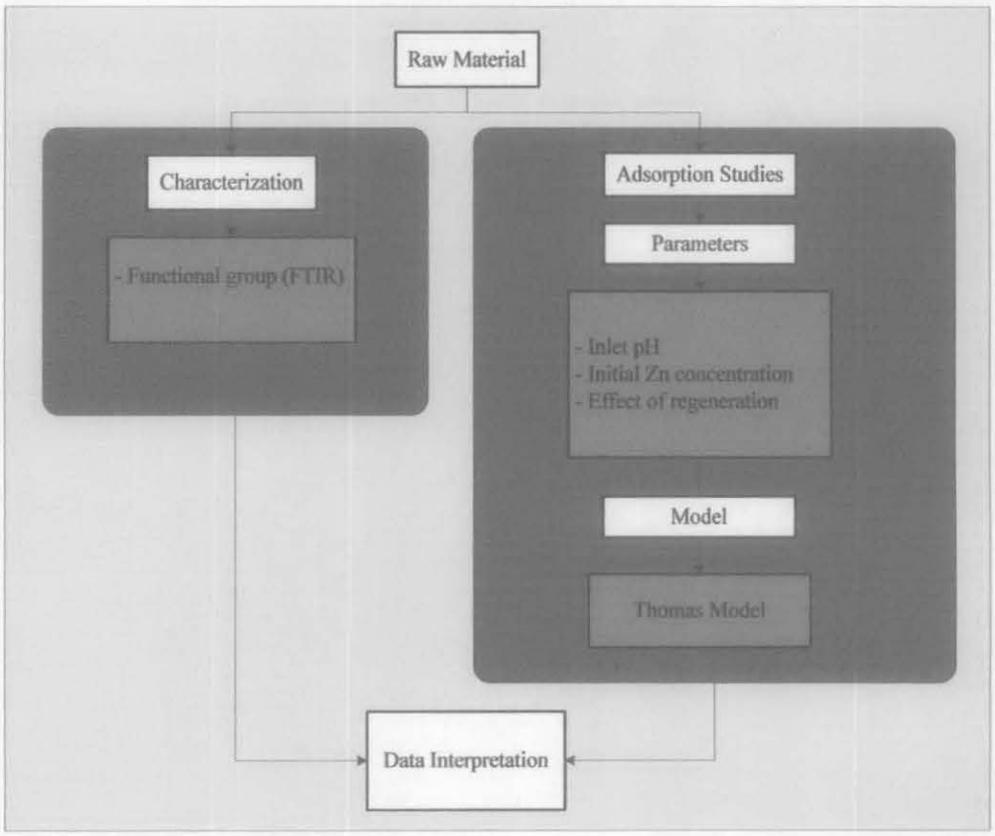


Figure 3.1: Flow chart of overall project works

3.2 Project Methodology

3.2.1 Overview

This experiment is conducted using column technique and the synthetic waste water is prepared by dissolving zinc sulfate ($ZnSO_4.7H_2O$) in distilled water. There are three parameters that will be included in this experiment namely initial metal concentration, inlet pH and effect of regeneration. All the experiments were carried out manipulating the mentioned parameters while keeping the temperature (25°C) and flow rate ($35cm^3/min$) constant. The diameter of the column used for this experiment is 2 cm and 60 cm height.

For the initial metal concentration, the parameters were varied at 50 ppm, 100 ppm and 150 ppm. Meanwhile for the pH of the solution, the parameters were varied at pH=3, pH=5 and pH=7. The inlet pH is adjusted using 5% NaOH and 5% H_2SO_4. Lastly, the regeneration experiment is carried out at pH 3 with initial concentration 100 ppm.

The pH of the test water is tested using a pH meter and the concentration of the outlet samples were tested using atomic absorption spectrophotometer (AAS). Characterization of the resins will be determined by using the Fourier Transform Infrared Spectroscopy (FTIR).

3.2.2 Pretreatment of the Resin

The resins need to be pre-treated before the experiments were carried out. The method used in the pretreatment is rinsing the resin in downward flow pattern by using deionized water excessively. The Hydrogen ion (H^+) in the deionized water will replace the Sodium ion (Na^+) in the resins. The complete procedure is attached in the Appendix.

3.2.3 Regeneration of the Resin

The resins will be exhausted after continuous usage and it can be regenerated. The ability of the resin to be regenerated is important as it will be cost effective in the industry. The resins are regenerated using 5% sulfuric acid (H_2SO_4) solution in a downward flow pattern. Minimum contact time of 40 minutes is allowed in the regeneration with constant flow rate of 35cm^3/min. After that, the resin is rinsed with deionized water.

3.3 Tools and Materials

3.3.1 Tool: Ion Exchange Unit

The ion exchange unit is the main equipment used in this experiment, specifically SOLTEQ Ion Exchange Unit (Model: TR02). The equipment consists of two columns which are cationic column and anionic column. Each column has a diameter of 2 cm and length of 60 cm. In this project work, only the cationic column was used.

Figure 3.2: SOLTEQ Ion Exchange Unit (Model: TR02)

3.3.2 Tool: Atomic Absorption Spectrophotometer (AAS)

The outlet concentrations of the sample were tested using the AAS.

Figure 3.3: Atomic Absorption Spectrophotometer

3.3.3 Material: Resin

A synthetic strong acid cation resin, Lewatit S 1467, produced by Lanxess was used in the experimental studies. The resin is in Na^+ ionic form with sulfonic acid functional group. It is light brown, gel type beads that have crosslinked polystyrene matric. The physical and chemical properties of the resin are tabulated below:

Table 3.1: Physical and Chemical Properties

Resin	Lewatit S 1467
Total Capacity	2.0 eq/L
Mean Bead Size	0.60 mm
Maximum Swelling	8% (Na^+ to H^+)
Bulk Density	8.20 g/l

Figure 3.4: Lewatit S 1467 resin

3.3.4 Material: Chemicals

Zinc sulfate ($ZnSo_4.7H_2O$) made by HmBG chemicals was used to prepare the synthetic wastewater. In order to regenerate the resin, sulfuric acid (H_2SO_4) manufactured by Merck chemical was used. For pH adjustment, the following chemicals are used namely sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) manufactured by Merck chemical.

Figure 3.5: Zinc sulfate ($ZnSo_4.7H_2O$)

3.4 Resin Characterization

3.4.1 FTIR (Fourier Transform Infra Red)

FTIR (Fourier Transform Infra Red) will be used to characterize the resin in this experiment. The FTIR is widely used to determine the structure of organics compound and can identify the presence of certain functional groups within a molecule. FTIR technique is an analytical method used to identify the chemical structure of many inorganic chemical and also organics materials or compound. Most FTIR units operate within the range of 400-4000 cm^{-1} wave number. The wave number is used as these numbers are directly proportional to energy. Functional group tends to adsorb a photon of infrared radiation. Hence, the energy increase and it is associated with bond vibrations involving in the stretching and bending of bonds. FTIR analysis can be applied to small quantities of materials, whether solid, liquid, or gaseous.

3.5 Gantt Chart and Key Milestone

The project work is divided into two parts in 8 months two semester period. For Final Year Project 1 (FYP 1), the research work is done. The experimental works is carried out during Final Year Project 2 (FYP 2).

Timelines for FYP 1

No.	Activities /Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Selection of Project Topic														
2	Preliminary Research Work														
3	Submission of Extended Proposal														
4	Proposal Defence														
5	Project work continues														
6	Submission of Interim Draft Report														
7	Submission of Interim Report														

Timelines for FYP 2

No.	Activities /Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Project work continues														
2	Submission of progress report														
3	Project work continues														
4	Pre EDX														
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)														

Process Milestone

Figure 3.6: Gantt charts and key milestone

CHAPTER 4

RESULT AND DISCUSSION

4.1 Resin Characterization

4.1.1 FTIR Analysis

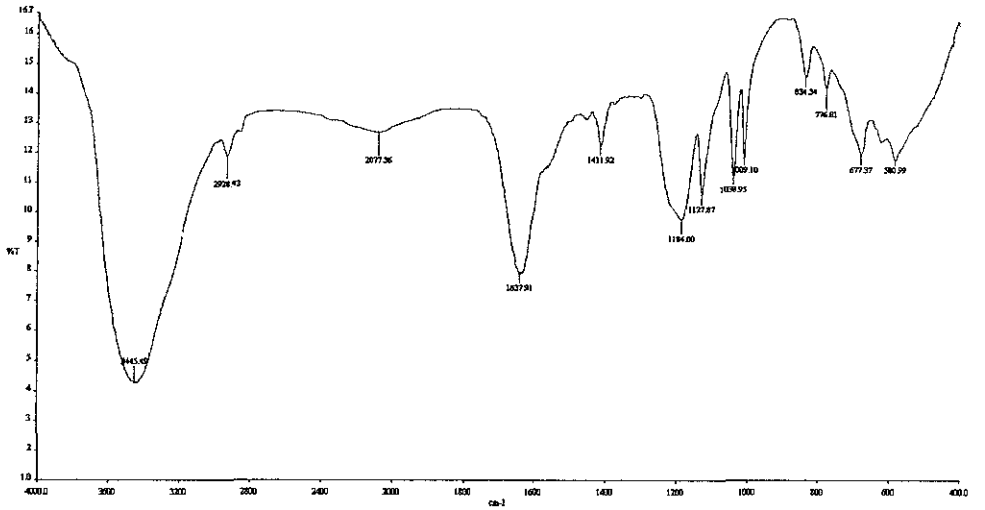


Figure 4.1: After pre-treatment with deionized water

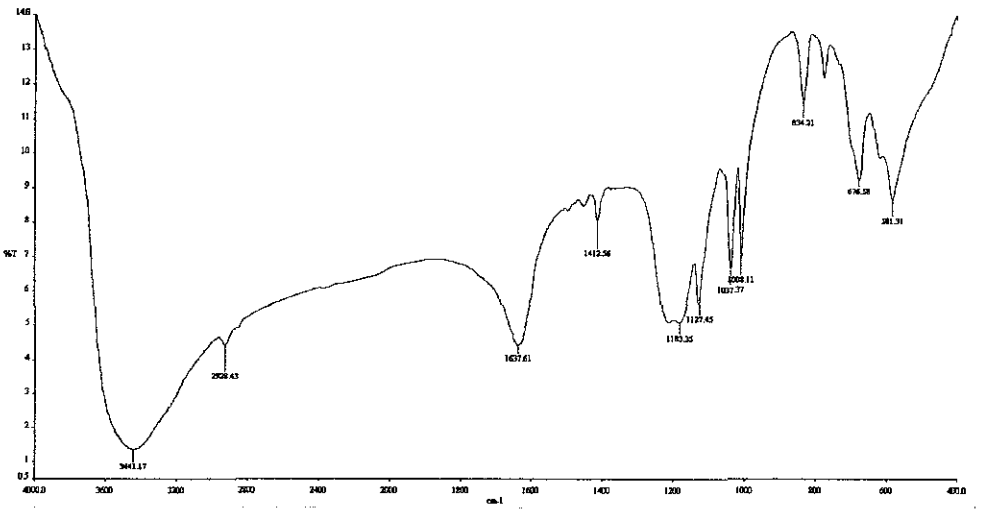


Figure 4.2: After zinc loading

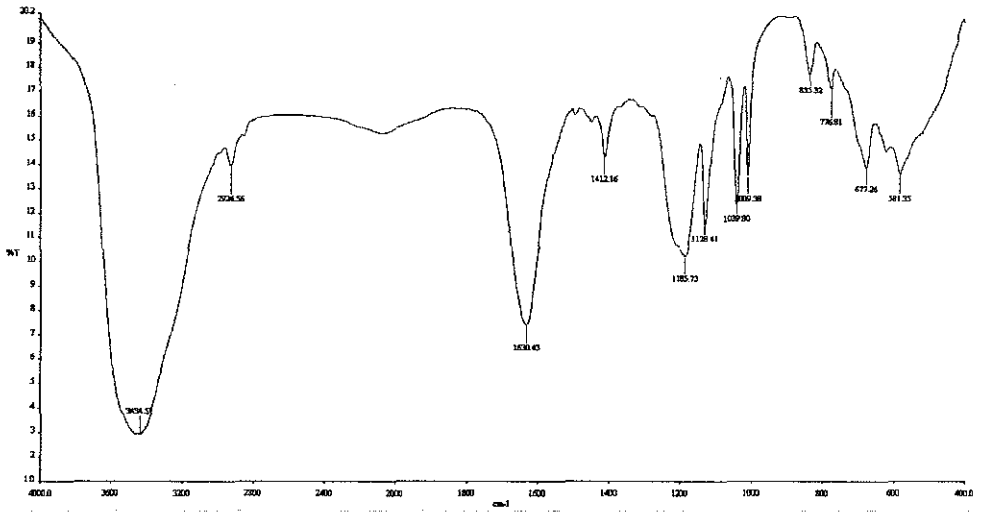


Figure 4.3: After regeneration with sulfuric acid

The FTIR is used to determine the functional group available in the cation resin. Three resin samples were analyze; resin after pretreatment with deionized water, resin after zinc loading and resin after regeneration with sulfuric acid. Referring to figure 4.1, it can be observed that a broad peak at 3445 cm^{-1} which indicates the OH group. This is due to the presence of water in the resin. The band at 1637 indicates that the stretching vibration of primary amine group. After the zinc loading, it can be seen on figure 4.2 that the values of every peak are decreasing. After regeneration, it can be observed that the peaks are increasing back to its initial band. This shows that the resin can be reuse after regeneration has been done.

4.2 Effect of Initial concentration

For the effect of initial concentration, the experiment is carried out at 50 ppm, 100 ppm and 150 ppm. The pH of the synthetic wastewater solution is prepared at pH=5 and the flow rate is kept constant at 35cm^3/min. the cation column if filled up to 10 cm height in the column.

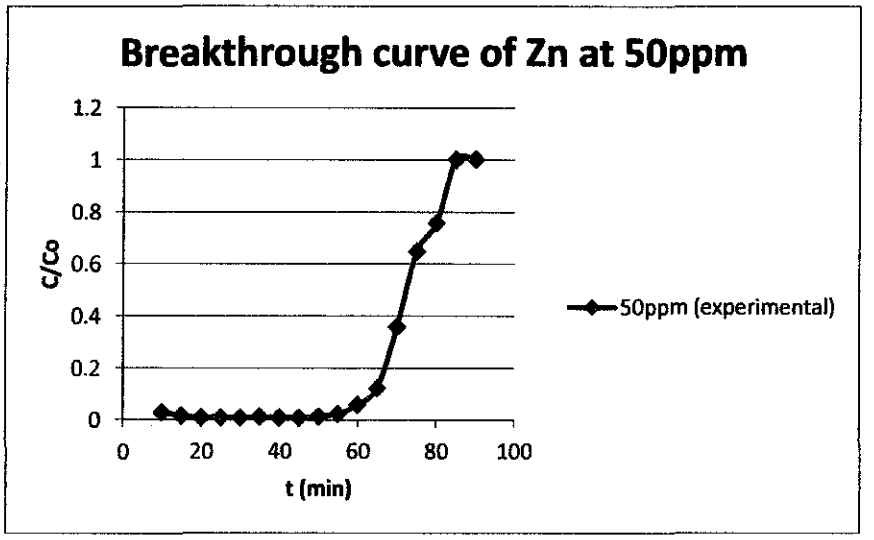


Figure 4.4: Breakthrough curve of Zn(II) at 50 ppm

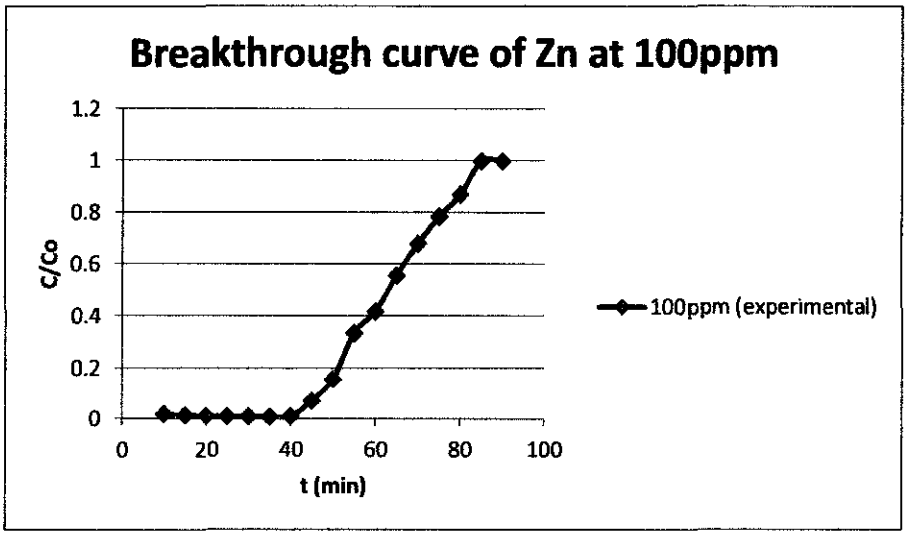


Figure 4.5: Breakthrough curve of Zn(II) at 100 ppm

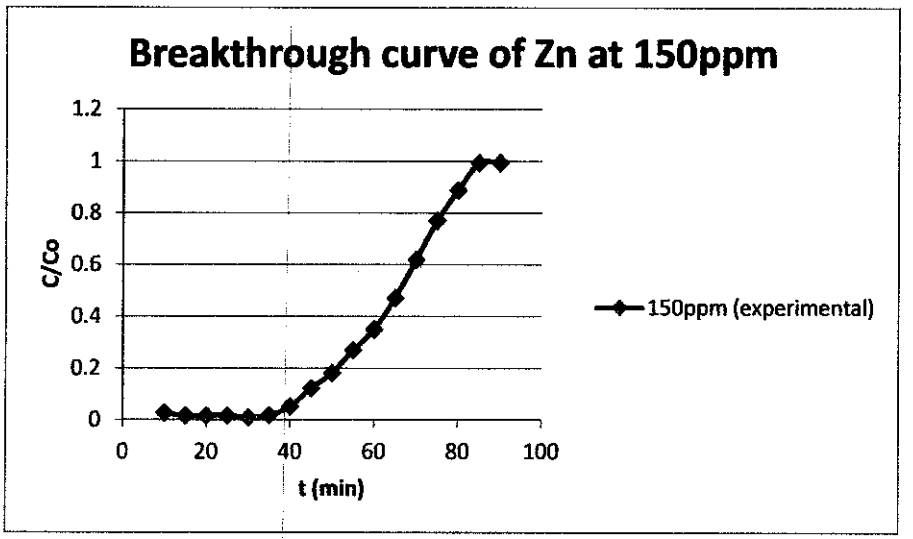


Figure 4.6: Breakthrough curve of Zn(II) at 150 ppm

Table 4.1: Breakthrough time for different initial concentration

Initial concentration (ppm)	Breakthrough time (min)
50	55
100	40
150	30

Referring to the figure 4.4, 4.5 and 4.6, the breakthrough curves for different initial metal concentration is shown. Table 4.1 shows the breakthrough time for each initial concentration variables. After the breakthrough have been reached, the resin in exhausted and can't absorb anymore contaminant. Regeneration is needed in order to reuse the exhausted resin. It is shown in Table 4.1 that breakthrough time for initial concentration at 50ppm is 55 minutes meanwhile the breakthrough concentration for initial concentration at 150ppm is 30 minutes. The breakthrough time decrease with increasing initial zinc concentration. It can be justified that the exchange sites of the resin reach maximum saturation faster when there are more zinc ion in the solution. The amount of zinc ion increase as the concentration of zinc increases and therefore decreasing the breakthrough time needed.

Similar trend is studied by Ozturk & Kose (2007) that the phenomenon is due to the driving force of the concentration gradient, as the increase in the initial metal ion concentration. It is also reported that in the study an increase in initial metal concentration will also increase the amount of metal absorbed. Another study by Zhang et al. (2010) concluded that the effect of initial Zn(II) concentration will increase as the concentration increase but only in the range of 10 to 40 mg L^{-1}.

Won & S.Hun (2006) reported that for continuous flow ion exchange column, the first order reversible adsorption model such as Thomas's Model is selected for the kinetic studies. As per discussed in the literature review, Thomas Model will be used to analyze kinetic data in this experiment. The graphs below show the determination of Thomas parameters and exchange capacity for different inlet concentration.

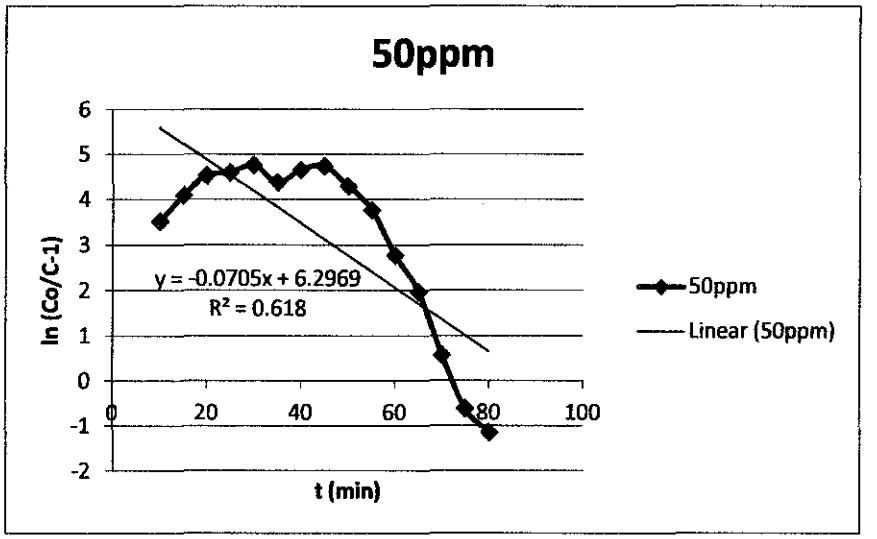


Figure 4.7: Graph for determination of Thomas Parameters (50 ppm)

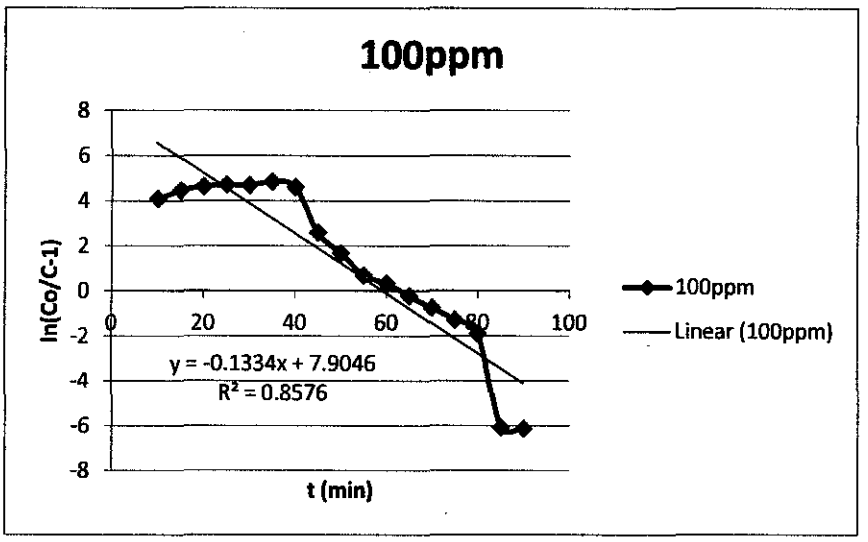


Figure 4.8: Graph for determination of Thomas Parameters (100 ppm)

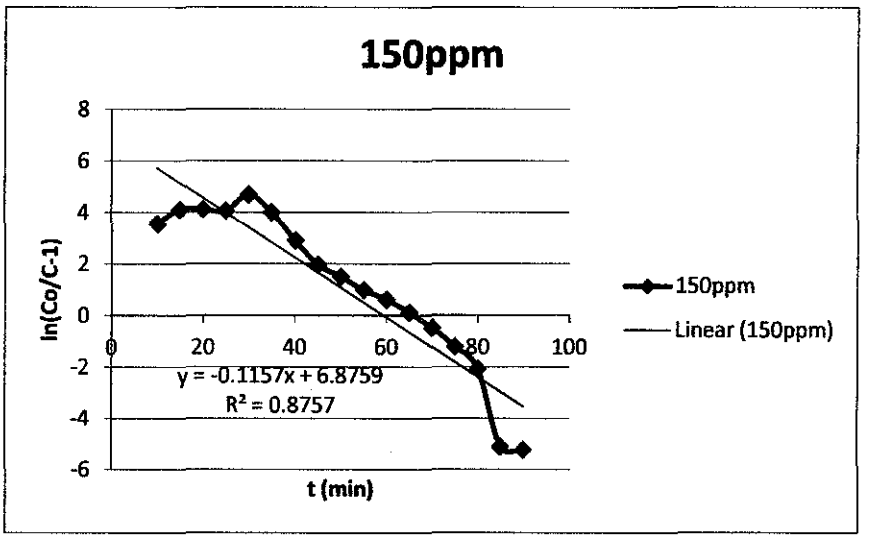


Figure 4.9: Graph for determination of Thomas Parameters (150 ppm)

Table 4.2: Properties of Ion Exchange for Different Initial Concentration

Initial Concentration (ppm)	Exchange Capacity, q_o (mol/kg)	k_{Th}
50	4.491	0.002
100	0.125	0.092
150	0.201	0.050

The value of exchange capacity, q_o and Thomas coefficient, k_{Th} is determined based on graph ln((Co/C)-1) versus t as illustrated in the Figure 4.7, 4.8 and 4.9. Table 4.2 shows that as the concentration are increasing from 100ppm to 150ppm, the exchange capacity also increase from 0.125mol/kg to 0.201mol/kg. Besides that, it also can be concluded that the exchange capacity is inversely proportional to the Thomas coefficient. Based on the values of q_o and k_{Th} obtained, the breakthrough curve can be constructed.

4.3 Effect of pH

The extractability of the cation phase from the solution phase is pH dependent because of it will affect the solubility of metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction is mentioned in Zhang et al (2010) report.

The effect of pH on zinc removal for this project work is carried out at initial zinc concentration of 100ppm, temperature of 25°C and flow rate of 35cm^3/min. The pH of the synthetic wastewater is decreased using sulfuric acid (H_2SO_4) to pH 3 and is increased to pH 7 using sodium hydroxide (NaOH).

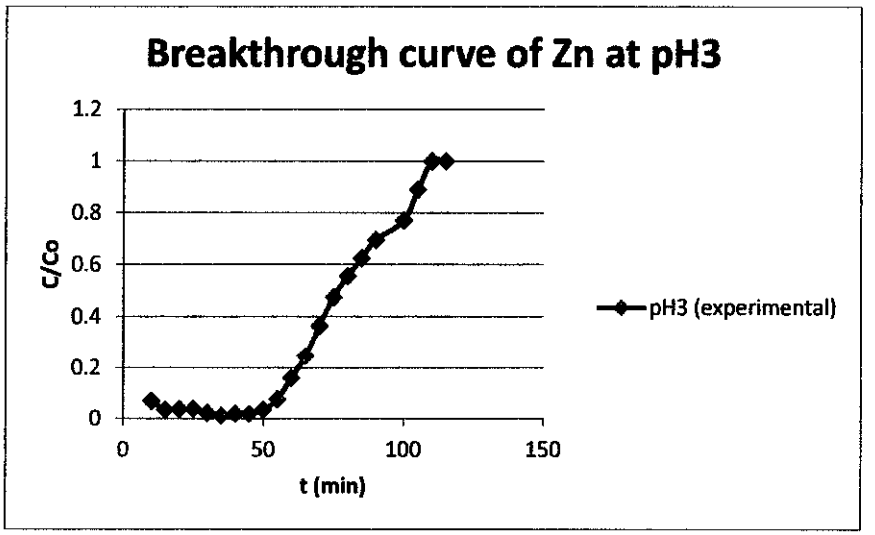


Figure 4.10: Breakthrough curve of Zn(II) at pH 3

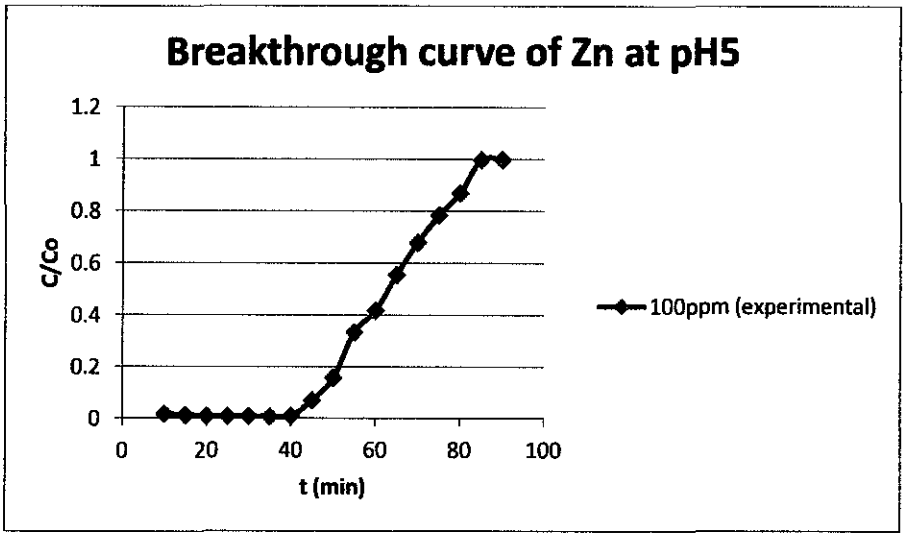


Figure 4.11: Breakthrough curve of Zn(II) at pH 5

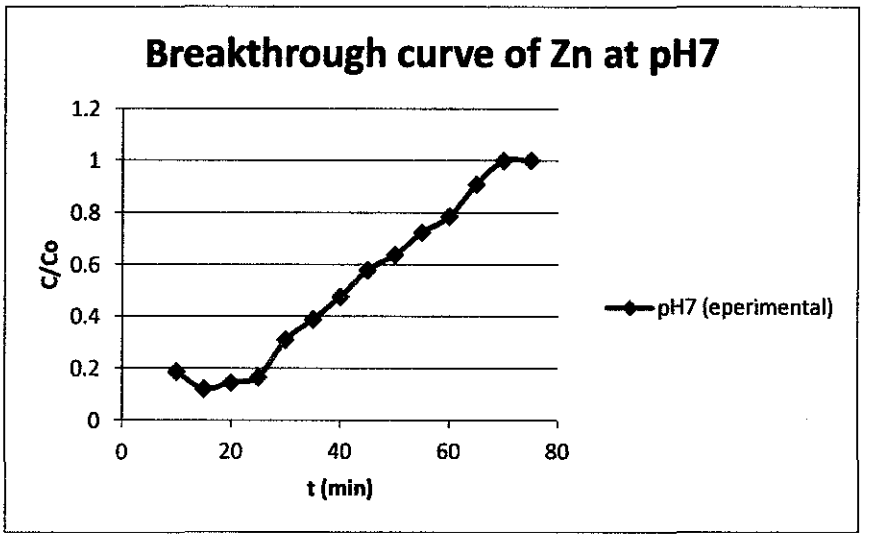


Figure 4.12: Breakthrough curve of Zn(II) at pH 7

Table 4.3: Breakthrough time for different pH value

pH value	Breakthrough time (min)
3	35
5	40
7	15

Figure 4.10, 4.11 and 4.12 shows the breakthrough curve of zinc at different pH value. Based on the table 4.3, the breakthrough time for pH 3 to pH 5 will increase as the pH increase. This is justified by the presence of H^+ ion in the solution is higher at lower pH value. Thus the zinc ion needs to compete with the hydrogen ion present in the solution during the ion exchange process. Meanwhile, at higher pH value, decrease in removal efficiency can be justified by the formation of $Zn(OH)_2$ due to the reaction of Zn^{2+} with OH^-. Precipitation may occur in this condition thus affecting the resin's performance. Based on the result, the best pH is 5 in order to optimize the system. The graphs below show the determination of Thomas parameters and exchange capacity for different pH values.

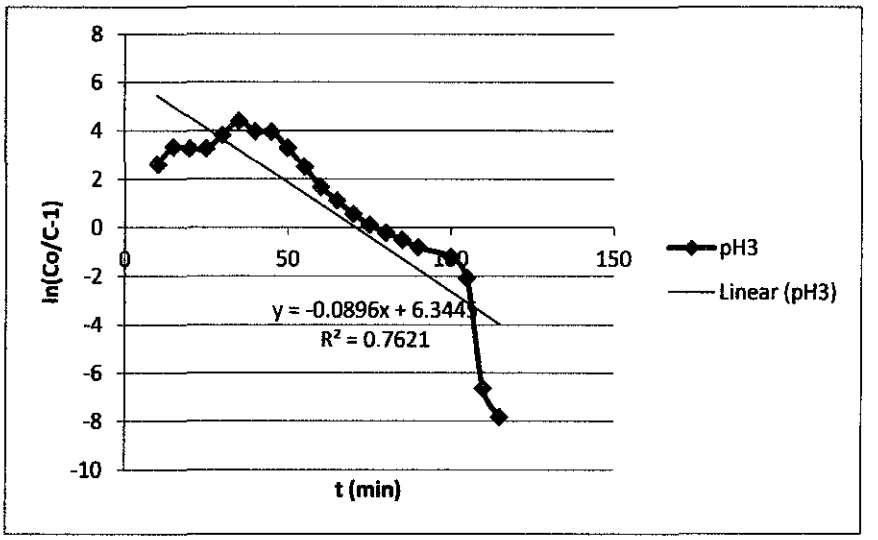


Figure 4.13: Graph for determination of Thomas Parameters (pH 3)

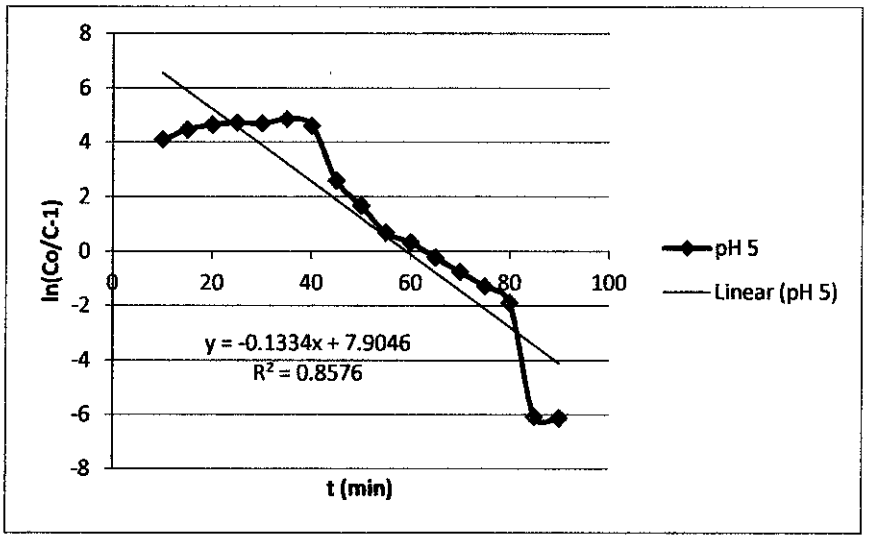


Figure 4.14: Graph for determination of Thomas Parameters (pH 5)

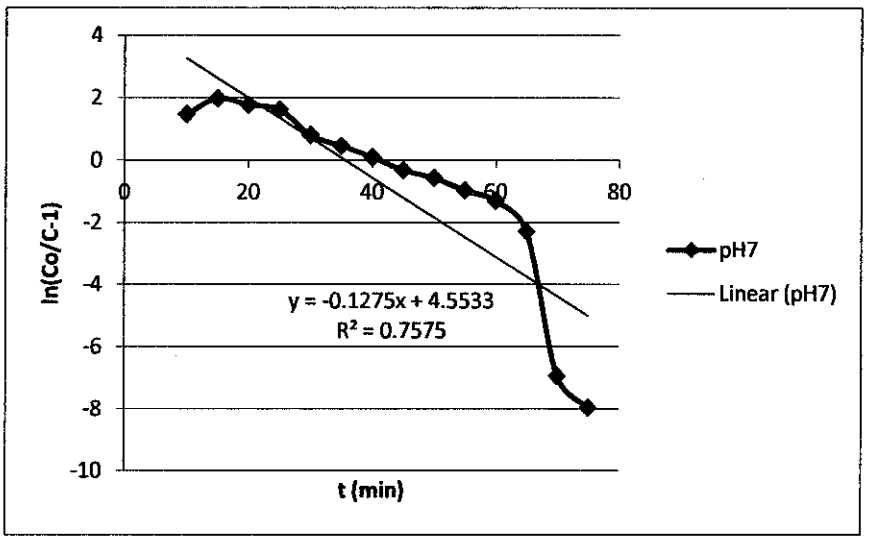


Figure 4.15: Graph for determination of Thomas Parameters (pH 7)

Table 4.4: Properties of Ion Exchange for Different Initial Concentration

pH value	Exchange Capacity, q_o (mol/kg)	k_{Th}
3	0.157	0.059
5	0.125	0.092
7	0.075	0.089

The value of exchange capacity and Thomas coefficient is determined by the plot of ln((Co/C)-1) versus time as illustrated in Figure 4.13, 4.14 and 4.15. Based on table 4.4, it is clearly shown that the exchange capacity will decrease as the pH value increase. Zhang et al. (2010) reported that for Zn(II) removal at pH higher than 6, forming of $Zn(OH)^+$ species will promotes a reduction of the exchange capacity. This is due to the diminution of the formal charge of the metallic ion.

4.4 Effect of Regeneration

The ability of the resin that can be regenerated upon exhaustion is very important as it can minimize the cost of operation in the industry. In this project, Lewatit S 1467 is regenerated with 5% sulfuric acid as proposed by the manufacturer. The H^+ ion in the acid solution will exchange with the Zn^{2+} in the immobile particle due to selectivity.

A contact time of one hour with the flow rate of $35cm^3/min$ is allowed for the regeneration process. The breakthrough time for virgin resin is 35 minutes and the breakthrough time for the regenerated resin is 40 minutes. The exchange capacity of virgin and regenerated resin is calculated using Thomas model.

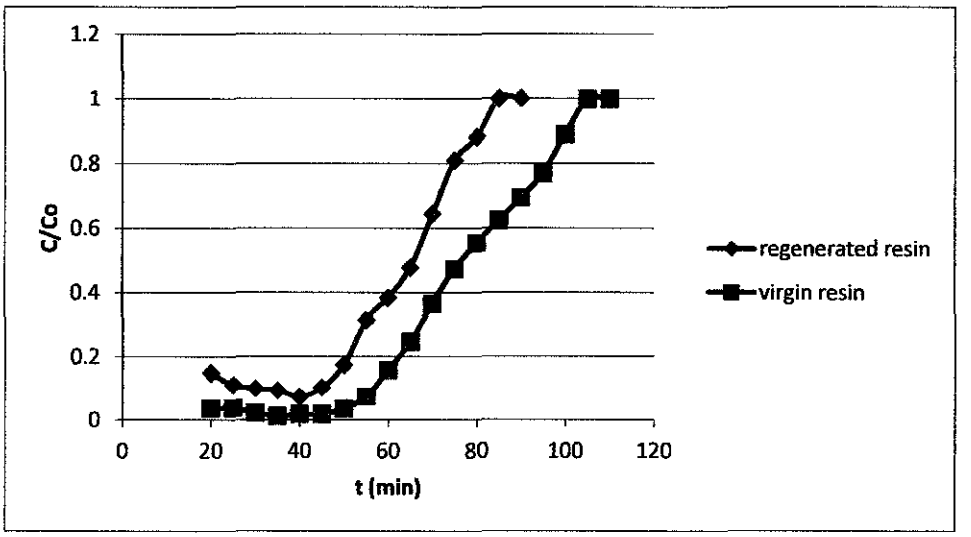


Figure 4.16: Breakthrough curve of virgin resin and regenerated resin

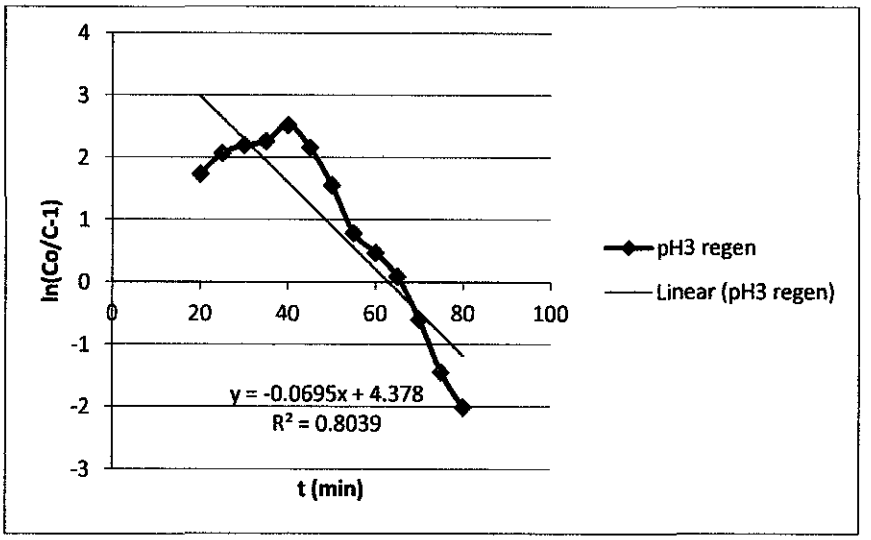


Figure 4.17: Graph for determination of Thomas Parameters for regenerated resin

Table 4.5: Properties of Ion Exchange for Regenerated Resin

Resin	Exchange Capacity, q_o (mol/kg)	k_{Th}
Virgin resin	0.157	0.059
Regenerated resin	0.130	0.049

The result in Table 4.5 shows the calculated value for the exchange capacity based on Thomas model after the regeneration process. The result indicates that there is decrease in exchange capacity of the regenerated resin. Decrease of 17% of the exchange capacity after regeneration and it can be concluded that the resin can be reuse after regeneration.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

This project works contribute to a better understanding of the ability of the ion exchange resin to remove the selected metal which is zinc from synthetic wastewater. The results from the experiment determine the optimum values for the parameter tested such as pH, initial metal concentration and effect of regeneration.

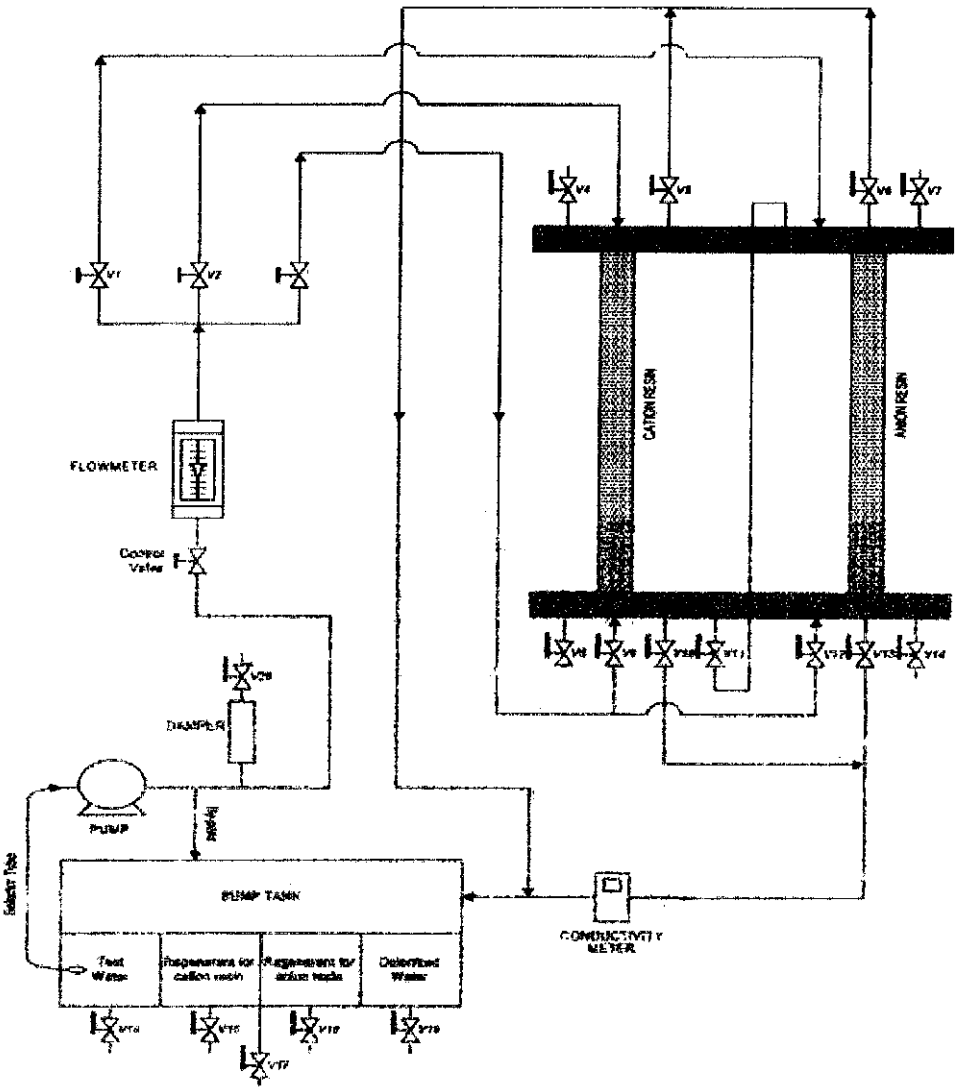
For initial metal concentration, it will affect the breakthrough time and the exchange capacity. The breakthrough time decrease with increasing initial metal concentration. Thus, the optimum operating parameters is at lower initial metal concentration. For pH, the optimum pH value for zinc removal is 5. At pH below than 3, the competition of Zn^{2+} with H^{+} makes the ion exchange process less effective. At higher pH than 7, chemical precipitation will form. Based on the project works, there is a slight decrease in the exchange capacity and it can be concluded that the resin can be regenerated upon exhaustion.

5.2 Recommendation

This project can be improved with some recommendations. A few factors that made the experimental data to be less reliable have been identified. Firstly is to run each experiment at least twice so that the data gathered can be verified. Next is to make sure the whole ion exchange system is free from previous experiment contaminant before a new experiment is started. This is due to the fact that it can affect the next experiment results. Another recommendation that can be made for this project works in the future is to lower the range for initial concentration experiments. Since the maximum concentration limit that can be detected by the Atomic Adsorption Spectrophotometer (AAS) is 4ppm which is small, the outlet samples need to be diluted thus making the experiment data less accurate. Lastly, the project work can be further improved with the experiments of other variables such as resin dosage and flow rates.

APPENDICES

APPENDIX A: Schematic Diagram of Ion Exchange Unit



APPENDIX B: Ion Exchange Unit Operational Procedures

> **Experiment Procedures**

a) Pre-treatment of resin.

1. Wash the resin with deionized water in the column.
2. Rinsing is stopped when the conductivity meter reading is close to conductivity reading of the deionized water.
3. Dry the resin in vacuum oven at 60°C overnight.

b) Preparation of solution

1. Prepare the aqueous solutions by dissolving single or binary metal sulfate in distilled water.
2. Adjust the pH to be in range 2.0-14.0 by adding a small amount of 5% H_2SO_4 or 5% NaOH.

c) Fixed bed experiments

1. Carry out the experiment at 25°C using the ion exchange unit.
2. Put the cation resins into the bed (up to 10cm of the column).
3. Fed the top of the bed with the synthetic wastewater solution (50ppm) at 35cm^3/min until the breakthrough curve was completed.
4. Take the samples in the outlet for every 5 minutes.
5. Determine the outlet concentrations using atomic absorption spectrophotometer.
6. Repeat step 4 to step 6 with different initial zinc concentrations (100ppm and 150ppm).
7. Repeat the experiment with other variables which is inlet pH values (pH=3, pH=5 and pH=7).

APPENDIX C: Raw Data

Breakthrough time for initial concentration 50ppm

time	C	C
min	ppm	mol/m3
0	45.3045	0.692634
5	12.2325	0.187016
10	1.302	0.019906
15	0.744	0.011375
20	0.4845	0.007407
25	0.4545	0.006949
30	0.384	0.005871
35	0.5655	0.008646
40	0.4275	0.006536
45	0.3945	0.006031
50	0.6105	0.009334
55	1.0305	0.015755
60	2.6705	0.040828
65	5.573	0.085202
70	16.3195	0.249499
75	29.387	0.449281
80	34.357	0.525264
85	45.42	0.6944
90	45.447	0.694813

Breakthrough time for initial concentration 100ppm

time	C	C
min	ppm	mol/m3
0	95.091	1.453791
5	13.002	0.19878
10	1.563	0.023896
15	1.086	0.016603
20	0.909	0.013897
25	0.84	0.012842
30	0.864	0.013209
35	0.738	0.011283
40	0.939	0.014356
45	6.639	0.1015
50	14.924	0.228164
55	31.738	0.485224
60	39.669	0.606476
65	52.774	0.806831
70	64.528	0.986531
75	74.492	1.138865
80	82.567	1.262319
85	94.872	1.450443
90	94.883	1.450611

Breakthrough time for initial concentration 150ppm

time	C	C
min	ppm	mol/m3
0	151.45	2.31543
5	15.56	0.237888
10	4.19	0.064058
15	2.47	0.037762
20	2.44	0.037304
25	2.57	0.039291
30	1.38	0.021098
35	2.75	0.042043
40	7.8	0.11925
45	18.56	0.283753
50	27.54	0.421043
55	40.96	0.626213
60	53.07	0.811356
65	71.39	1.09144
70	93.7	1.432524
75	116.62	1.782935
80	134.59	2.057668
85	150.54	2.301518
90	150.64	2.303047

Breakthrough time for pH 3

time	C	C
min	ppm	mol/m3
0	100.03	1.5293
5	16.4125	0.250921
10	6.835	0.104496
15	3.45	0.052745
20	3.7025	0.056605
25	3.7025	0.056605
30	2.1575	0.032985
35	1.22	0.018652
40	1.8575	0.028398
45	1.89	0.028895
50	3.575	0.054656
55	7.4875	0.114472
60	15.9075	0.2432
65	24.6775	0.37728
70	36.4725	0.557607
75	47.425	0.725053
80	55.4725	0.848087
85	62.465	0.954991
90	69.4725	1.062124
95	77.017	1.177468
100	89.0184	1.36095
105	99.899	1.527297
110	99.99	1.528689

Breakthrough time for pH 7

time	C	C
min	ppm	mol/m3
0	93.28	1.426103
5	46.9675	0.718059
10	17.35	0.265254
15	11.31	0.172912
20	13.5925	0.207808
25	15.435	0.235977
30	28.805	0.440383
35	36.175	0.553058
40	44.3025	0.677315
45	53.9225	0.82439
50	59.4575	0.909011
55	67.48	1.031662
60	73.2375	1.119685
65	84.7025	1.294967
70	93.19	1.424727
75	93.2475	1.425606

Breakthrough time for pH 3 regeneration

time	C	C
min	ppm	mol/m3
0	93.2425	1.42553
5	61.3075	0.937295
10	35.7675	0.546828
15	21.12	0.322891
20	13.9975	0.214
25	10.4775	0.160184
30	9.3475	0.142908
35	8.8125	0.134729
40	6.95	0.106254
45	9.6825	0.14803
50	16.28	0.248895
55	29.2075	0.446536
60	35.8225	0.547669
65	44.585	0.681634
70	60.145	0.919522
75	75.525	1.154658
80	82.2425	1.257357
85	93.2725	1.425989
90	93.3675	1.427441

REFERENCES

Alyuz, B., & Veli, S. (2009), Kinetics and equilibrium studies for the removal of nickel and zinc from aqueous solutions by ion exchange resins, J. Hazard. Mater. 167 482–488.

Cavaco, S.A., Fernandes, S., Quina, M.M., & Ferreira, L.M. (2007), Removal of chromium from electroplating industry effluents by ion exchange resins, J. Hazard. Mater. 144 634–638.

Donia, A.M., Atia, A.A., & Mabrouk, D.H. (2011), Fast kinetic and efficient removal of As(V) from aqueous solution using anion exchange resins, J. Hazard. Mater. 191 1–7.

Edebali, S., & Pehlivan, E. (2010), Evaluation of Amberlite IRA96 and Dowex 1×8 ion-exchange resins for the removal of Cr(VI) from aqueous solution, Chem. Eng. J. 161 161–166.

Haghsheno, R., Mohebbi, A., Hashemipour, H., & Sarrafi, A. (2008), Study of kinetic and fixed bed operation of removal of sulfate anions from an industrial wastewater by an anion exchange resin, J. Hazard. Mater. 166 961–966.

Harland, C.E. (1994), Ion Exchange: Theory and Practice, 2nd Edition, The Royal Society of Chemistry.

Kose, T.E., & Ozturk, N. (2007), Boron removal from aqueous solutions by ion-exchange resin: Column sorption–elution studies, J. Hazard. Mater. 152 744–749.

Kołodynska, D. (2011), Application of strongly basic anion exchangers for removal of heavy metal ions in the presence of green chelating agent, Chem. Eng. J. 168 994–1007.

Lenntech (n.d). Zinc. Retrieved August 25, 2001 from http://www.lenntech.com/periodic/elements/zn.htm.

Lin, L.-C., & Juang, R.-S. (2005), Ion-exchange equilibria of Cu(II) and Zn(II) from aqueous solutions with Chelex 100 and Amberlite IRC 748 resins, Chem. Eng. J. 112 211–218.

Lin, L.-C., Li, J.-K., & Juang, R.-S. (2007), Removal of Cu(II) and Ni(II) from aqueous solutions using batch and fixed-bed ion exchange processes, De salination 225 249–259.

Misak, N.Z. (1995), Adsorption isotherms in ion exchange reactions. Further treatments and remarks on the application of the Langmuir isotherm, Colloids Surf. A: Physicochem. Eng. Asp. 97 129–140.

Ozturk, N., & Kose, T.E. (2007), Boron removal from aqueous solution by ion-exchange resin: Batch studies, Desalination 227 (2008) 233-240.

Parameter limits of effluent of Standards A and B, Environmental Quality Act of 1974. The Malaysia Environmental Quality (Sewage and Industrial Effluents) Regulations, 2009.

Pehlivan, E., & Cetin, S. (2008), Sorption of Cr(VI) ions on two Lewatit-anion exchange resins and their quantitative determination using UV–visible spectrophotometer, J. Hazard. Mater. 163 448–453.

Rao, K.S., Chaudhury, G.R., & Mishra, B.K. (2010), Kinetics and equilibrium studies for the removal of cadmium ions from aqueous solutions using Duolite ES 467 resin, International Journal of Mineral Processing 97 68–73.

Shah, R., & Devi, S. (1997), Preconcentration and separation of palladium(II) and platinum(IV) on a dithizone anchored poly(vinylpyridine)-based chelating resin, Anal. Chim. Acta 341 217–224.

Shek, T.-H., Ma, A., Lee, V.K.C., & McKay, G. (2008), Kinetics of zinc ions removal from effluents using ion exchange resin, Chem. Eng. J. 146 63–70.

Won, B., & S.Hun, S. (2006), Effect of operating conditions on the removal of Pb(II) by microporous titanosilicate ETS-10 in a fixed bed column. Journal of Colloid and Interface Science,305, 218-225.

Zhang, Y., Li, Y., Yang, L.-Q., Ma, X.-J., Wang, L.-Y., & Ye, Z.-F. (2010), Characterization and adsorption mechanism of Zn2+ removal by PVA/EDTA resin in polluted water, J. Hazard. Mater. 178 1046–1054.