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REMOVAL OF COPPER IONS FROM SYNTHETIC AND INDUSTRIAL WASTEWATER USING CATION EXCHANGE RESIN

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**A project report submitted in partial fulfilment of the
requirements for the award of Bachelor of Engineering
(Hons.) Chemical Engineering**

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DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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APPROVAL FOR SUBMISSION

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ABSTRACT

In an industrialized nation like Malaysia, many manufacturing plants release wastewater which needs to be treated whereby increasing the demand for wastewater treatment. Cation exchange resin is one of the most effective methods to remove Cu(II) ion from synthetic and industrial wastewater and it can be used for multiple servicing cycle. In this research, the aim was to remove Cu(II) from synthetic wastewater using cation exchange resin. The corresponding objective was to study the properties, operating parameters (pH, initial concentration, rein bed height, flowrate of wastewater) of cation exchange resin on Cu(II) adsorption. Durability test was performed after optimizing all parameters studied. This research provides an insight on how cation exchange resin behaves under different conditions and provide guidelines for future advanced research in this field. From this research, it was found that cation exchange resin is capable of achieving > 97% adsorption efficiency towards Cu(II) enabling it a suitable wastewater treatment method in various industries. Industrial wastewater collected from air-conditioner manufacturing factory was treated with cation exchange resin shown decent adsorption result whereby fulfilling the Malaysian Discharging Industrial Effluent Standard.

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LIST OF SYMBOLS / ABBREVIATIONS

C_e	final concentration, mg/l
C_o	initial concentration, mg/l
h	bed height, cm
q	absorption capacity, mg/g
V	volume, cm^3
W	Weight, g
BV	bed volume, ml

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CHAPTER 1

INTRODUCTION

1.1 General Introduction

Ion exchange is very useful for industrial application in purification of solution such as industrial effluent treatment, demonetization, water softening, and etc. It is popularly used for heavy metal removal from industrial effluent, removal of nitrate compound or fluoride. Ion exchange resin can be separated into 2 categories: cation exchange resin for removal of positive ion (cation) and anion exchange resin for removal of negative ion (anion). The resin is a bead-like polymer with fixed functional group attached to the backbone of the polymer matrix. The type of functional group will determine the selectivity in terms of inhibition or rejection of the ionic species. Cation exchange resin is responsible for exchanging positive ions such as $Cu^{2+}, Ca^{2+}\ and\ Fe^{2+}.$ On the other hand, anion exchange resin is used to exchange negative ion such as $Cl^{-}\ and\ OH^{-}$.

Almost all ion exchange resins share the same type of polymer matrix which is styrene-divinylbenzene (DVB) co-polymer. This matrix is responsible for holding the exchange functional group in a stable structure due to its insoluble properties in all pH range during service lifetime. Cation exchange resin serves a wide range of applications and can be further distinguished into different types of cation exchange resins, either weakly acidic or strongly acidic acid cation exchange resin. Chelating resin is one of the weak cation exchange resins which has high selectivity towards heavy metal, particularly copper. It has a iminodiacetate functional group which is able to form complexes with metal ions even in high concentration of calcium and sodium salt.

Ion exchange resin works differently under different parameters and conditions, e.g. pH range, initial metal concentration, bed height, and solution blow rates. For instance, cation exchange resin does not behave similarly at all pH values. At some point, cation exchange resin may behave as anion exchanger under very low/ acidic pH. Thus, optimum pH condition shall be investigated to bring out the best operating performance of the exchange resin. Different pH values also affect the absorption capacity of metal ion into the resin. In industrial effluent treatment regardless of scaling, operators seek for the best absorption capability of exchange resin to efficiently remove heavy metals from effluent, so that the cost can be reduced. In order to achieve the best absorption capability, we need to provide optimal conditions in every parameter mentioned earlier.

1.2 Problem Statement

In a developing country like Malaysia, industrialization serves an important role to further improve the national economy. When industrialization is significant, it consumes large amount of chemical raw materials for processing, thus abundant wastes such as chemical effluent are released to the environment which may contain hazardous components typically heavy metals. Heavy metals are generally the most highly tenacious pollutants in industrial effluent (Akpor, Ohiobor and Olaolu, 2014).

In fact, heavy metals are considered as one of the most persistent pollutants in industrial effluent. Heavy metals have an atomic density larger than 6 g/cm^3 which are refereed as trace metals. Toxic heavy metals commonly found in industrial effluent include lead, mercury, copper, nickel, chromium, zinc, and etc. Discharge of heavy metals into water bodies brings health and environmental issues if the released concentration is high. Heavy metals indeed also occur naturally and enter the environment in insignificant amount through different paths such as vegetation, rock leaching, ore mining (Akpor, Ohiobor and Olaolu, 2014). Despite natural occurrence of heavy metals from leaching, the accumulation of heavy metals in the environment, typically aquatic bodies, through direct and indirect activities such as industrialization, construction and fabrication is also dominant (Akpor, Ohiobor and Olaolu, 2014). Due to the high solubility property of heavy metal in water bodies, it can be easily absorbed by aquatic living organism (Barakat, 2011).

This project was focused on removal of copper, Cu(II) from synthetic and industrial wastewater using cation exchange resin. The efficiency of removing copper from industrial effluent by cation exchange resin made it more appreciable for this project. Copper serves as an essential engineering metal, mainly used in engineering processes and alloy manufacturing. With respect to its function, copper is commonly found in various industrial sources including paint engineering, semiconductor and printed circuit board manufacturing, electronics plating, wood preservation and other manufacturing and fabricating operation. However, copper is persistent in the environment due to its toxicity and non-biodegradable nature, leading to harmful biochemical effects, hazards and toxicity to human and environment. Once copper enters the food chain, it will accumulate in human body in large quantity. Over-accumulation of copper beyond permitted amount will cause thoughtful health disorder (Babel and Kurniawan, 2004). Usually, excessive intake of copper causes capillary damage, mucosal irritation, central nervous system disorder, and etc. (Shrivastava, 2009).

There are many other ways, for instance membrane filtration, flocculation, coagulation, biological methods, to remove Cu(II) from industrial effluent. Among these treatments, cation exchange resin is found to be economically feasible and effective in the copper removal. Improved sorption capacity and adsorbent of cation exchange resin hold great potential on heavy metal removals from industrial effluent (Gaikwad and Sapkal, 2010). Nevertheless, cation exchange resin has other advantages over other metal removal methods which will be discussed later.

Generally, ion exchange process undergoes convenient operation and only requires low cost material. Most importantly, it is very reliable and effective in removing heavy metals from industrial effluent, particularly wastewater with low heavy metal concentration which is hard to be treated using other treatment (Gunatilake, 2015). Some argue that biological treatment is the most cost-efficient and the absorbents are abundant (Gunatilake, 2015). Yet, the biological method faces difficulties in removing toxic inorganic compounds from various industries (Gunatilake, 2015). So, ion exchange method still plays an important role on heavy metal removal apart from other methods even though the cost is slightly higher.

1.3 Aim and Objectives

The target of this project was to remove copper ion (Cu(II)) from synthetic effluent by using cation exchange resin provided by i-Chem Solution Sdn. Bhd., a wastewater treatment company based in Puchong, Selangor. The objectives of this research included:

a. To identify the properties (absorption capacity and durability) of cation exchange resin.

b. To determine the effects of operating parameters (pH, initial Cu(II) concentration, bed height, and flowrate) on absorption efficiency of cation exchange resin.

c. To investigate the performance of cation exchanging process in different solution (synthetic and industrial wastewater).

1.4 Scope and Limitation of the Study

The scope of present research only covered a portion of the study of ion exchange in wastewater treatment. The parameter study in this research covered initial Cu(II) concentration, resin bed height. pH, wastewater flowrate, availability of chelating agent. In fact, there are many other factors which also affects absorption efficiency of cation exchange resin such as temperature, pressure, source of wastewater etc. But they were not the parameters to be investigated in this study.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In an advanced industrialization generation, heavy metals are considerably the most persistent pollutants in wastewater. Great amount of heavy metals that were discharged in wastewater not only harms the environment, but also bring huge impacts to our health. These environmental impacts due to heavy metals was mostly attributed to industrial sources, Exposure of heavy metals to humans occur through different kind of routes, typically by ingestion of solid food or liquid, and inhalation of airborne dust and fumes. Apart of bringing various harms towards human, we must not neglect the fact that heavy metals in wastewater also strikes negative impacts to marine and aquatic ecosystem e.g. habitat wrecking, extinction of aquatic species, toxicity from chemical effluent.

The most typical toxic heavy metals in wastewater are nickel, copper, cadmium, zinc, iron, mercury etc. Usually heavy metals were released by factories/workshops of various industries, which increase wastewater treatment cost if the effluent releasing rate is high. As an insight, wastewater treatment is an essential aspect to prevent and to reduce the negative effects of toxicity of heavy metals in wastewater. The main purpose for wastewater treatment is to remove all potential hazards to the ecosystem and all relevant information will be review in detail throughout this literature review.

2.1.1 Sources of Heavy Metals in Industrial Effluent

In general, the presence of heavy metal in wastewater originate naturally and human activities. Natural sources such as natural volcano eruptions, erosion of soil, landfill etc.; human factors include electroplating & semiconductor manufacturing industries, metal parts fabrication and finishing, mining and extraction etc. (Akpor, Ohiobor and Olaolu, 2014). For instance, electroplating, electrolysis, coating industries usually generated toxic chemical waste which compose of nickel, zinc, lead, copper, cadmium etc.

Electroplating and metal finishing by means of electrochemical process involve the accumulation of thin protective layers into the desired metal surfaces

(Akpor, Ohiobor and Olaolu, 2014). During this process, heavy metals such as copper maybe released into the wastewater. The release of heavy metal is usually through disposal or spillage of process water bath and rinsing of metal products. On top of that, it showed that industrial effluent treatment and cleaning of process vessels and tanks also produce substantial concentration toxic heavy metal-containing sludge (Cushnie, 1985).

In addition, metal mining activities and smelting process contribute a major sources of heavy metal exposure to the environment. From earlier research, significant concentration of heavy metal deposits was found in soil, water, crops and vegetable in nearby location where these activities take places (Wei et al., 2008). Moreover, one of the major contributor of heavy metal pollutants in wastewater is textile industries. These industries involve dying process during textile production. These dying process or coloration utilizes compounds such as copper, nickel which has high toxicity towards the environment.

2.1.2 Malaysian Standards of Industrial Effluent

The Department of Environment Malaysia (DOE) regulates the industrial effluent treatment system as a mandatory legislative requirement in Malaysia. The regulation which regulates the industrial effluent system falls under the Environmental Quality Regulations (EQR) 2009.

According to Regulation 11, Sub-regulation 1a, b in EQR 2009, it held that nobody is allowed to discharge contaminated industrial effluent of any species with the concentration greater than the upper limit of Standard A or Standard B.

For Sub-regulation 2, it regulates that when 2 or more metals specified in the 5th schedule exist in the industrial effluent, the metals concentration must not exceed:

- For Standard A: 0.5 mg/L, or
- For Standard B: 3 mg/L for insoluble form, and 1 mg/L for soluble form.

Table 2.1 shows the acceptable concentration for discharging industrial effluent in Standard A and B. These standards were extracted from the 5th schedule pursuance with Sub-regulation 11(1) and 11(2) of EQR 2009. This project focus on removal of copper, so parameter displayed for other metal are irrelevant.

Table 2.1: Acceptable Concentration for Discharging Industrial Effluent in Standard A and B.

Parameters	**Units**	**Standard**	
		A	**B**
pH	nil	6.0 - 9.0	5.5 - 9.0
Temperature	°C	40	40
Copper	mg/L	0.20	1.0

2.1.3 Effect of Heavy Metal Polluted Industrial Effluent

Untreated wastewater with contaminated heavy metals brings different kind of health and environmental issues when released to the environment. Heavy metals such as Copper, Nickel, and Chromium are the most health hazardous among all. Heavy metals are highly soluble in liquid environment, so it is easily absorbed by living organism, which directly affects fishes and aquatic plants. As these organisms enters the food chain, we as human being is the final consumer and high concentration of heavy metals will accumulate in our bodies. Despite heavy metals is sometimes essential to our health, ingestion of uncontrolled level may cause serious health impacts. For instances, Arsenic is a hazardous element which cause cancer, organ damage, reduced growth, and even fatality if ingested in great dose. Heavy metals such as lead or mercury may cause body cells being attacked by own immune system, known as autoimmunity. This further induce serious health disorder e.g. kidney failure, arthritis, breakdown of nervous system and brain failure of foetus of pregnant woman. In fact, growing children absorb higher concentration of heavy metal through ingestion than adults, because they consume more and absorb more from their food for weight gaining purpose when growing.

According to study, heavy metals in industrial effluent provides great threats to soil and the plants growing there, followed by human or animal consuming such contaminated plants allowing them to get into the food chain, leading to severe harmful effects (Saidi, 2010). Typically, overdose of heavy metals from vegetables or land-grown fruits will accumulate in kidneys, which subsequently leads to kidney malfunction.

Copper as an example, although it provides essential nutritional value to humans; high concentration of copper in water bodies, especially drinking water can lead to anaemia, vomiting, diarrhoea, some even leads to kidney and liver damage for serious case (Akpor, Ohiobor and Olaolu, 2014). It is reported that ingestion of copper leads gastro-intestinal illnesses, hepatotoxic and nephron poisoning effects (Shivastava, 2009). High toxicity nature of copper induces irritation of central nervous system, damaging blood capillary mucosal irritation etc.

Apart of bringing tremendous threats towards human beings, heavy metals also directly pollute soil ecosystem by toxicity of heavy metals. Plants which grows on polluted soils may encounter low growth rate, photosynthesis inhibition, reduced chlorophyll synthesis and lower activity of enzyme. As if heavy metals present in high concentration in the soil, it inhibits the plants from nutrient intake, metabolic processes, chlorosys etc. Besides, heavy metal polluted industrial effluent will affect the quality of receiving water bodies such as river or sea, it also highly varies and depend on the chemical composition of the discharged effluent from the industries (Akpor, Ohiobor and Olaolu, 2014). In terms of aquatic ecosystems, dissolves heavy metals will decrease the dissolved oxygen content, which eventually lowered the aquatic population of the affected water bodies.

2.2 Methods for Removal of Heavy/Trace Metals from Industrial Effluent

There are several methods used to remove suspended heavy metals from varying industrial effluent e.g. chemical (hydroxide or sulfide) precipitation, biological treatment, electrochemical treatment, cation exchange etc.

2.2.1 Chemical Precipitation

In the manufacturing industry, chemical precipitation is considerably the utmost popular technique of removing heavy metals from industrial effluent. This is because the operation can be done conveniently and cost saving. The chemical precipitation process produces precipitate by converting dissolved metal ions into insoluble heavy metal precipitates as metal hydroxide, phosphate and carbonate (Gunatilake, 2015). The mechanism of this process is by reacting metal solution with precipitant to produce insoluble metal precipitate. Then, coagulants were used to increase the floc size and to be removed as sludge.

Among all chemical precipitation technique, hydroxide precipitation is the dominating heavy removal technique in the industry due to low operating cost and ease of operation (Huisman et al., 2006). Based on simple handling and operation, cost effective, different hydroxides can be employed which is usually lime, which is commonly used in industrial settings as precipitant (Baltpurvins et al., 1997).

Common hydroxides e.g. calcium hydroxide, $Ca(OH)_2$ also known as lime can be used to remove Cu(II) ions from industrial effluent. According to research, maximum copper precipitation rate occurs at optimum pH of 12.0 for NaOH as precipitant, where the dissolved copper concentration can be reduced from 48.49 mg/L to 0.70 mg/L (Mirbagheri and Hosseini, 2005).

A simple concept of hydroxide precipitation mechanism can be presented as follows:

$$M^{2+} + 2(OH)^{-} \leftrightarrow M(OH)_2$$

where M^{2+} representing the dissolved metal ions, $2(OH)^{-}$ represents hydroxide ion (precipitant) and and $M(OH)_2$ represents metal hydroxide(Barakat,2011). During precipitation process, major parameters such as pH and temperature significantly affects the heavy metal removal, pH optimally between 9-11. The most common precipitant technique used is metal hydroxide using lime as precipitant agent due to low cost of lime, relative simplicity and their abundant availability, and safe and convenient operation.

However, as a drawback, hydroxide precipitation produces large amount of low density sludge which arise disposal complications (Kongsricharoern and Polprasert, 1995). The process consumes much time and require large amount of precipitant to remove the heavy metal into compliancy level. It also requires further treatment after the precipitation process due to its excessive sludge production (Barakat,2010). Lastly, metal hydroxide precipitation will be halt in when there is complexing agent in the effluent.

Apart of hydroxide precipitation, other types of precipitation method e.g. sulfide precipitation is also an efficient method for heavy metal treatment from industrial effluent. The core advantages of sulphide precipitation are the precipitate of metal sulphide is way lesser compared to hydroxide precipitation. Besides, sulfide precipitation able to achieve high heavy metal removal percentage over large pH range than hydroxide precipitation due to its non-amphoteric properties. Sulfide precipitation also produces improved thickening and dewatering metal sulfide sludges (Fu and Wang, 2011).

2.2.2 Coagulation and Flocculation

Nowadays, usually, coagulation and flocculation process usually works hand in hand with precipitation. This is because metal precipitation produced very fine particles, so coagulation and flocculation are used to coagulate the fine particles and remove them as a sludge. Coagulation is the process of colloids destabilization by elimination of their repulsion force. A coagulant is a metallic salt is used to reduce the colloidal particles net surface charge to stabilize by electrostatic repulsion process (Benefield, 1982). Ferrous sulfate and aluminium sulfate are the most widely used coagulant in conventional industrial effluent treatment. Both ferrous and aluminium sulfate are capable of neutralizing particle charges and impurities enmeshment on the amorphous precipitates, which makes it a promising method of removing heavy metal from industrial effluent.

On the other hand, flocculation the process of addition polymerization of small destabilized particles into large aggregates or clumps for simpler removal. It increases the particle size continuously through addition collision polymerization whereby interaction and additional collision with organic polymers. Note that flocculation does not neutralised particles charge but only increase particle size through polymerization. As the destabilized particle were flocculated and floc is form, it can be easily removed by filtration and floatation. Several types of flocculant are being deployed in treatment of industrial effluent these days, e.g. polyferric sulfate, polyaluminium chloride and polyacrylamide (Fu and Wang, 2010). Nevertheless, direct flocculation in fresh industrial effluent is impractical and ineffective; which requires pre-treatment such as chemical precipitation before flocculation.

Coagulation-flocculation process basically cannot remove heavy metals from industrial effluent completely (Chang and Wang, 2007). Hence, pre-treatment such as precipitation must be done before coagulation-flocculation process. According to Plattes et al. (2007), which used 3-step treatment (chemical precipitation, coagulation, flocculation) to remove tungsten from industrial effluent by employing ferric oxide. Efficiency as high as 99% of tungsten removal was achieved under acidic condition, pH less than 6.0.

2.2.3 Electrochemical Treatment

Another popular technology of removing heavy metals from wastewater effluent is through electrochemical treatment, whereby passing current through an electrolyte or aqueous metal-bearing solution which contain an insoluble anode and a cathode. Electrochemical treatment works in a way by precipitating dissolved heavy metal ions in weak acidic catholyte as metal hydroxides. Basically, the few steps of electrochemical wastewater treatments are electrooxidation, electroflotation, electrodeposition, and electrocoagulation.

Electrocoagulation is an electrolytic process by passing an electric current through the industrial effluent (electrolyte) to destabilize the dissolved and suspended heavy metal ions. It works almost alike with chemical coagulation, whereby reducing the net surface charge of colloidal particle. By removing the surface charge, there is no longer any repulsive force between particles, enabling them to approach each other. Short distance between particles induces Van de Waal's forces to hold the colloids together allowing aggregation of particles. Electrocoagulation uses aluminium (Al) or iron (Fe) electrode to dissolve aluminium or iron ion to produce coagulants (Chen, 2004). Figure 2.1 illustrates the mechanism of an electrocoagulation reactor. Aluminium is used as anode while an inert material is used in cathode.

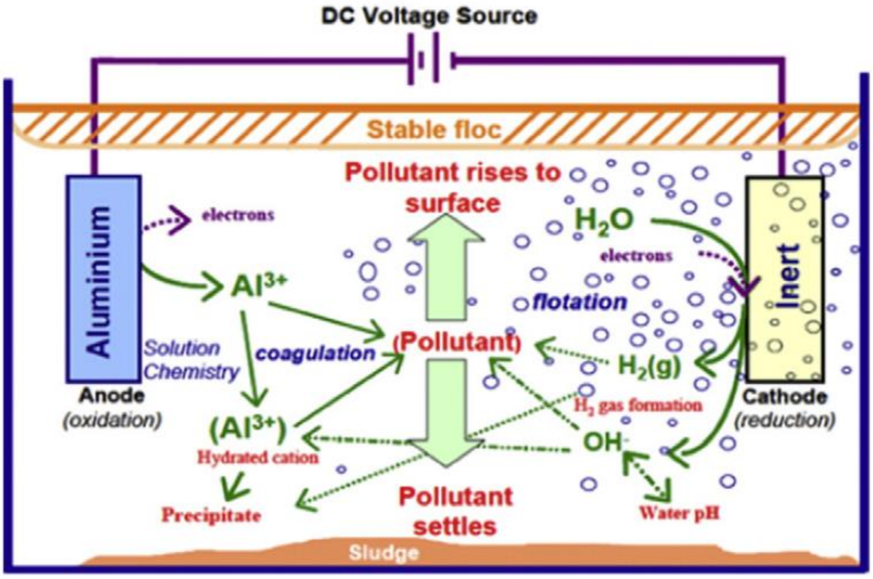


Figure 2.1: Interactions on an Electrocoagulation Reactor (Avivid Water Technology)

At the anode, the aluminium undergoes oxidation; whereby losing electrons and oxidized into cations (metal ions). On the inert cathode, water hydrolyzation occurs producing hydroxyl group (OH-) and hydrogen gas (H_2). At the same time, free mobile electrons from anode destabilized the surface charges of suspended heavy metals producing agglomerates. Finally, agglomerates begin to sink to the bottom of the tank and can be removed through filtration.

Electroflotation works almost the same way as electrocoagulation. The only difference is, electroflotation produces particulates which floats onto the wastewater surface instead of sink to the bottom of the tank (Erick, 2011). The floatation of particulates was assisted by the formation of hydrogen gas at the anode. Figure 2.2 illustrate a typical electroflotation process.

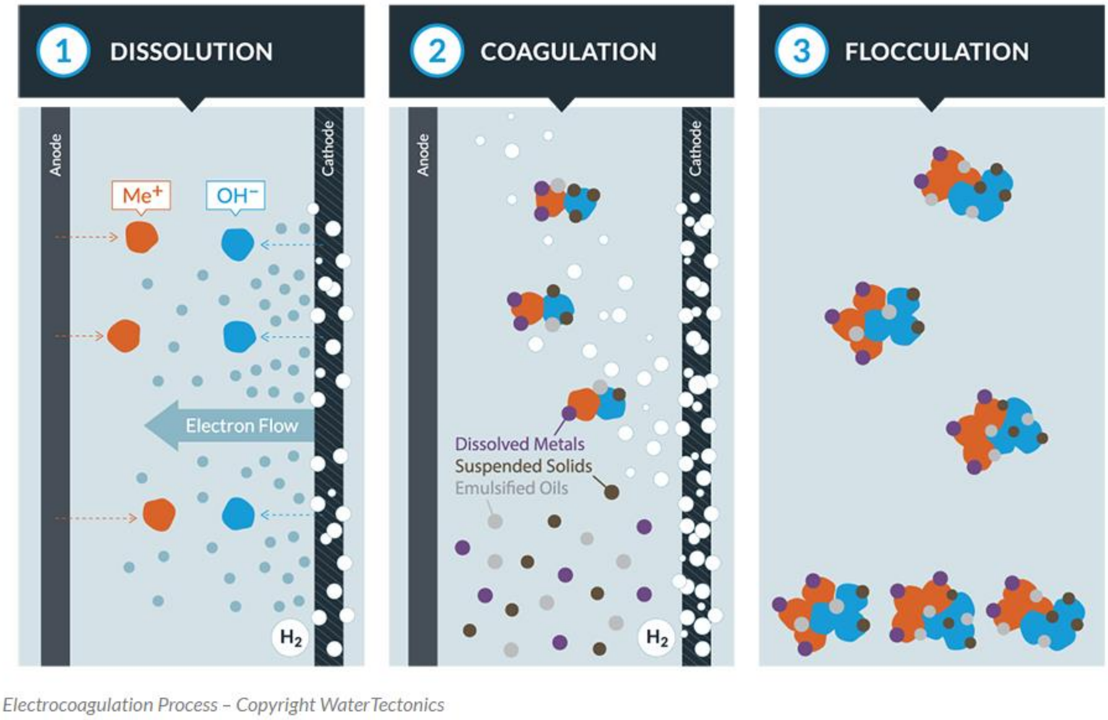


Figure 2.2: Process of Electroflotation (Water Tectonics)

Take iron (Fe) as anode:

$$Fe \rightarrow Fe^{2+} + 2e$$

$$H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e$$

Cathode:

$$2H_2O + 2e \rightarrow 2OH^- + H_2$$

The first reaction shows the formation of coagulants through electrode oxidation. Meanwhile, water hydrolysis occurs at the cathode forming bubbles of hydrogen gas. The hydrogen gas aids the particulates to floats to the water surfaces.

Coagulation by formation of metal hydroxide also known as colloids electrodestabilization. It is a typical precipitation method for heavy metals through electrolytic oxidation and destabilizing contaminants to produce floc (Gunatilake, 2015). In electrocoagulation, electrolytic oxidation of anode generates the coagulant. During the process, dissolve and charged metal ions react with appropriate anion in order to be removed from the effluent. Electrochemical treatment produce less sludge than chemical precipitation and do not require any chemical.

2.2.4 Ion Exchange

Ion exchange is the most regularly employed method in industrial wastewater treatment industry. It only involves minimal cost equipment and material which is very cost effective and high efficiency. Typically, ion exchange resin functioned as medium for ion exchange; cationic exchange resin is used for removal of heavy metals. Cation exchange resin is insoluble solid particularly sphere shaped porous structure which can absorb positive charged ion such as heavy metals from industrial effluent and replace it with other less hazardous ions to the wastewater in equal amount. For instances, positively charges hydrogen and sodium ions in cationic exchange resin are exchanged with hazardous heavy metal ion such as copper, zinc, nickel, chromium ion, etc. It also works in the same way for negatively charged ion exchange process.

2.2.5 Membrane Filtration

Suspended solid and inorganic compound can be easily removed by membrane filtration without any chemical reaction, it works by trapping suspended ions or molecule onto a semi-permeable membrane, whereby removing particular elements or compound from the stream. Membrane filtration usually divided into various types, such as ultrafiltration, nanofiltration, reverse osmosis (RO), polymer-supported ultrafiltration and complexation-ultrafiltration (Barakat, 2011). Each filtration method can be utilized depending on the sizes and types of particle we wanted to trap and retained. In ultrafiltration, a permeable membrane which has pore size approximately 5-20nm is used to separate suspended solids, macromolecules, heavy metals and other inorganic compound with molecular weight between 1000-100,000Da from industrial affluent (Gunatilake, 2015). Larger size molecules such as heavy metal and macromolecules will be retain onto the membrane while allowing low molecular solutes and water which has smaller size than pore of the membrane to flow through the passage. Ultrafiltration is capable of achieving removal efficiency more than 90.0% from a 10–112 mg/l metal concentration under pressure between 2–5 bar and pH ranging 5-9.5. Moreover, ultrafiltration can operate with lesser driving force, moreover it requires only small because the membrane have great packing density (Gunatilake, 2015). Nevertheless, the drawback of membrane filtration is the fouling of membrane. The longer the serving time of the filtration membrane, the more molecule it traps. From time to time, the membrane starts fouling hence decreasing the ultrafiltration performance. Fouling of membrane leads numerous adversative effects on membrane filtration system e.g. declination of flux, greater pressure drop, and increase possibility of degradation of membrane.

According to studies, treatment of industrial effluent using nanofiltration and reversed osmosis (RO) to remove copper and cadmium ions were investigated (Abu Qdaisa and Moussab, 2004). It is found that reverse osmosis can achieve high removal efficiency for both copper and cadmium, achieving 98% and 99% removal efficiency respectively. In contrary, nanofiltration can only remove 90% of copper from the same effluent source. Figure 2.3 demonstrate the effect concentration of Cu(II) ions in the permeate on reverse osmosis (RO) and NF. From the figure, with the same initial concentration of copper ion on both method, the total dissolved solid (TDS) in permeate of RO is significantly lower than NF.

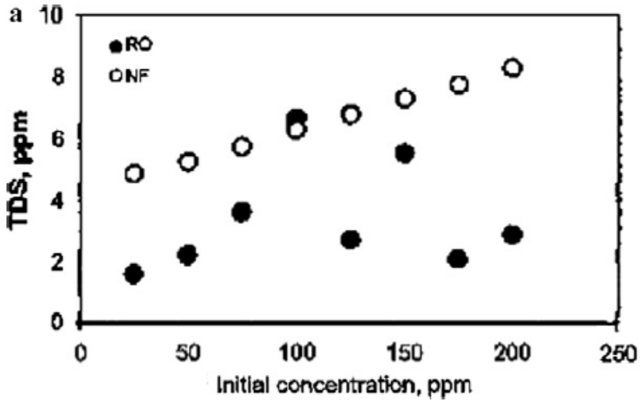


Figure 2.3: Comparison of Total Dissolved Solid Concentration Between RO And NF (Abu Qdaisa and Moussab, 2004)

Another effective technique of removing heavy metal from industrial effluent is polymer-supported ultrafiltration (PSU) (Rether and Schuster, 2003). This method works in 2 steps; selecting acid-base water soluble ligands to bind targeted heavy metal to create larger size macromolecule, followed by ultrafiltration to separate out the metal polymer-bind macromolecule, subsequently producing metal free effluent. Figure 2.4 illustrates the working principles of PSU. Polymer-supported ultrafiltration consist of polychelatogens of high selectivity on binding target ion from complex effluent. Complexation of the target ion are trapped prior the membrane, allowing other non-targeted element to pass through as permeate.

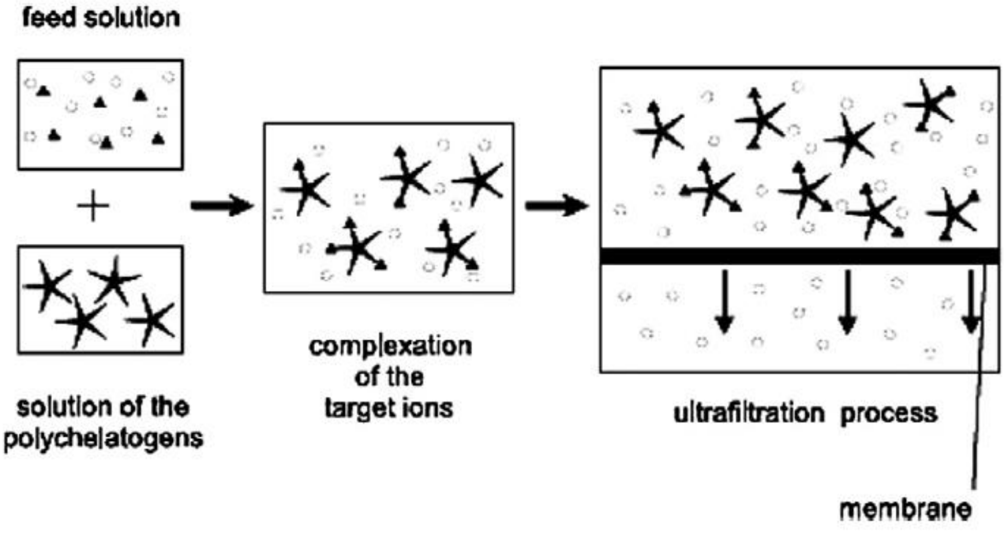


Figure 2.4: Principles of Polymer-supported Ultrafiltration (PSU) Technique (Rether and Schuster, 2003)

Therefore, the idea of PSU is complexing the metal ion onto the polymer so that the size of ion can be artificially increased. Hence, when a metal-containing effluent is added with macroligands (Macromolecules with ligand function), complexed metal ions is retained as a concentrated product onto ultrafiltration membrane (Crini et al., 2014).

Advantages of PSU includes high selectivity upon selective binding agent/polychelatogen. It has rapid reaction kinetics and ultrafiltration in PSU can operate in low-energy conditions (Barakat, 2011). On top of that, homogeneous metal ions can be removed or recovered, even in low concentration. The main drawback of PSU is that a detailed technical knowledge is required prior to operation and the price of PSU membrane is costly (Crini et al., 2014).

2.2.6 Biological Method

In biological method, it removes pollutants from wastewater by using biological techniques. It utilizes microorganism to settle the solids in the wastewater. Common techniques include using trickling filters, activated sludge for treating wastewater. In heavy metal removal wise, the biological method commonly used is biosorption. Biosorption utilizes adsorption and chelation to removes heavy metal from industrial wastewater. Typical sources of bio-adsorbent produced from varying agriculture waste depending to the ecosystem. Advantages of bio-adsorbent are fairly cheap which can easily be derived from industrial by-product, agriculture waste, modified biopolymers and can be used for heavy metal removal from metal-contaminated water. Recent research focus on heavy metal removal from industrial effluent by using agriculture by-products through biosorption. Basically, usage of resourceful by-products such as, coconut husk, rice husk, palm husk can be modified and heated to activated carbon which can absorb heavy metals.

Table 2.2: Pros and Cons on Different Wastewater Treatment Method

Wastewater treatment method	Advantages	Disadvantages
Chemical Precipitation	Cost efficient, easy handling operation.	Produce significant amount of sludge which requires extra treatment to remove.
Coagulation and Flocculation	Decrease time required for suspended solid settlement.	Require pre-treatment such as chemical coagulation
Electrochemical Treatment	Less chemical required, less sludge production.	High capital cost, require high electric supply
Ion Exchange	High absorption capacity, great removal effeciency.	Ion exchange resin need to be regenerated after exhaustion.
Membrane Filtration	High removal efficiency.	Membrane fouling, high operating cost.
Biological Method	Low cost of biosorbents, rapid adsorption.	Low selectivity, still under experimental phase.

2.3 Fundamental of Ion Exchange

All ions were electrically charged, either net positively or negatively charged. In general, positively charged ions are known as “Cation” while negatively charged ions are called “Anions”. Figure 2.5 shows a rough proportion of ions found in water, depending on the water source.

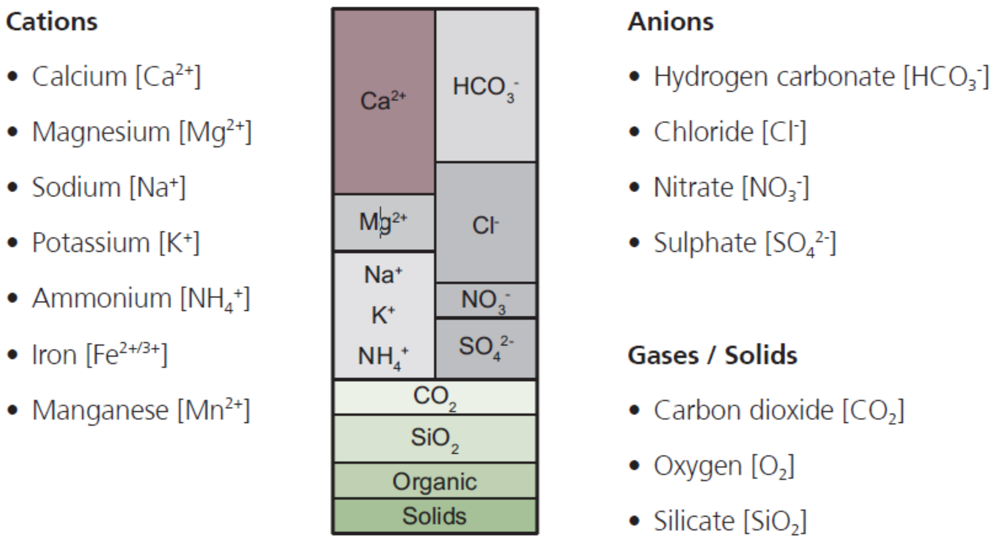


Figure 2.5: Typical Ions Found in Water (Hydrogroup)

Ion exchange is a reversible ion interchanging process between an insoluble solid also known as ion exchange material and a liquid. This process does not permanently change the structure of the solid after ion exchange process (Wheaton and Lefevre, 2017). Ion exchange resins are generally insoluble polymers with active sites which allows exchanging of ions with the same charges from a solution. The outstanding popularity of using ion exchange resin in treating industrial effluent is that the resin can be reuse multiple cycle after regeneration.

In heavy metal, Copper(II) ion extraction:

$$\boldsymbol{2RNa^{+} + Cu^{2+} \leftrightarrow R_2Cu^{2+} + 2Na^{+}}$$

R denotes the exchange medium (resin) in sodium form is readily to exchange for copper ions, thus remove copper ions from industrial effluent and replace it with equal amount of sodium ions. After period of time, the resin will be exhausted, whereby fully loaded with copper and needed to be regenerate. The exhausted resin can be treated with sodium chloride solution, whereby removing the copper and regenerate back to sodium form, to be used on another operation cycle.

Ion exchange process in the resin is a reversible reaction, where regeneration can be done for multiple times. Exchange of ions depends on the favourability of the active sites towards the mobile ions. When a more favourable ion is contacted, ion exchange occurs by releasing equivalent charges of ion to compensate the newly binded ion.

2.3.1 Physical Properties of Ion Exchange Resins

Generally, ion exchange resin is a resin which manufacture synthetically by adding functional groups into a crosslinked polymer. The active sites of the exchange resin, is known as ion exchangers. The insoluble exchangers hold the mobile ions with opposing charge which responsible for exchanging cation or anion. The backbone structures of the resin polymers consist of various type of functional groups which added through addition or condensation polymerization. By using the right manufacturing process and technology with polymerization method and condition, porosity and particle size of resin can be optimized and controlled.

A typical ion exchange resins is made from cross-linked co-polymer (thermosets) matrix and evenly distributed with ion-active sites all over the polymer structure for ion exchange process to occur. A cation exchange resin has numerous negatively charged functional group within the polymer matrix and accompanied with exchangeable cations (positive ions). Basically, ion exchange resin is beads form along with specific porosity and zise depending on the application.

2.3.2 Chemical Properties of Ion Exchange Resins

The exchange capacity of ion exchange resin can be expressed in the total number of active sites for ion (Wheaton and Lefevre, 2017). It is normally determined by using a measured quantity of fully generated resin. The ions are then being removed from a solution, whereby the number of ions were measured through normal analytical methods. The absorption capacity of ion exchange resin usually expressed in resin dry weight. The wet volume and weight is dependent on percentage of divinylbenzene (DVB) on the DVB and polystyrene polymer matrix. Figure 2.6 illustrates the relationship between the wet weight and wet volume capacity with the DVB percentage. The higher the composition of DVB in the polymer backbone, the greater the wet weight/volume capacity.

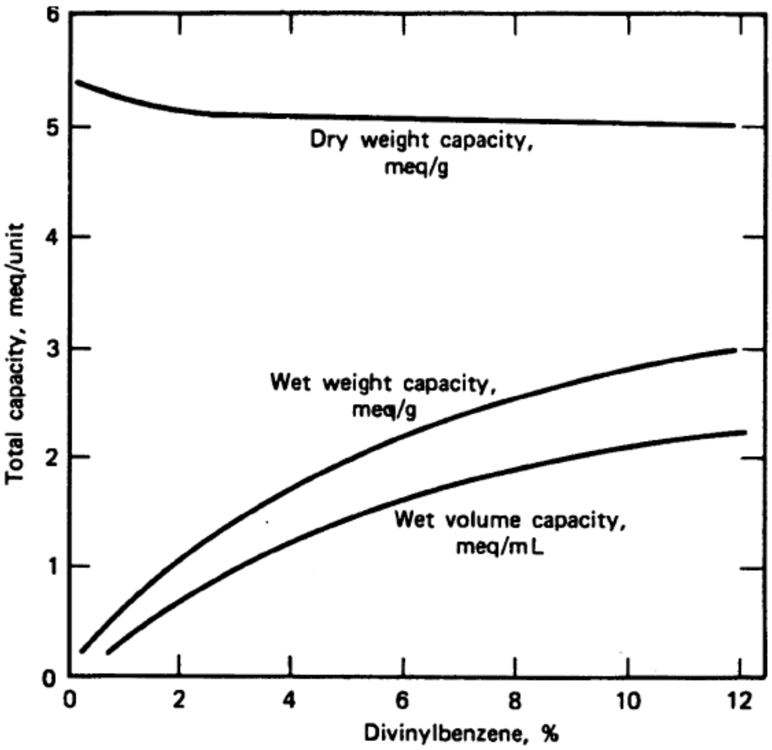


Figure 2.6: Total Capacity vs. Cross-Linkage (Percent DVB) Polystyrene (Wheaton, 2017)

In terms of ion selectivity, ion exchange process can be reversed, enabling the regeneration of ion exchange resins. It can be done by contact the exchange resin to an excess of electrolyte, so that the resin can be regenerated to the original salt form.

$$\boldsymbol{RA^{+}} + \boldsymbol{B^{+}} \leftrightarrow \boldsymbol{RB^{+}} + \boldsymbol{A^{+}}$$

where B^{+} refer to the positive ion suspended in the electrolyte.

If B is not in excess, exchange of ion cannot be done and will establish a chemical equilibrium which dependent on the ratios of A^+ and B^+ ions and resins' selectivity/affinity. Generally, the selectivity coefficient of the reaction is expressed by:

$$\boldsymbol{K_A^B} = \frac{\boldsymbol{\bar{m}_B}}{\boldsymbol{\bar{m}_A}} \times \frac{\boldsymbol{m_A}}{\boldsymbol{m_B}} \tag{2.1}$$

where m and $\bar{m}$ refers to the concentration if ion in the solution and resin, respectively.

2.3.3 Structure and Manufacture of Ion Exchange Resin

Synthetic ion exchange resin is manufactured by introducing variety of functional groups such as sulfonic group, iminoacetate group into 3D crosslinked polymer matrix. The polymer matrix is also known as the backbone of the exchange resin which is a co-polymer, typically combination of styrene with divinyl benzene (DVB) according to ITOCHU Chemicals America INC. The crosslinked polymers synthesis is shown in the schematic diagram below. The DVB is responsible for crosslinking of the copolymer matrix.

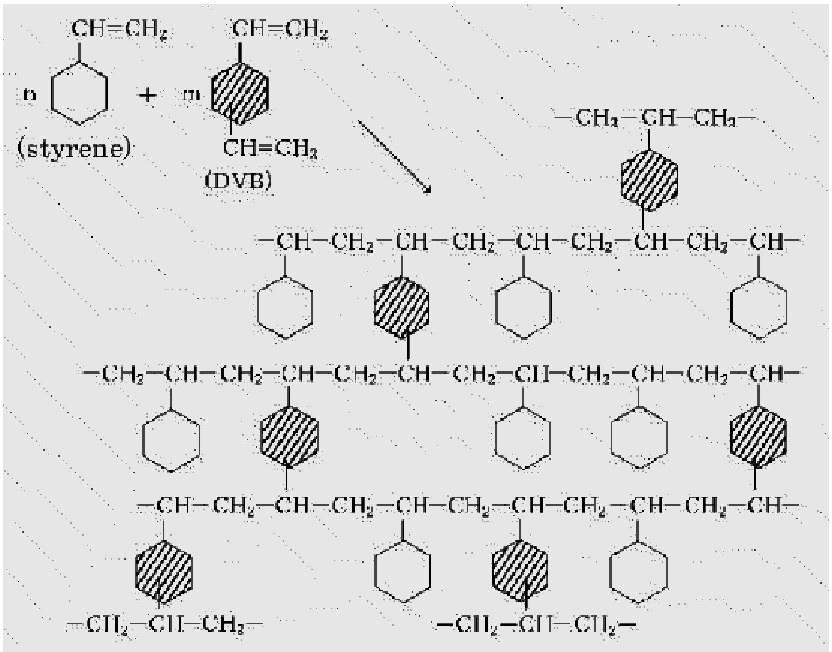


Figure 2.7: Chemical Structure of DVB Co-polymer (ITOCHU, 2017)

The most standard ion exchange resin for industrial use is shaped into spherical beads, with diameters of 0.3 - 1.2 mm (ITOCHU, 2017). Manufacture of ion exchange resin involves a crosslinked bead copolymer with addition of functional groups. For instances, strong acid cation resins undergo sulfonation, or chelating resin involves addition of iminodiacetate group. For weak acid cation exchange resin, it is manufacture by co-polymerization between acrylic acid or methacrylic acid with divinyl benzene (DVB) as cross-linking agent. During the manufacturing process, ester from acid in suspension undergo polymerization then hydrolysed to produce functional acid group.

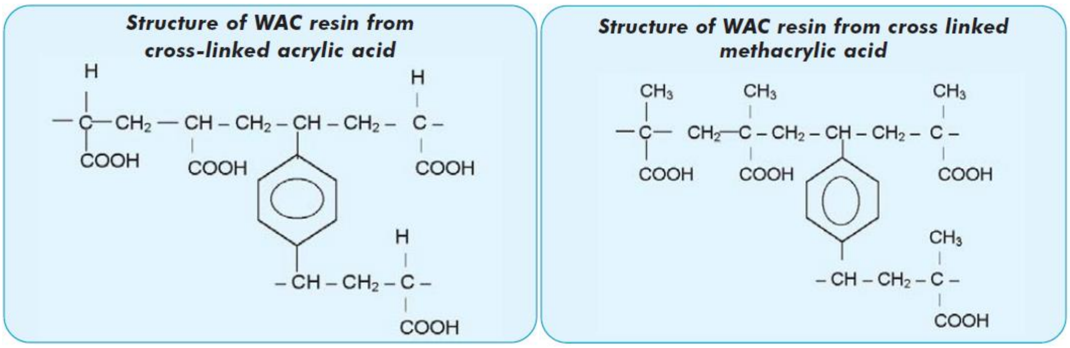


Figure 2.8: Structure of Weak Acid Cationic Resin (left) and Strong Acid Cationic Resin (right) (WaterTech, 2004)

In other words, production of ion exchange resin involves addition of functional groups to the backbone of these crosslinked-polymer structures. For instances, ion exchangeable groups such as iminodiacetate group or sulfonic groups are known as “fixed ions” because they are permanently bonded to the crosslinked polymer structure and do not leaves. On the other hand, “counter ions” or mobile ions are used to neutralized with the fixed ion, e.g. fixed sulfonic acid group SO_3^- is being neutralized by mobile H^+ion (ITOCHU, 2017).

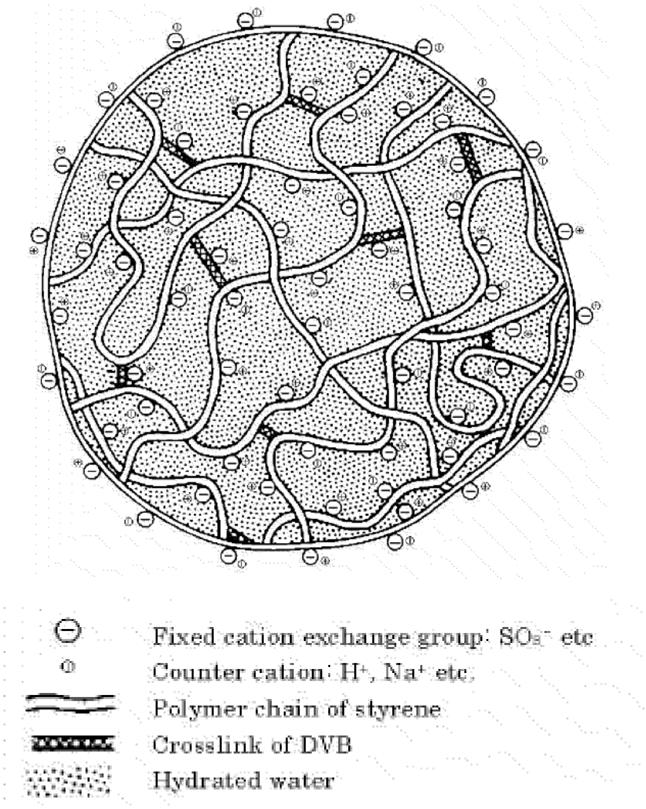


Figure 2.9: Resin Bead in Expanded View (ITOCHU, 2017)

Figure 2.9 shows a conventional cation exchange resin structure. We shall imagine the resin structure as a complete 3D structure or a sphere. DVB forms the crosslink in the resin where crosslink density varies with the ratio of DVB: Styrene. During manufacturing, if the ratio of DVB: Styrene is higher, crosslink also becomes higher in copolymerization resulting a denser network and structure. In contrary, if the ratio is lower, less crosslink is created which creates a sparse network. Form here, we know that DVB acts as a crosslinking agent which links the styrene branch into a denser structure (ITOCHU, 2017). Concentration of crosslinking can be calculated by identifying the amount of DVB on the copolymer.

Ion exchange resin has micropores for increasing number of ion exchange sites where ion can diffuse into them to exchange ions. When the crosslinkage is higher, the size of micropores becomes smaller, making ions harder to diffuse into the micropores. However, producing less crosslinkage for easier ion diffusion doesn’t necessarily means better. This is because when the crosslink is too low, they become sparse and more difficult to handle because they become soft and physically weak as a resin.

As mention earlier, styrene and DVB do not absorb water. Nevertheless, they can gain strong water absorbability after added with ion-exchangeable functional groups as they have swelling properties in water. The polymer matrix is capable to expands its size and the volume increases by hydration and the nature of osmotic pressure. The degree of hydration and swelling is stabilized at equilibrium between expansion and contraction force of the polymer chains. Hence, lower crosslinkage resin tends to absorb more water and swell more due to lower contraction force by the crosslinkage. On the other hand, high crosslinking resin has more contracting force due to its abundant crosslinkage, thus less swelling.

2.3.4 Types of Ion Exchange Resins

Ion exchange resin can be divide into few types by their functional group either attracting positive ion (cation) or negative ion (anion).

1. Cation exchange resin
    - Strong acid cation exchange resins
        - ➢ Functional groups obtain from strong acid e.g. R-SO_3H (sulfonic group)
    - Weak acid cation exchange resins

        - Functional groups obtain from weak acids, e.g., R-COOH (carboxylic acid group).
    - Chelating resins
        - Functional groups e.g. (iminodiacetate group)
2. Anion exchange resin
    - Strong basic anion exchange resins
        - Functional groups obtain from quaternary ammonium compounds, e.g. R-N-OH.
    - Weak basic cation exchange resins
        - Functional groups obtain from amine groups, R-NH_3OH or R-R'-NH_2OH.

Tables 2.3 and 2.4 shows a comparison between strongly acidic cation exchange resin and weakly acidic cationic exchange resin, and comparison between strong base cation exchange resin and weak base cationic exchange resin, respectively.

Table 2.3: Comparison Between Strong Acidic Cation Exchange Resin and Weak Acidic Cationic Exchange Resin.

Strong acid cation exchange resin	**Weak acid cation exchange resin**
▪ Strong acidity as mineral acid	▪ Weak acidity as organic acid
▪ Able to dissociate in all pH range (aqueous solution)	▪ Only can dissociate in neutral to alkaline range (aqueous solution)
▪ Can be regenerated by hydrochloric acid (HCl) and sulphuric acid (H_2SO_4)	▪ Can be regenerated by hydrochloric acid (HCl) and sulphuric acid (H_2SO_4)
▪ Hard to be regenerated (more regenerants is required)	▪ Easy to be regenerated
▪ High rate of reaction	▪ Lower rate of reaction

Table 2.4: Comparison Between Strong Base Cation Exchange Resin and Weak Base Cationic Exchange Resin.

Strong base anion exchange resin	Weak base anion exchange resin
▪ Caustic alkali for strong base	▪ Ammonium hydroxide for ammonium hydroxide
▪ Able to dissociate in all pH range (aqueous solution)	▪ Only can dissociate in acidic to neutral range (aqueous solution)
▪ Hard to be regenerated (more regenerants is required)	▪ Easy to be regenerated
▪ Higher rate of reaction	▪ Lower rate of reaction
▪ Resin can be regenerated by NaOH	▪ Resin can be regenerated by NaOH

2.4 Mechanism of Ion Exchange Resins

As a recap, the backbone of the exchange resin is the copolymer matrix which is insoluble, whereby fixed ion or ion exchangeable group (positively charged or negatively charged) is permanently attached to the matrix which cannot be removed or replaced. From there, each fixed ion must be neutralized with a counter ion to preserve the electrical charge of the ion exchange resin. Counter ion aka mobile ion can move in or out of the resin matrix. In other words, counterion can be attached to or detached from the ion exchangeable group.

Figure 2.10 shows a schematic diagram of a cation (left) and anion (right) exchange resin beads (Lenntech, 2008). The fixed ion for cation exchange resin are sulfonate group SO_3^- which permanently attached to the copolymer matrix. Every sulfonate is bonded with an equal counteract charges of mobile ions, which is sodium ion Na^+ in this case. On the other hand, anion exchange resin has quaternary ammonium group (N^+R_3) as fixed ion. Every ion going into the resin has to be replaced with an ion going out to preserve electrical neutrality. In ion exchange theory, only ions of same electric sign (either both positively charged or both negatively charged) can be exchange.

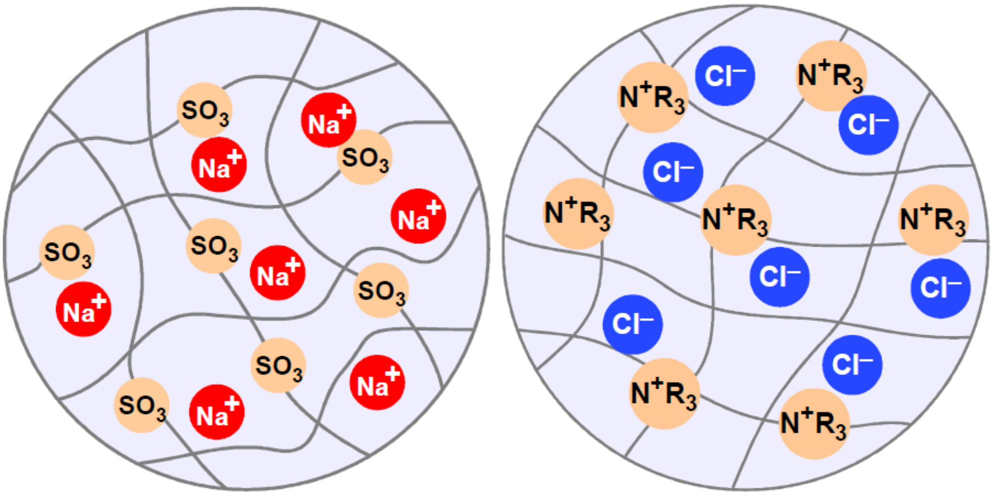


Figure 2.10: Schematic Diagram of Typical Cation (left) and Anion (right) Exchange Resin (Lenntech, 2008)

One may have thought of making an ion exchange resin which able to exchange cation as well as anion. In fact, it can be manufacture but it has no working purpose. This is because the fixed anion and fixed anion will have neutralized each other so that it is impossible to exchange with foreign ions. Thus, it is important to distinguish both cationic and anionic exchange resin.

A simple water softening process shall illustrate the mechanism of ion exchange resin. We usually encounter water hardness in raw water. Hardness refers to significant amount of dissolved magnesium and calcium ion present in the water, where it may accumulate and build up eventually blocking pipes. So, water softening is used to remove the calcium and magnesium ion by replacing them with a more soluble ion e.g. sodium or hydrogen ion.

During the softening process, cation exchange resin is used which positively charged sodium Na^+ion acts as the mobile ion. As the hard water pass through the cation exchanged resin-filled column, ion exchange occurs. Since calcium and magnesium are divalent cation, each Ca^{2+} and Mg^{2+} moved into the resin is replaced by two Na^+ ions moving out from the resin, again to achieve neutralization. The exchange reaction written as:

$$2RNa + Ca^{2+} \rightarrow R_2Ca + 2Na^+$$

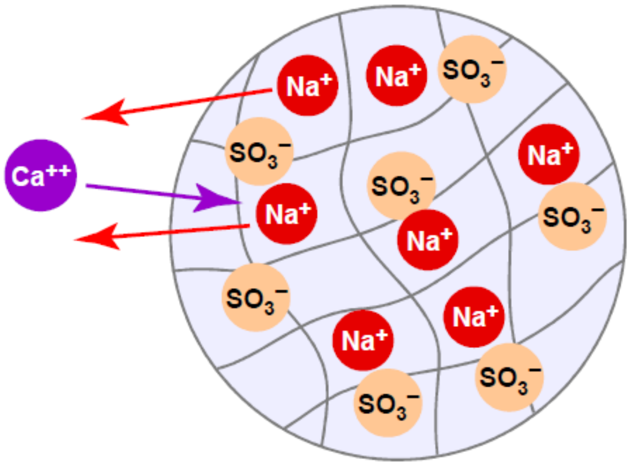


Figure 2.11: Sodium Exchange in a Cation Resin Bead

Figure 2.11 illustrates initial mobile ion of the resin is Na^+. For every Ca^{2+} ion moves into the resin beads is replaced by two Na^+ions leaving the resin. To top of that, the cation exchange process takes place only when the cation exchange resin has a higher affinity for the calcium and magnesium ion than for sodium. In layman terms, the resin prefers calcium and magnesium over sodium.

Sulfonic acid group affinity for cations changes with the cationic charges and the ionic size. Normally large ions with high valency has the greatest affinity.

Order of affinity for some common cations is approximately:

$$\boldsymbol{Hg^{2+} < Li^+ < H^+ < Na^+ < K^+, NH_4{}^+ < Cd^{2+} < Ag^+ < Mn^{2+} < Mg^{2+} < Zn^{2+} < Cu^{2+} < Ni^{2+} < Co^{2+} < Ca^{2+} < Sr^{2+} < Pb^{2+} < Al^{3+} < Fe^{3+}}$$

Order of affinity for some common anion is approximately:

$$\boldsymbol{OH^-, F^- < HCO_3{}^- < Cl^- < Br^- < NO_3{}^- < HSO_4{}^- < PO_4{}^- < CrO_4{}^- < SO_4{}^{2-}}$$

2.4.1 Working Mechanism of Chelating Ion Exchange Resins

In this project, chelating resin was selected to be used for copper (Cu) removal from industrial effluent. A chelating resin is a class of cation exchange resin which has minor difference from conventional acid and basic ion exchange resin. Chelating resin has a high selectivity towards divalent ions over monovalent ions such as

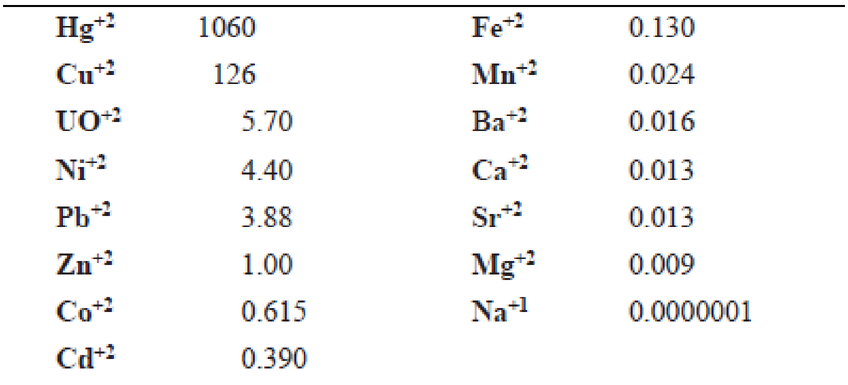
$Cu^{2+}, Pb^{2+}, Ni^{2+}$ and other divalent heavy metal ions. A chelating resin has a microporous structure, it is a styrene divinylbenzene copolymer with iminodiacetate acid functional groups.

Iminoacetate acid group is the chelating group mainly used in metal cation removal from aqueous solution due to its nature which can form complex with metal ions even in the presence of high concentration of sodium salts. Chelating resin usually undergoes swelling due to the tendency of dilution of the resin itself (Zagorodni, 2006). The iminodiacetate acid group is the chelating group for binding divalent heavy metal ions. Chelating resin sometimes was classified into weakly acidic cation exchange resin due to availability of carboxylic acid group. However, chelating resin has a higher selectivity towards divalent metal ions which make chelating resins different from ordinary weak acid cation exchange resin.

Table 2.5 were obtained from BIO-RAD Laboratories, lists the selectivity factor for various cations of Chelax chelating resin. With Zinc (Zn) ion as a reference cation, it measures quantitively the affinity of the resin displayed for other cation as compared to Zn.

Selectivity for Divalent Cation

Table 2.5: Selectivity for Divalent Cation



Hg^{+2}	1060	**Fe^{+2}**	0.130
Cu^{+2}	126	**Mn^{+2}**	0.024
UO^{+2}	5.70	**Ba^{+2}**	0.016
Ni^{+2}	4.40	**Ca^{+2}**	0.013
Pb^{+2}	3.88	**Sr^{+2}**	0.013
Zn^{+2}	1.00	**Mg^{+2}**	0.009
Co^{+2}	0.615	**Na^{+1}**	0.0000001
Cd^{+2}	0.390		

Chelating resin can be used in both batch and column techniques in absorption of element. As there are various types of chelating resin available commercially, operators have few options for selecting resin for their desired purpose (Kagaya, Gemmei and Inoue, 2014).

2.4.2 Operating Parameters of Chelating Ion Exchange Resins

2.4.2.1 pH

The performance of metal extraction on the chelating resin is fundamentally predicted based on the functional group (ligand) with the metal ion in the solution (Kagaya, Gemmei and Inoue, 2014). According to Kayaga, the absorption of Cu(II) ions using iminodiacetate group chelating resin increased when the pH of the solution increased. The recovery of Cu ion in various pH is shown in Figure 2.12.

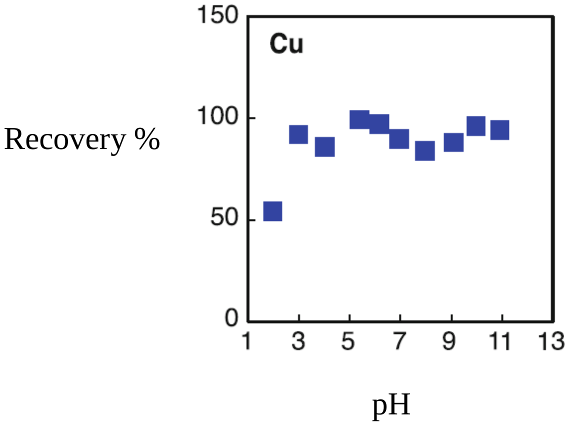


Figure 2.12: Recovery of Cu(II) on Different pH Using Iminodiacetate Group Chelating Resin (Chelax-100)

According to Chelax, chelating resin exhibits stable absorption performance at pH ranging from 3 to 12. Generally, the absorption capability is primarily affected by the pH. Absorption level was very low below pH 2 and rose sharply from pH 3 to 4. It reached a maximum absorption capacity at pH 5 and above (Bio-Rad, 2000). The reason behind the ineffective absorption of chelating resin at low pH is due to the convertible behaviour to anion exchanger. It can be described as in Figure 2.13. From Figure 2.13, the structure of the resin exchange group changes with their pH. At pH below 4, the resin will tend to behave as anion exchange resin, which is unfavourable for cation exchange such as Cu(II) ion.

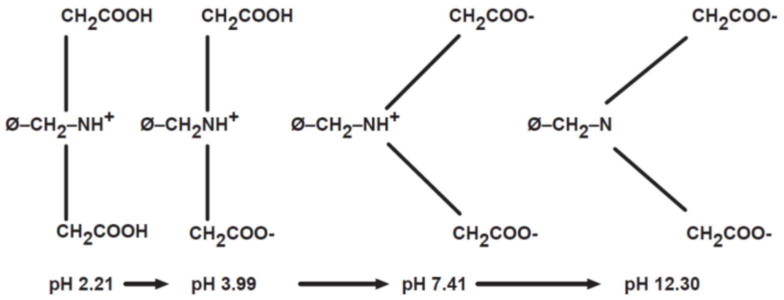


Figure 2.13: Transformation in Structure of Iminodiacetate Chelating Resin in Different pH (Bio-Rad, 2000)

2.4.2.2 Initial Concentration of Cu(II)

In ion exchange process, the initial concentration of Cu(II) needs to be optimized to ensure that the ion exchange resin performs well. Theoretically, when the initial concentration of Cu(II) increases, the uptake of metal ions by the resin also increases. However, when the concentration is increased to a certain saturation point, the concentration of metal ion no longer affects the metal ion uptake of the resin. So, the resin absorption capacity serves as an essential factor to determine the amount of resin required to quantitatively absorb a certain amount of metal ion in the solution (Fadel, El-Bahy and Abdelaziz, 2016). Figure 2.14 shows the optimal concentration of different metal ions. Based on the graph, it is identified that the resin capacity reach to the peak at pH 14 according to the trend for Cu ions. Further increase of concentration of metal in the solution will not enhance the resin capacity.

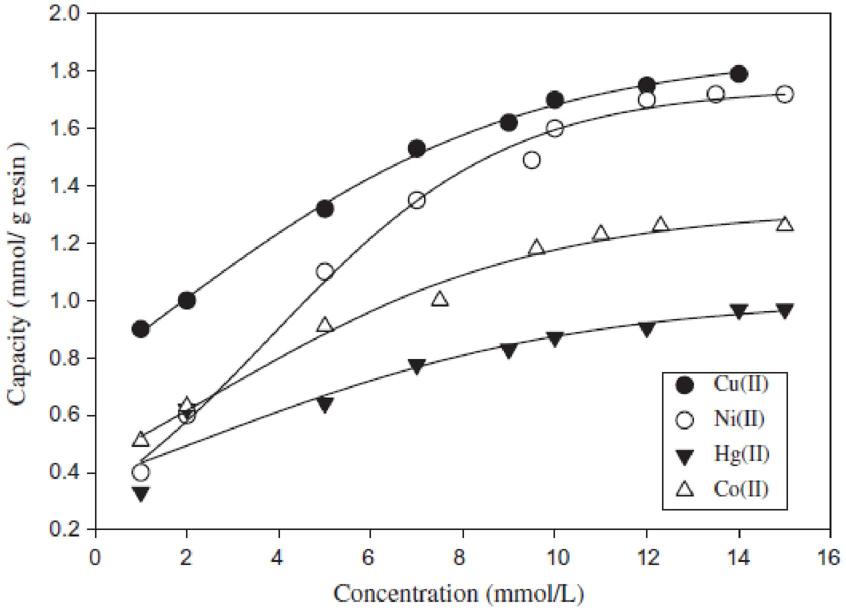


Figure 2.14: Effect of Initial Concentration of Metal Ions On Resin Absorption Capacity

2.4.2.3 Wastewater Flow Rate

Flow rate of effluent certainly will affect the absorption rate of resin. Figure 2.15 shows the relative concentration of a metal solution versus time. It was shown that when the flow rate was higher, the duration needed for the metal ion to breakthrough completely was shorter. This was due to the fact that more metal ion was exchanged in a shorter amount of time, where the resin was exhausted sooner. Thus, it is uncappable of absorbing metal ion when it is fully loaded.

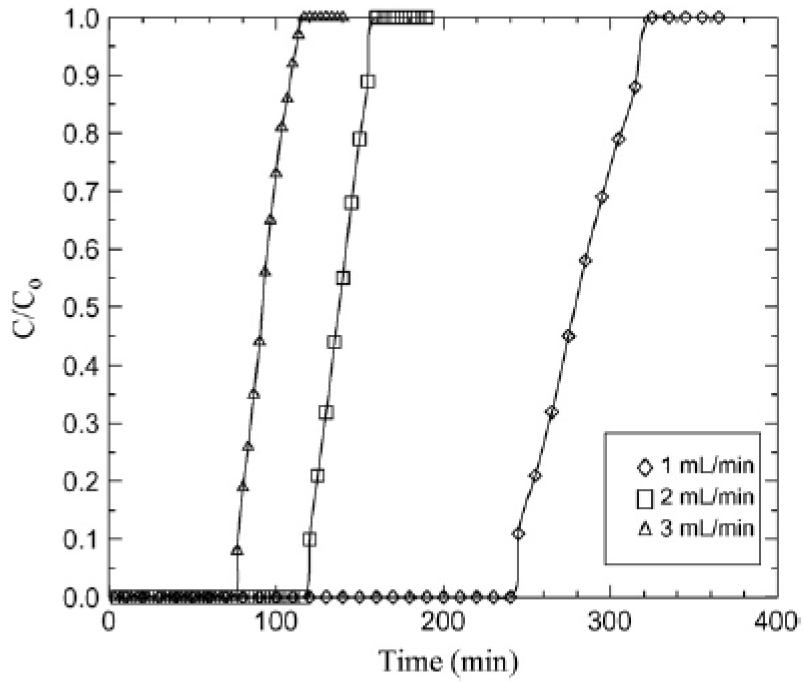


Figure 2.15: Effect of Wastewater Flow Rate on Metal Uptake

2.4.3 Regeneration of Ion Exchange Resins

When a chelating cation exchange resin no longer can remove heavy metal from aqueous solution due to exhaustion, it need to be regenerated to be reused for another operation cycle. For now, the most effective solvent to remove the metal ions from the chelating resin is acids, e.g. hydrochloric acid, sulphuric acid. Although concentrated salt aqueous solution such as sodium chloride, NaCl (aq) is quite feasible to elute selective ion from resin, it is inefficient for eluting heavy metals which is strongly absorbed to the resin.

Generally, regeneration of exhausted chelating resin involves 2 processes. The first step is to convert the metal-binded resin to hydrogen form by reacting with hydrochloric acid.

Take copper Cu(II) loaded resin as example:

$$\textbf{\textit{Resin-Cu}} + \textbf{\textit{2HCl}} \rightarrow \textbf{\textit{Resin-H}} + \boldsymbol{CuCl_2}$$

By reacting the copper-loaded resin with hydrochloric acid, copper ion will be removed from the resin and replaced by hydrogen ion. This is due to the fact that hydrogen has higher affinity than copper towards the resin. Therefore, copper will bond with the chloride ion to produce copper(II) chloride.

In the next step, hydrogen form resin can be converted to the desired ionic from using desired cation hydroxide solution. E.g. desired ionic form is in sodium, Na.

$$\textbf{Resin-H} + \textbf{NaOH} \rightarrow \textbf{Resin-Na} + H_2O$$

2.4.3.1 Co-current Regeneration System

Regeneration of Chelating resin can be conducted in two ways, either by co-current or counter-current system. Basically, co-current regeneration system is most widely used in the industries. In co-current regeneration system, the regenerant flows with the same path and direction as the effluent, either both streams from the top to bottom or both from bottom to the top. Practically, chelating resins are not completely converted to H form after regeneration because complete regeneration consumes huge amount of regenerant which is not feasible. Hence, the bottom part of the resin is more contaminated with metal ions than top part of the resin bed after regeneration process (Dardel, 2016). So, during the next operation cycle, the lower contaminated resin will encounter metal ion leakage due to the displacement of contaminated ion, whereby there is no readily regenerated resin further down as a backup. Co-current regeneration system can be represented in Figure 2.16.

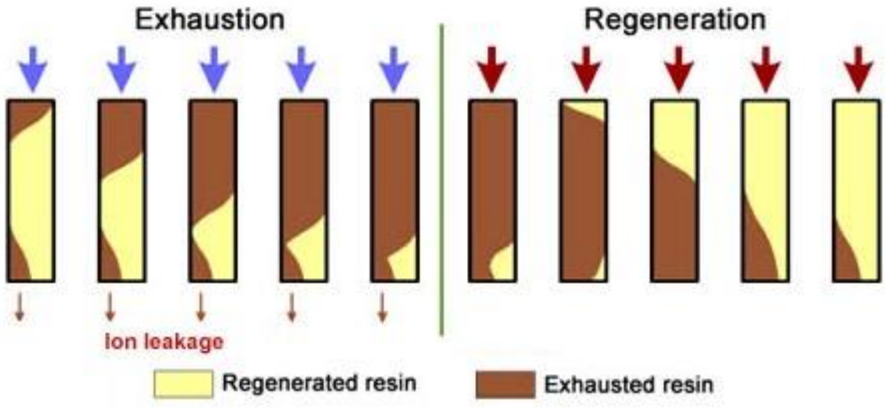


Figure 2.16: Co-current Regeneration System (Dardel, 2016)

Table 2.6: Advantages and Disadvantages of Co-current Regeneration System

Advantages	Disadvantages
Proven process	Higher capital cost
Simple resin cleaning operation	Significant contaminated ion leakage
Reliable regeneration	Poorer water quality

2.4.3.2 Counter-current Regeneration System

In contrary, the counter-current regeneration performed by reverting the flow direction of the regenerant. It means that the regenerant flows in a reversed direction of the effluent flow. It is usually done in downflow of loads pairing with upflow regeneration. By using counter-current regeneration system, the regenerant needs not to push the metal ions through the uncontaminated resin bed. The unexhausted/ less exhausted resin at the bottom layer is regenerated first, followed by the top layer (Dardel, 2016). By then, the contaminated ion is pushed to the top and the lower part is the cleanest. So, leakage of contaminated ion is less likely to occur. Counter-current regeneration is illustrated in Figure 2.17.

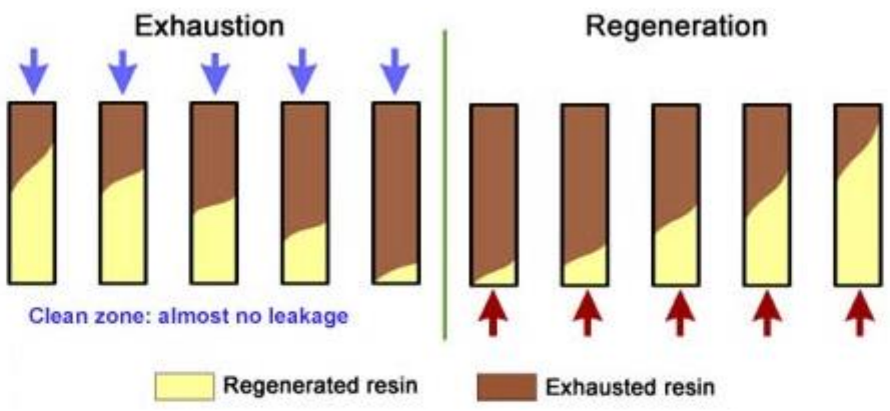


Figure 2.17: Counter-current Regeneration System (Dardel, 2016)

Table 2.7: Advantages and Disadvantages of Counter-current Regeneration System

Advantages	Disadvantages
High efficiency	Much higher capital cost
Treated water has purer quality	Complex regeneration technique
Low leakage of ion	Multiple regeneration cycle required

2.5 Uses and Applications of Ion Exchange Resins

There are various applications of ion exchange resin such as water softening, demineralization, wastewater treatment etc.

2.5.1 Demineralisation

Demineralisation of natural water is also known as deionization. Natural water consists of a variety of dissolved ion, both cation and anion. To deionize the water, both cation and anion exchange resins are employed at the same time. A typical setup is to pass the untreated water through cation exchange resin bed first. During this step, dissolved cations from the water exchange with hydrogen ion from the resin, so that the effluent is low in acidity. Then, the water is allowed to flow through a bed of hydroxide to form anion exchange resin. Anions from natural water are removed and replaced by hydroxide ions. Finally, both hydrogen and hydroxide ions released from cation and anion exchange resins respectively react to produce water (pure H_2O).

2.5.2 Water Softening

Ion exchange resin can be used for water softening. In this application, cation exchange resin present in sodium form can be used to remove calcium (Ca) and magnesium (Mg) ions which are usually found in hard water. Hard ions in the aqueous solution are replaced with an equivalent amount of sodium ion. Calcium and magnesium ions have a higher affinity than sodium ion, so they are preferable to be bound to the resin. During exhaustion, the resin can be regenerated by passing regenerant through the resin to replace bound ions on the resin. For normal cation exchange resin, concentrated salt solution such as sodium chloride (NaCl) can be used to regenerate the exhausted resin.

CHAPTER 3

METHODOLOGY AND WORK PLAN

3.1 Introduction

This project involved experimenting 2 different types of wastewater samples for which each sample was conducted chronologically as follows:

1) Synthetic wastewater containing copper (Cu(II)) ions only.
2) Industrial wastewater collected from air-conditioner manufacturing factory located in Selangor.

3.1.1 Preparation of Synthetic Wastewater Containing Cu(II)

An exact weight of 1 g of analytical grade copper(II) sulfate $CuSO_4 \cdot 5H_2O$ was prepared and added into 1 L of deionized water. It was allowed to be dissolved in the deionized water to produce the stock concentrated solution of synthetic Cu(II) solution. Then, the stock concentrated Cu(II) solution is further diluted into desired concentration by adding deionized water.

3.2 Preparation of Chelating Resin

In this research, chelating resin HM100 was obtained from a wastewater treatment company (i-Chem Solution Sdn. Bhd.) which is based in Puchong, Selangor. It was a co-polymer of styrene and divinylbenzene, DVB with iminodiacetate acid functional group, which is mainly used for heavy metal removal from industrial effluent. The chemical nature of iminodiacetate group was that they were able to form metal-resin complexes with metal ions even in the presence of high concentration of calcium and sodium salts. The chelating resin had a high selectivity towards Cu(II) ions and the relative affinity is in accordance with the following sequence:

$$H^+ > Cu^{2+} > Pb^{2+} > Ni^{2+} > Zn^{2+} > Co^{2+} > Cd^{2+} > Fe^{2+} > Mn^{2+} > Ca^{2+} > Mg^{2+} > Ba^{2+} > Sr^{2+} > Na^{2+}$$

3.3 Experimental Setup

3.3.1 Materials

Chelating resin with iminodiacetate group, HM100 was obtained from a wastewater treatment company. HCl is used as regenerant for HM100 chelating resin. HCl and NaOH was used for pH neutralization and conditioning. Analytical grade copper(II) sulfate salt $CuSO_4 \cdot 5H_2O$ was used for preparation of Cu(II) synthetic wastewater. Deionized water was required for slow rinse and as a solvent for Cu(II) ions. Silver nitrate solution worked as an indicator for chloride ions.

3.3.2 Apparatus and Equipment

Apparatus in this research included

- A glass chromatography column with a tap to act as a containing medium for the resin.
- A membrane to support the resin from leaking out of the column.
- A separating funnel to contain more solution to flow through the chromatography column
- A retort stand to support the chromatography column
- A beaker to contain the effluent

Instruments in this research included

- A digital laboratory scale for weighing chemicals with precision of $\pm$ 0.0001 g.
- A pH meter to measure the pH value of the solution. It is used to standardize solution from pH 0 - 10.
- Inductively-Coupled-Plasma Atomic Emission Spectroscopy (ICP) is used to measure Cu(II) in the solution, also to quantify the concentration of Cu(II).
- Scanning Electron Microscopic (SEM) to visualize the surface of resin.
- Energy-dispersive X-ray Spectroscopy (EDX) to identify the surface composition of the resin.

3.3.3 Column Setup

A chromatography column was prepared and it had a 0-porosity sintered disc at the bottom part of the column as a platform to hold and support the resin bed. The stopcock at the outlet of the chromatography column was used to adjust the flowrate. Deionized water as initially filled into the column followed by desired volume of resin. It is important to maintain the water level inside the column 2 - 3 cm above the resin bed. If the column runs out of water, backwashing shall be done, whereby water was replenished from the bottom through the outlet of column to displace trapped air through the top of the column.

Subsequently, a pear-shaped separating funnel was perfectly fitted to the inlet of the chromatography column to contain more volume of solution.

Column specification: Length: ~ 30 cm, Internal Diameter: ~ 1.9 cm

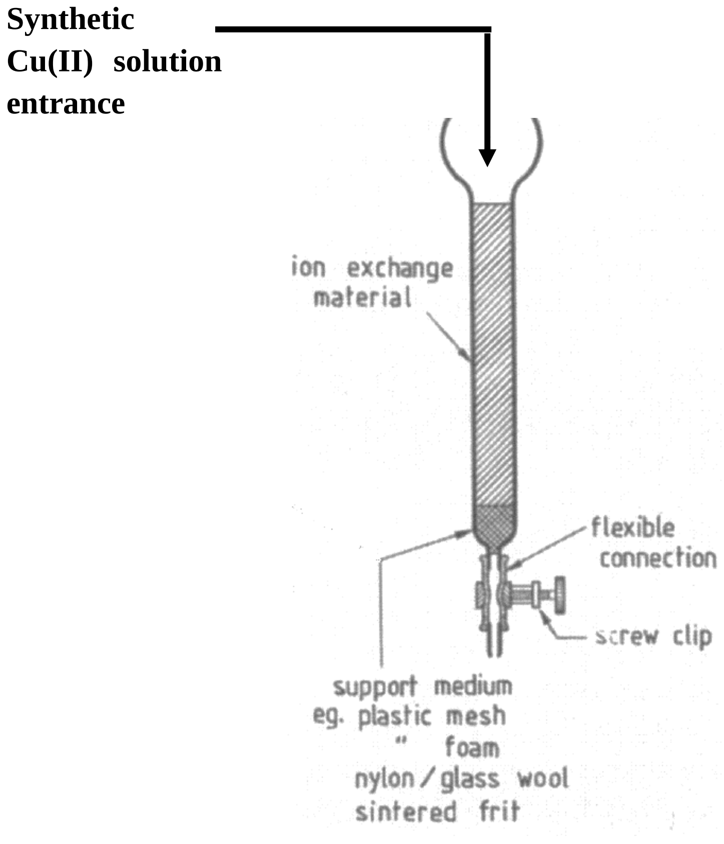


Figure 3.1: Column Setup

3.4 Column Test

The parameters to be tested for column absorption of Cu(II) were:

- pH of synthetic wastewater
- initial concentration of Cu(II)
- bed height of iminodiacetate chelating resin, and
- flow rate of synthetic wastewater

Each of these parameters was optimized one after another. Figure 3.2 shows the experimental sequence of parameter optimization in chronological order.

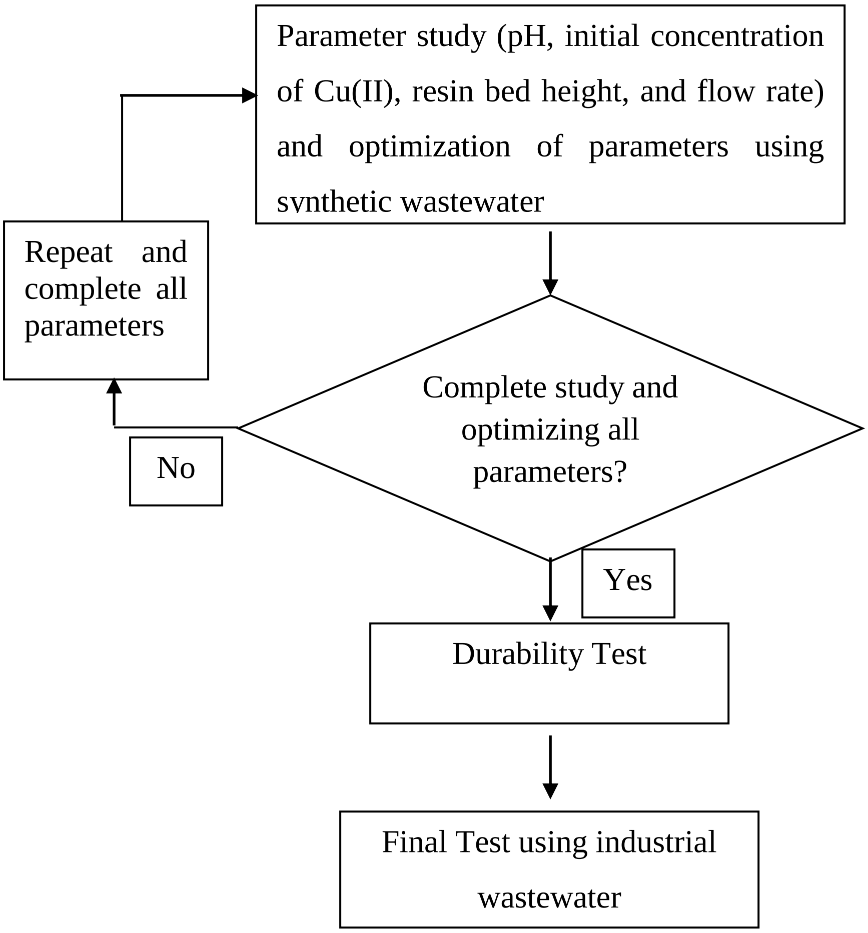


Figure 3.2: Experimental Procedure

3.4.1 Measurement of Resin Bed Volume

Resin bed volume was measured under wet condition where resin is poured into a measuring cylinder along with deionized water enough for the resin to fully submersed below the water surface by 2 - 3 cm. As if resin floats onto the surface of water, gently knock the side of cylinder to settle down the resins. After 5 minutes, the resins were fully settled down and the reading of the cylinder at the height of settled resin is termed as bed volume.

3.4.2 Bed Volume

Practically, resin volume and column size vary by their applications. So, amount/ volume of servicing solution and regenerant was conveniently determined by relating the bed volume (BV) of resin. For example, assuming a regenerant flow rate of 5 BV is required. If the resin used is 20 ml, 5 BV of regenerant required would be 100 ml.

3.4.3 Benchmark Selection

Based on the suggested operating conditions provided along with the chelating product specification, the flow rate of solution can be benchmarked. According to the specification, the suggested service flowrate is 6 to 32 BV/hr.

Assuming the glass column used for the column test has a diameter of 2 cm, resin bed height at 9 cm. The bed volume can be calculated as follows:

$$V_{\text{cylinder}}, \text{Bed Volume} = \pi r^2 h \tag{3.1}$$

$$= \pi(1cm)^2(9cm)$$

$$= 28.27cm^3 \approx 28.27ml$$

Lower boundary (6 BV/hr): $6 \times 28.27\ ml/hr = 169.62ml/hr = 2.287\ ml/min$

Upper boundary (32 BV/hr): $32 \times 28.27\ ml/hr = 904.64ml/hr = 15.077\ ml/min$

3.5 Optimization of Absorption Operating Parameters

3.5.1 Determination of Optimal pH and Its Effect on Cu(II) Absorption

The optimum pH value of synthetic wastewater was determined through column and batch method. In the column method, 1 L of 50 mg/L Cu(II) synthetic solution was allowed to flow through the resin bed of 10 cm. The pH of the Cu(II) solution was fixed to the desired value using 1 M HCl or 1 M NaOH prior to the experiment.

In the batch method, 100 mL of synthetic wastewater contained Cu(II) with concentration of 50 mg/L was shaken in a shaking incubator at 25°C for a certain amount of time. Th pH value of the wastewater was adjusted to the desired pH using 0.5 M hydrochloric acid or 0.5 M sodium hydroxide prior to the experiment.

Adsorption capacity can be calculated by determining the initial (C_o) and final (C_e) concentration of Cu(II) in the solution for varying pH in the range of 2 and 10. The concentration of Cu(II) in the solution can be analysed using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

A graph of adsorption capacity, q (mg/g) versus pH can be plotted upon completion. From the graph, we can illustrate the trend of adsorption capacity of chelating resin by varying pH condition.

3.5.2 Determination of Optimal Initial Cu(II) Concentration and Its Effect on Cu(II) Absorption

Initial concentration of Cu(II) in the synthetic wastewater can be optimized using the same concept in pH research. Initial concentration study was performed at optimal pH. A range of 100 mL synthetic wastewater with Cu(II) concentration ranging from 20 to 100 mg/L was shaken in a shaking incubator at 25°C for certain amount of time.

3.5.3 Determination of Optimal Column Bed Height and Its Effect on Cu(II) Absorption

After determining the optimal pH value and initial concentration of Cu(II), the following test requires optimization of column bed height. The column bed height was adjusted from 2.5 to 15.0 cm. 500 mL of Cu(II) synthetic wastewater with optimal pH and initial concentration was allowed to flow through different column bed height. The purpose of this test was to determine the minimum bed height required to effectively remove Cu(II) from the synthetic wastewater or to prevent major breakthrough of Cu(II) through the resin bed.

3.5.4 Determination of Optimal Flowrate and Its Effect on Cu(II) Absorption

Using the optimal pH, initial concentration, and column bed height by earlier experiment, the last parameter to be investigated is the flowrate of synthetic wastewater. Synthetic Cu(II) wastewater with optimal pH, initial concentration and bed height were allowed to flow through the resin bed with different flow rate. The flow rate was adjusted in the range between 1 and 70 mL/min. This test was to find out the minimum contact time required to effectively adsorb the Cu(II) ion from the synthetic wastewater to prevent breakthrough of Cu(II) through the resin bed.

3.6 Regeneration of Exhausted Resin

The resin was subjected to regeneration after each servicing cycle. The regeneration involved 2 steps, regeneration using HCl and slow rinse using deionized water.

Regeneration was performed using 1 L of 10% HCl flowing through the exhausted resin to remove the bound Cu(II) ion from the resin, replacing it with 2 H^+ ions. It was followed by slow rinse using deionized water to remove the chloride ions (Cl^-) from HCl trapped in the resin bed. Silver nitrate was periodically dropped into the slow rinsed water as an indicator to check the presence of chloride ions. If the solution turns cloudy, it indicated the presence of chloride ion. Hence, the slow rinse process was continued until the slow rinsed water remain colourless after dropping with silver nitrate indicator.

3.6.1 Durability Test

The durability of the resin was examined through multiple servicing and regeneration cycle by comparing the adsorption capacity percentage for every consecutive cycle.

An expected trend of adsorption capacity percentage after multiple regeneration cycle is shown in Figure 3.3.

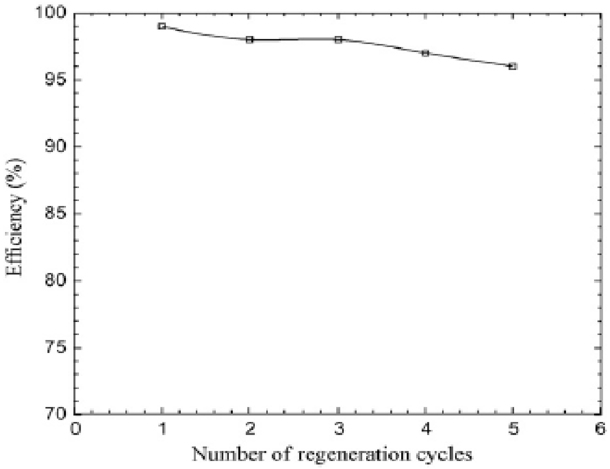


Figure 3.3: Trend of absorption capacity percentage after multiple regeneration cycle

3.7 Cu(II) Absorption from Industrial Wastewater Collected from Air-Conditioner Manufacturing Factory

Industrial wastewater was usually composed of a variety of organic and inorganic components, where complexes are often found in industrial effluent. This absorption test is carried out using the optimum parameters determined from Cu(II) synthetic solution.

3.8 Chemical Analysis

This research requires measurements of Cu(II) concentration which involved analytical measurement equipment. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) was employed to detect Cu(II) ion in the wastewater. This analytical technique deploys inductively coupled plasma to excite component elements, include atoms and ions. Spectrum rays were emitted when the excited atoms return to the low energy state. The type of element can be analysed based on the photon rays position. The advantages of ICP-OES was simultaneous analysis of multiple elements in the sample.

3.9 Data Analysis

Relative concentration of Cu(II) was determined using Equation 3.2:

$$Relative\ concentration = \frac{C_e(mg/L)}{C_o(mg/L)} \tag{3.2}$$

The efficiency of copper removal was calculated using Equation 3.3:

$$Removal\ efficiency, \% = \frac{C_o - C_e}{C_o} \times 100 \tag{3.3}$$

The adsorption capacity, q (mg/g) was calculated using Equation 3.4:

$$q = \frac{(C_o - C_e)V}{W} \tag{3.4}$$

where: C_o : initial concentration of Cu(II) ions (mg/L)

C_e : the final concentration of Cu(II) ions (mg/L)

V : volume of Cu(II) solution (L)

W : dry weight of resin (g)

Generally, resin regeneration efficiency was calculated using Equation 3.5.

$$Regeneration\ efficiency\ (\%) = \frac{(n)th\ run\ total\ absorption\ capacity(mg/g)}{1st\ run\ total\ absorption\ capacity(mg/g)} \times 100 \quad (3.5)$$

where n = 2, 3, 4, 5…

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

This chapter discussed the factors and parameters affecting the absorption of copper(II) ion onto iminodiacetate acid chelating resin. Isotherm and kinetic studies were also done after analysing the experimental result. From here onwards, the word “wastewater” and “synthetic wastewater” denotes the untreated wastewater or the influent. The word “effluent” denotes the treated wastewater solution.

4.2 Specification and Properties of Cation Exchange Resin

Specific name of resin : Iminodiacetate Chelating Resin
Resin matrix : Styrene divinylbenzene copolymer
Functional group : Iminodiacetate acid
Ionic form as shipped : Na^+
Moisture holding capacity : 55 – 65 %
Total capacity, mmol/ml : ≥ 1.3
Shipping weight, g/L : 700 to 800
Density, g/mL : 1.15 – 1.20
Uniformity coefficient : ≤ 1.7
Particle Size Range, mm : 0.315 to 1.25
Typical Reversible Swelling : $H^+ \rightarrow Na^+$:35 %
Granularity (0.315-1.25 mm) : ≥ 95 %

4.2.1 Recommended Operating Conditions

The manufacturer recommended the following operating conditions:

Maximum operating temperature : 80 ºC
pH range : 2 - 11
Minimum bed depth : 900 mm = 9 cm
Service flow rate : 6 – 32 BV/hr
Regenerant : HCl
Regenerant concentration : 5 - 10%

4.3 Surface Analysis of Resin

4.3.1 Scanning Electron Microscopic (SEM) Image of Iminodiacetate Chelating Resin

The resin images were captured at 3 different magnification (x150, x5,000 and x15,000) using SEM to investigate the difference on the surface of the resin before and after the adsorption of Cu(II) (Figures 4.1, 4.2 and 4.3). Based on Figure 4.3, it was found that the resin before adsorption had significant amount of visible tiny pores. On the other hand, no pores could be seen under the same magnification after adsorption of Cu(II) and it appeared to be saturated with a layer of element, which is Cu(II). This justification was supported by the EDX result which is discussed on the following part.

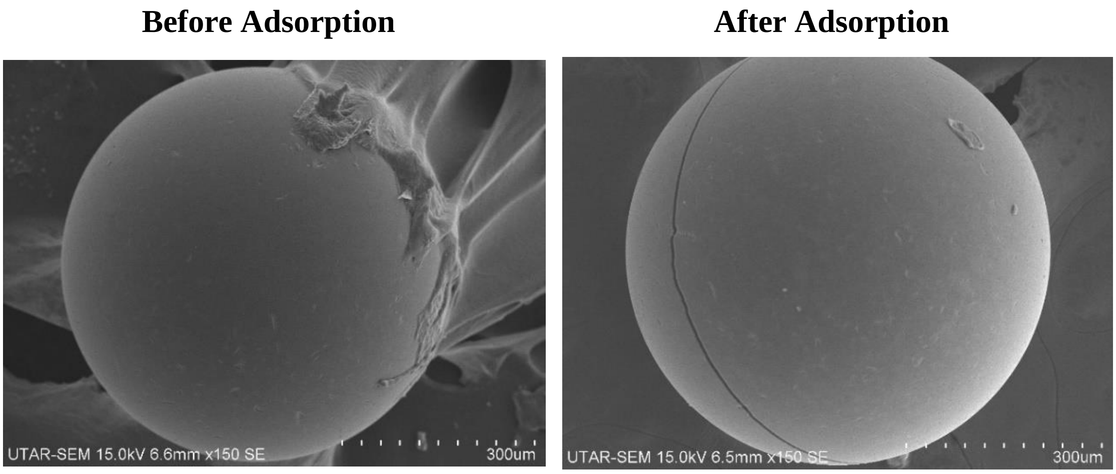

Before Adsorption After Adsorption

Figure 4.1: Iminodiacetate Chelating Resin SEM Image (x150)

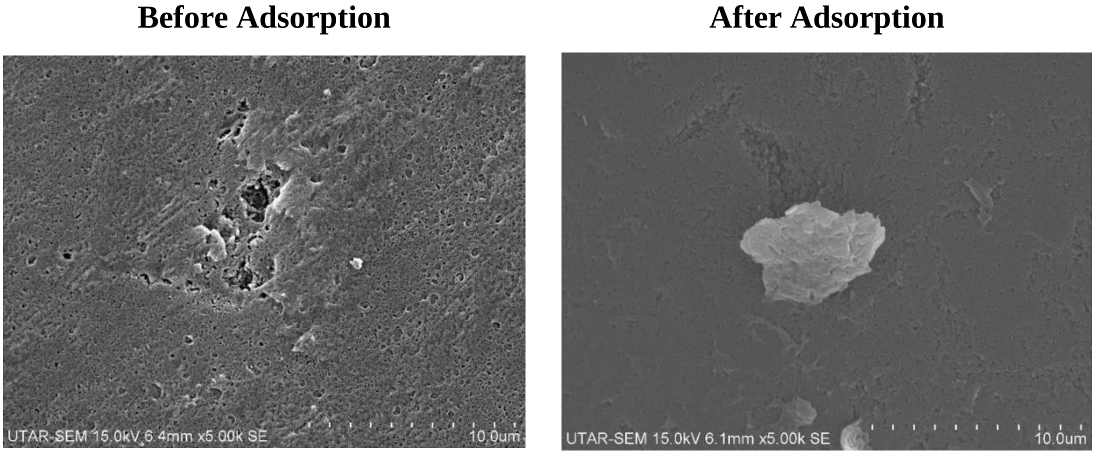

Before Adsorption After Adsorption

Figure 4.2: Iminodiacetate Chelating Resin SEM Image (x5,000)

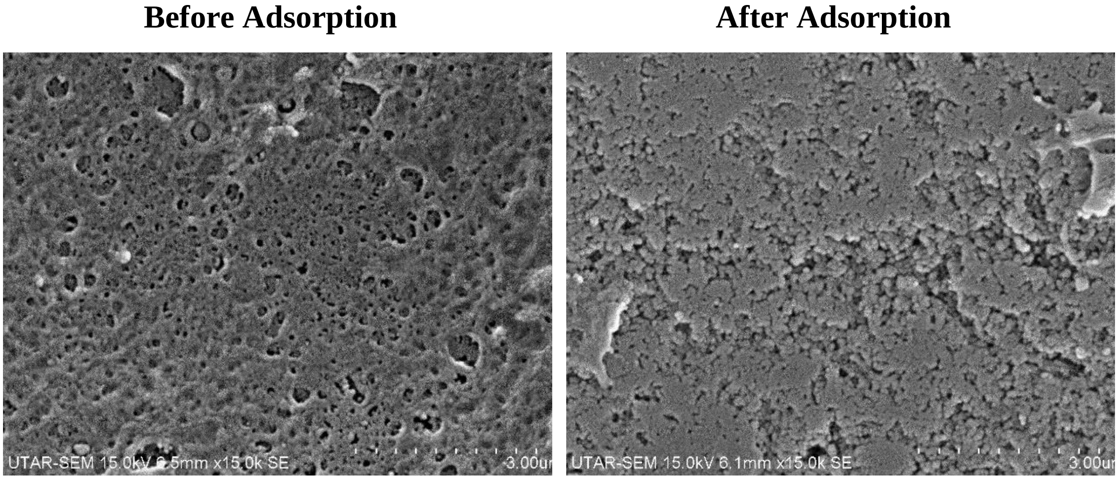
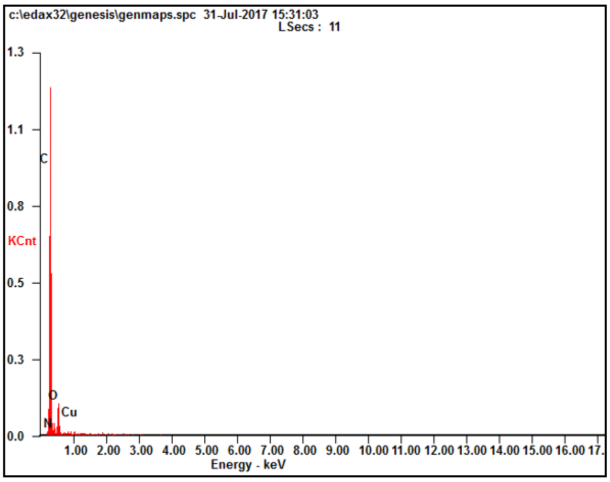

Before Adsorption **After Adsorption**

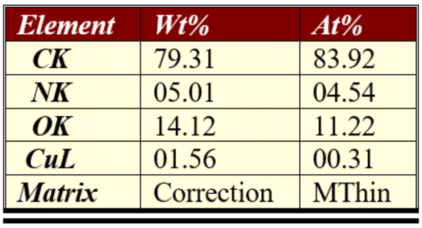
Figure 4.3: Iminodiacetate Chelating Resin SEM Image (x15,000)

4.3.2 Energy-dispersive X-ray Spectroscopy (EDX) Analysis

From the Microanalysis Report through EDX in Appendices 4, as a confirmation, a freshly regenerated resin showed no presence of Cu(II) on the surface. On the other hand, the resin after adsorption exhibit Cu(II) on the surface of the resin. For every iminodiacetate group (consist of single nitrogen ion), 2 hydrogen ions will be replaced by 1 Cu(II) ion during ion exchange process, and hence fulfilling the conservation of charges. In other words, the atomic percentage (At%) of Cu(II) could never exceed At% of N since one iminodiacetate group can hold at most one Cu(II) ion.

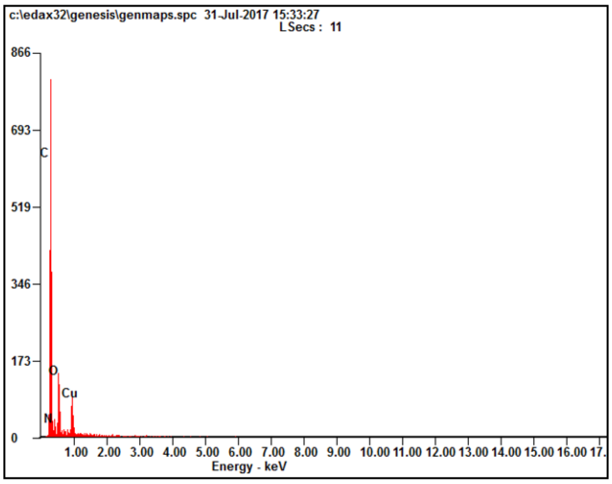
Based on the result for the resin after adsorption, the atomic percentage of N was 5.84% and atomic percentage of Cu(II) was 3.8%. This showed that the resin for that particular surface area was only 65% saturated with Cu(II) and would be further used prior to the regeneration.

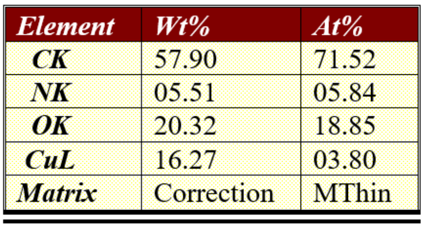




Element	Wt%	At%
CK	79.31	83.92
NK	05.01	04.54
OK	14.12	11.22
CuL	01.56	00.31
Matrix	Correction	MThin

Figure 4.4: EDX Report for Resin Before Adsorption





Element	Wt%	At%
CK	57.90	71.52
NK	05.51	05.84
OK	20.32	18.85
CuL	16.27	03.80
Matrix	Correction	MThin

Figure 4.5: EDX Report for Resin After Adsorption

4.4 Parameter Study

4.4.1 Effect of pH of Synthetic Wastewater

It is known that pH of wastewater will significantly affect the adsorption capability of chelating resin. Synthetic wastewater containing only copper(II) sulfate (ranging from 20 to 100 mg/L Cu) without adding any acid or base was tested to have pH value of 4.8-5.0. The pH of the synthetic wastewater was further adjusted by adding hydrochloric acid (HCl) and sodium hydroxide (NaOH).

4.4.1.1 pH Study by Column Method

The adsorption behaviour of copper on the chelating resin on different pH values was investigated by using both column and batch techniques. Figure 4.6 shows the result of removal efficiency of chelating resin at different pH values using column method. The fixed parameters of the column are tabulated in Table 4.1.

Table 4.1: Fixed Parameter of Column

Parameters	**Unit**	**Value**
Volume of Synthetic Wastewater	mL	1000
Initial concentration of Cu(II)	mg/L	50
Resin Bed Height	cm	10
Flow Rate	mL/min	5

The results from the column test shown that the efficiency of Cu(II) ion absorption increased slightly from pH 1.8-4.8. Despite various pH of the solution, the effluent concentration of Cu(II) ion remained in the range of 1.3 mg/L and showed removal efficiency approximately 97%. This slight difference of Cu(II) concentration in the effluent at different pH possibly due to excessive binding sites of chelating resin inside the column. Hence, the effect of pH was hardly be studied by using column. Batch test were further conducted to study the effect of pH towards adsorption of Cu(II) ion which provides a more significant result than column test.

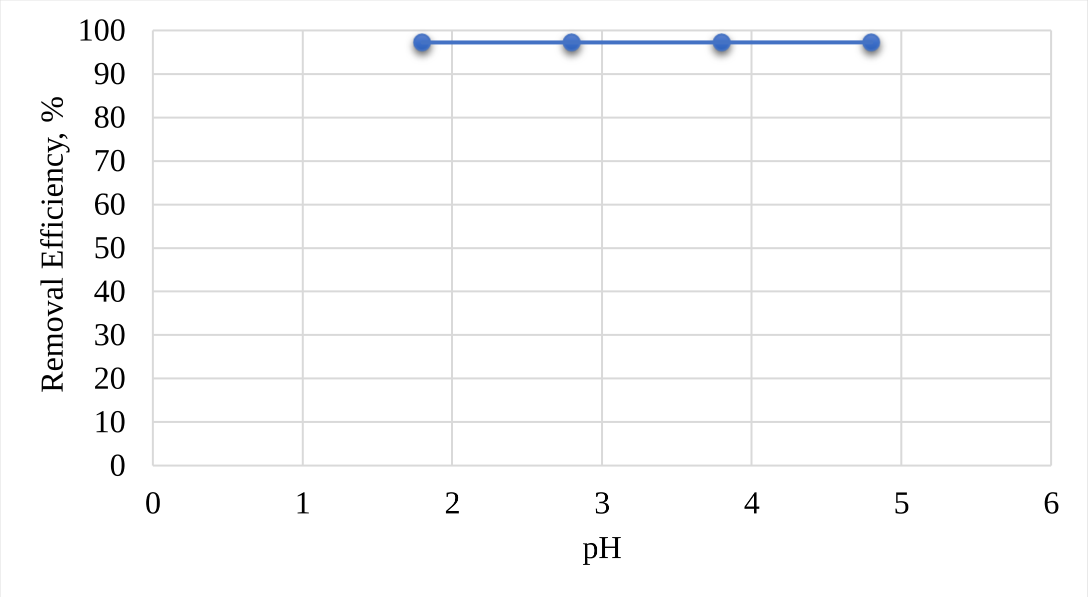


Figure 4.6: Effect of pH on the adsorption of Cu(II) ion using column method

4.4.1.2 pH Study by Batch Method

The adsorption test was performed at a pH value ranging from 1.0 to 9.0 using batch technique. Generally, the study of pH using batch technique showed significant adsorption results. Generally, the uptake of Cu(II) ions increased as the pH value increased due to the dissociation of iminodiacetate group of the resin for the chelation of Cu(II) ion. When the pH of wastewater was low, the hydrogen ion, H^+ concentration was high and easily bound itself to the iminodiacetate group of the resin. In other words, H^+ had the tendency to compete with Cu(II) or other cation for ion exchange sites, resulting in lower adsorption of targeted Cu(II) ion. Thus, at high concentration of H^+, the adsorption capacity of resin towards Cu(II) or any other similar cation decreased.

Results shown that adsorption was significantly low at acidic solution, pH 1 and 2, which may be attributed concentration of H^+ is higher than the Cu(II) ion, eventually competing for ion exchange sites and hinder the chelation of Copper. The optimum pH for Cu(II) adsorption was observed at pH 5-7 (slightly acidic-neutral), in which maximum adsorption capacity was found. It was observed that an increase of adsorption capacity at pH 9 might be due to the precipitation of hydroxide ion, OH^- thus forming insoluble copper(II) hydroxide precipitate which sank to the bottom of the effluent. The insoluble copper(II) hydroxide cannot be adsorbed by chelating resin as it uses the fundamental of ion exchange for adsorption, but not physical adsorption. However, insoluble precipitate can be removed by using other technique such as filtration. Any higher pH will also have resulted in formation of insoluble copper(II) hydroxide, which shows lower concentration of Cu(II) in the effluent, not due to the adsorption from the resin, but due to formation of precipitate. Therefore, based on the result from pH test, the optimum pH value found for Copper adsorption is 5-7. All following test were conducted at optimum pH ranges.

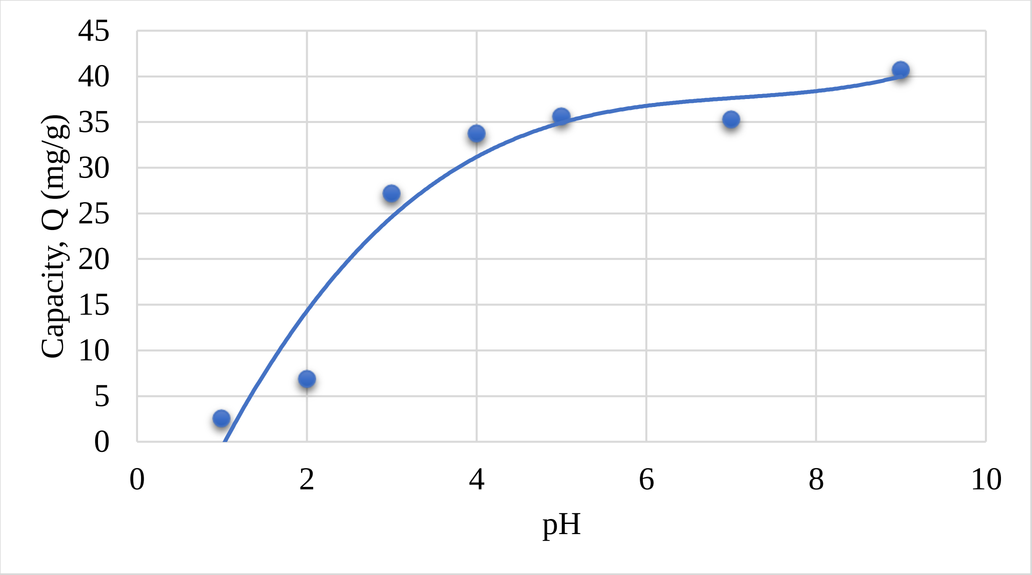


Figure 4.7: Adsorption capacity of resin at various pH

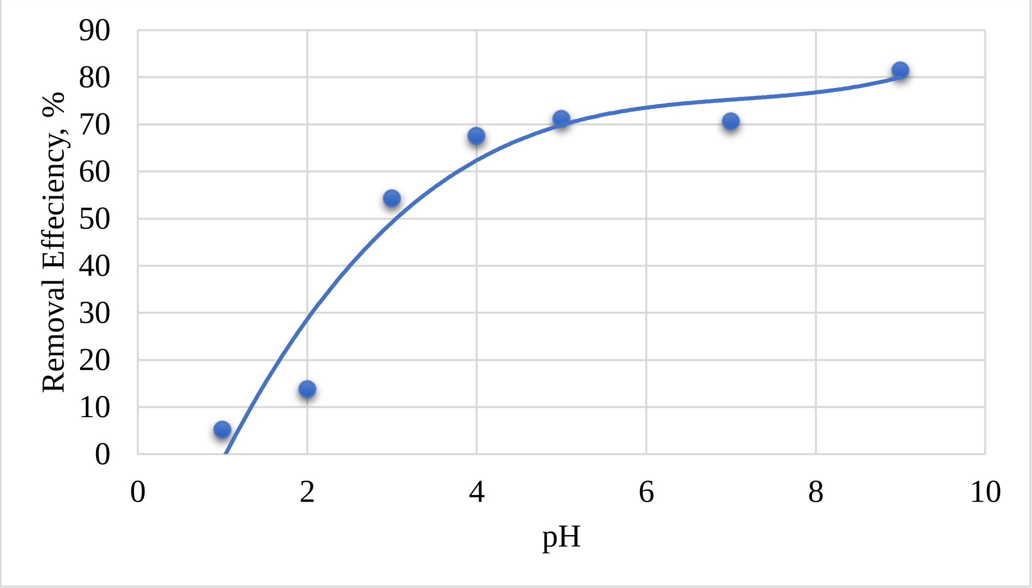


Figure 4.8: Effects of pH on the adsorption of Cu(II) ion using batch method

The effectiveness of Cu(II) adsorption was also been notified through the colour gradient of the resin (Figure 4.9). For wastewater at pH 2, the resin showed very light blue colour indicating low Cu(II) content on the surface. For wastewater at pH 6, on the other hand, showed darker blue colour, indicating higher Cu(II) content on the resin surface.

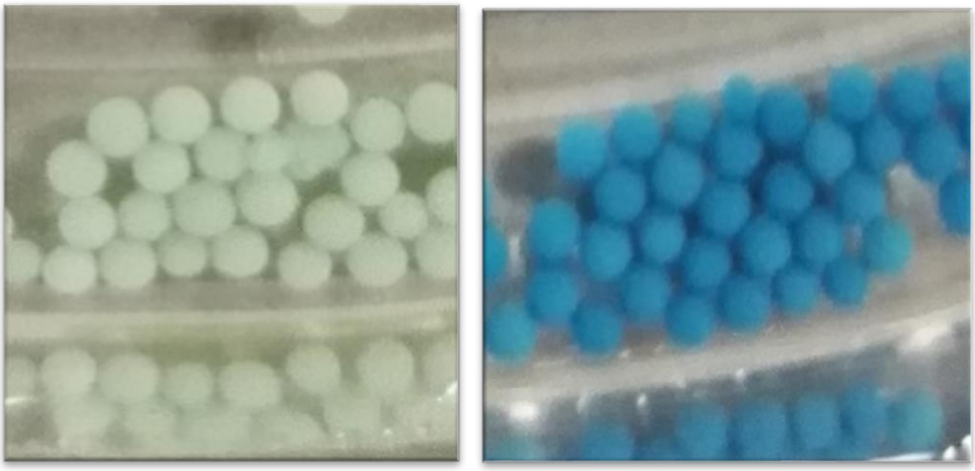


Figure 4.9: Comparison of resin colour at pH 2 (left) and pH 6 (right)

4.4.2 Effect of Initial Concentration of Synthetic Wastewater

Different initial Cu(II) concentrations shows different equilibrium adsorption capacities of the resin. It was found that the equilibrium adsorption capacity increased when initial Cu(II) concentration increased (Figure 4.10). Nevertheless, when the initial concentration reached the saturation capacity of the resin, further increase in the Cu(II) concentration, however, no longer improved the resin’s adsorption capacity. Thus, the highest achievable adsorption capacity of the chelating resin was observed when initial concentration of Cu(II) was at 80 mg/L, where the adsorption capacity reached 46.6 mg Cu(II)/ g resin. We need to identify the capacity of the resin, in order to determine the amount of the resin needed to effectively adsorb the Cu(II) ion from the wastewater quantitatively.

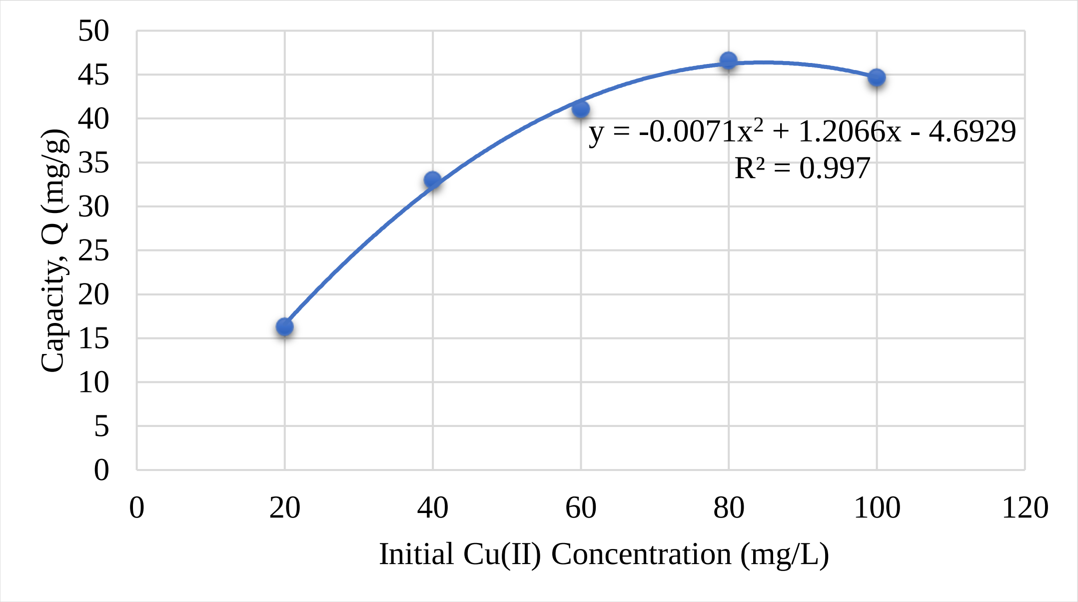


Figure 4.10: Effect of Initial Cu(II) Concentration on the Adsorption of Cu(II) Ion Using Batch Method

4.4.3 Effect of Resin Bed Height

Basically, the effect of resin bed height was investigated by using Cu(II) synthetic wastewater with optimal pH value of 5 and optimal concentration of 80 mg/L, as illustrated in Figure 4.11. It was found that Cu(II) concentration in the effluent was 5.34 mg/L when the column bed height was at 2.5 cm. The reason behind the breakthrough of Cu(II) was possibly due to insufficient/limited ion exchange site for Cu(II) adsorption. Instead, when the bed height was 5 cm and above, no significant breakthrough of Cu(II) was identified. This was probably due to availability of sufficient or excessive resin, providing a greater adsorption capacity as a whole for the adsorption of Cu(II).

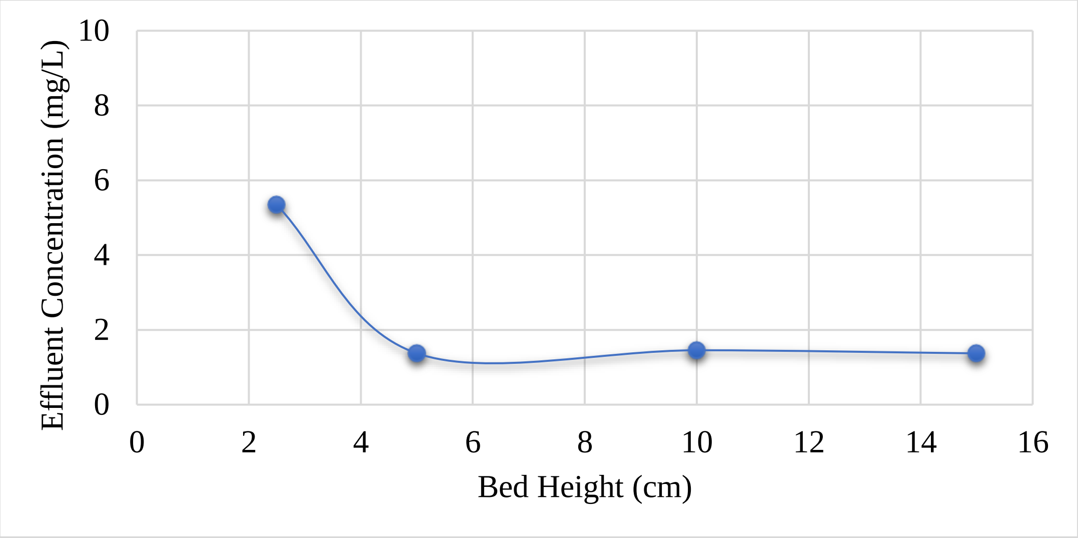


Figure 4.11: Effect of Column Bed Height on the Adsorption of Cu(II) Ion

4.4.4 Effect of Flowrate of Synthetic Wastewater

The effect of flowrate was studied at optimal operating conditions, where pH = 5, initial copper concentration = 80 mg/L, and bed height = 5 cm. It was reported that the wastewater flowrate had a relatively linear correlation (Figure 4.12).Generally, the concentration of Cu(II) in the effluent increased with increasing flowrate. This may be due to the fact that, when the flowrate is high, the contact time is shorter which reduces the efficiency of the adsorption/ ion exchange process. In other words, Cu(II) ion might straight away slipped through the gap within the resin beads due to high flow velocity. When the flowrate was at 5 mL/min, only insignificant amount of Cu(II) (1.3 mg/L) leaked through the resin bedThus, 5 mL/min was selected to be the optimal flowrate.

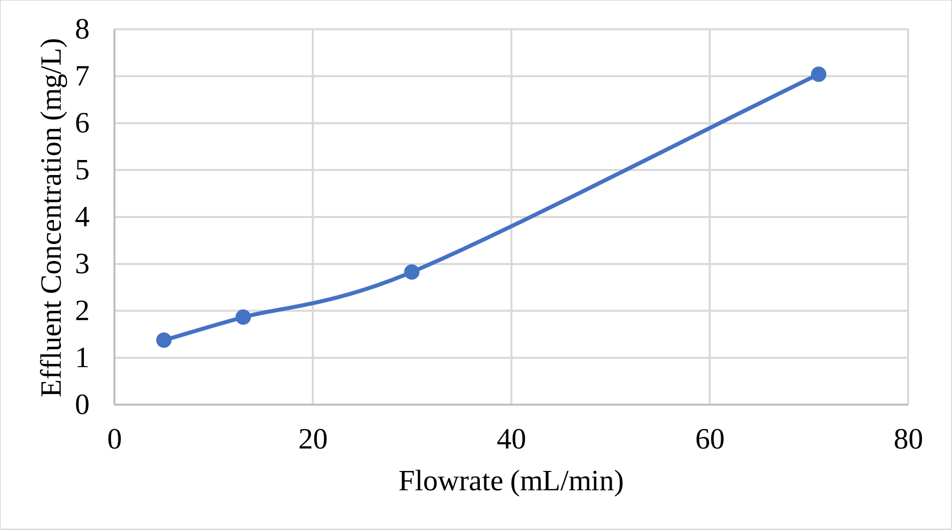


Figure 4.12: Effect of Wastewater Flowrate on the Adsorption of Cu(II) Ion

4.5 Adsorption Isotherms

As a part of current research, the adsorption isotherms were analysed by using Langmuir and Freundlich adsorption models.

4.5.1 Langmuir Isotherm

In Langmuir adsorption model, it is assumed that the surface of resin is homogeneous and all sites have equivalent binding force. It is also assumed that each site can only bind at most a single metal ion. Hence, the Langmuir adsorption model predicted that the adsorbate will be formed at the resin surface as a single layer, also known as monolayer coverage.

Langmuir adsorption model is formulated as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{KQ_m}$$

where:

C_e : Equilibrium concentration of metal ion (mg/L)

q_e : Equilibrium Adsorption capacity (mg Cu(II)/ g resin)

Q_m : Maximum adsorption capacity (mg Cu(II)/ g resin)

K : Langmuir constant

Langmuir equation can be expanded as a linear graphical equation, where:

$$\frac{C_e}{q_e} = \left(\frac{1}{Q_m}\right) C_e + \frac{1}{KQ_m}$$

$$y \;=\; m \quad x + \;\; c$$

From there, a graph of $\frac{C_e}{q_e}$ versus C_e was plotted in Figure 4.13, a straight line was obtained from the plot which indicated the adsorption of Cu(II) by iminodiacetate resin fits to Langmuir adsorption model. Thus, both Q_m and K values were obtained from the straight line's gradient and intercept, respectively.

Calculation of Q_m and K:

Gradient: $$0.02 = \frac{1}{Q_m}$$

$$\boldsymbol{Q_m = 50\ mg/g}$$

Intercept: $$0.0968 = \frac{1}{KQ_m}$$

$$0.0968 = \frac{1}{K(50)}$$

$$\boldsymbol{K = 0.20661}$$

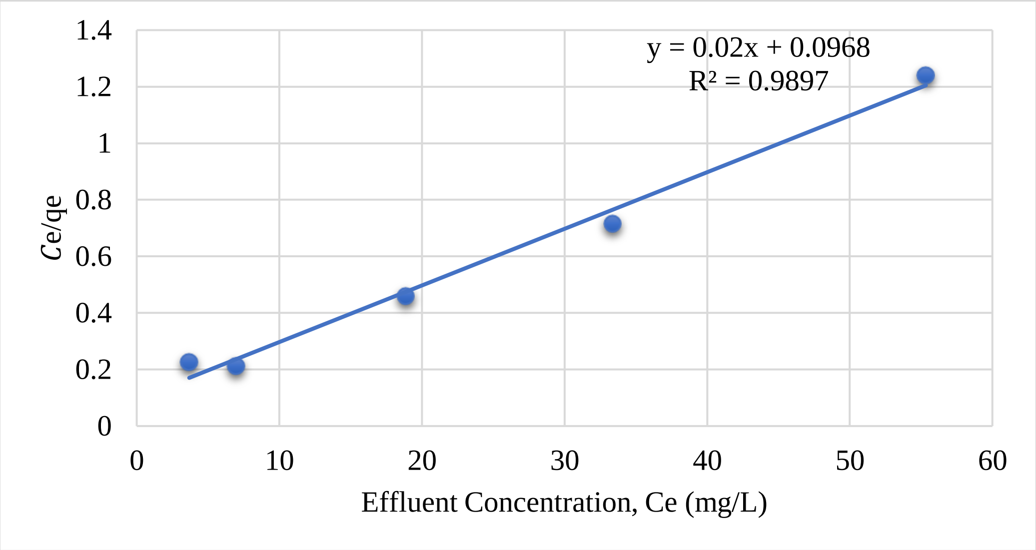


Figure 4.13: Plot of Linearized Langmuir Isotherm Model

The favourability on adsorption of copper using chelating resin was identified from a constant separation factor (R_{ads}). The equation of R_{ads} is expressed as follows:

$$R_{ads} = \frac{1}{1 + KC_o}$$

where,

K : Langmuir Constant (obtained from Y-intercept)

C_o : Initial concentration of Cu(II) (mg/L)

The Cu(II) adsorption using chelating resin is unfavourable when R_{ads} <1, linear when R_{ads} = 1, favourable when 0 < R_{ads} <1, and irreversible when R_{ads} = 0. The values of R_{ads} were calculated for all initial concentrations as shown in Table 4.2. It was proved that all R_{ads} values were found between 0 and 1, indicating the high favourability of resin for Cu(II) adsorption.

A graph of R_{ads} versus initial concentration has been plotted in Figure 4.14. It was shown that when the initial concentration of Cu(II) increased, the value of R_{ads} will decreased. This result showed that adsorption of Cu(II) was more favourable when the concentration of Cu(II) was higher.

Table 4.2: Parameters for Langmuir Isotherm

Langmuir Isotherm Model				
Initial concentration (mg/L)	***Final Concentration (mg/L)***	***Q (mg/g resin)***	***C_e/q_e***	***Constant Separation Factor, R_{ads}***
20	3.6840	16.3159	0.2257	0.1948
40	6.9753	33.0246	0.2112	0.1079
60	18.8853	41.1146	0.4593	0.0746
80	33.3820	46.6179	0.7160	0.0570
100	55.3318	44.6681	1.2387	0.0461
				0 < R_{ads} <1

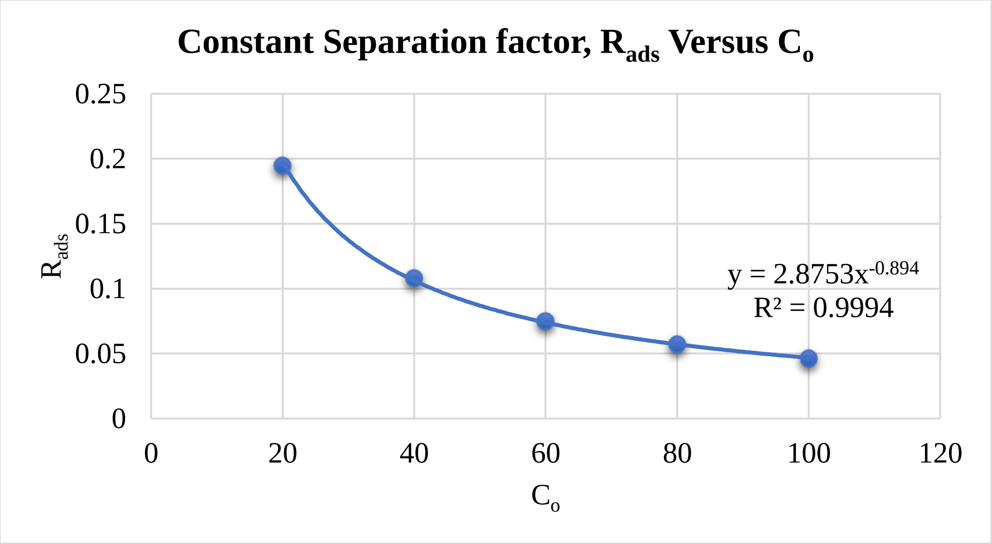


Figure 4.14:Plot of R_{ads} Versus Initial Concentration, C_o

4.5.2 Freundlich Isotherm

Another empirical model which is the Freundlich isotherm was fitted by the adsorption of copper. The Freundlich isotherm assumes multilayer adsorption on the surface of the adsorbent which differs from Langmuir assumptions of single layer adsorption.

The Linearized Freundlich equation can be expressed as follows,

$$\log q_e = n \log C_e + \log K_f$$

where,

C_e : Equilibrium concentration of metal ion (mg/L)

q_e : Equilibrium adsorption capacity (mg Cu(II)/ g resin)

K_f : Freundlich constant

n : Adsorption effectiveness

A graph of log q_e versus log C_e was plotted in Figure 4.15 and, thus the value of n and K_f can be identified from the gradient and the intercept, respectively.

Gradient, n : 0.3445

Intercept : $1.1226 = \log K_f$

$K_f = 13.26$

The value of n indicates the adsorption is unfavourable when $n > 1$, favourable when $0 < n < 1$, and irreversible when $n = 0$. The n value found in this study was suggesting constructive Freundlich model adsorption.

Table 4.3: Parameters for Freundlich Isotherm

Freundlich Isotherm Model				
Initial concentration (mg/L)	***Final Concentration (mg/L)***	***Q (mg/g resin)***	***Log q_e***	***Log C_e***
20	3.6840	16.3159	1.2126	0.5663
40	6.9753	33.0246	1.5188	0.8435
60	18.8853	41.1146	1.6139	1.2761
80	33.3820	46.6179	1.6685	1.5235
100	55.3318	44.6681	1.6499	1.7429

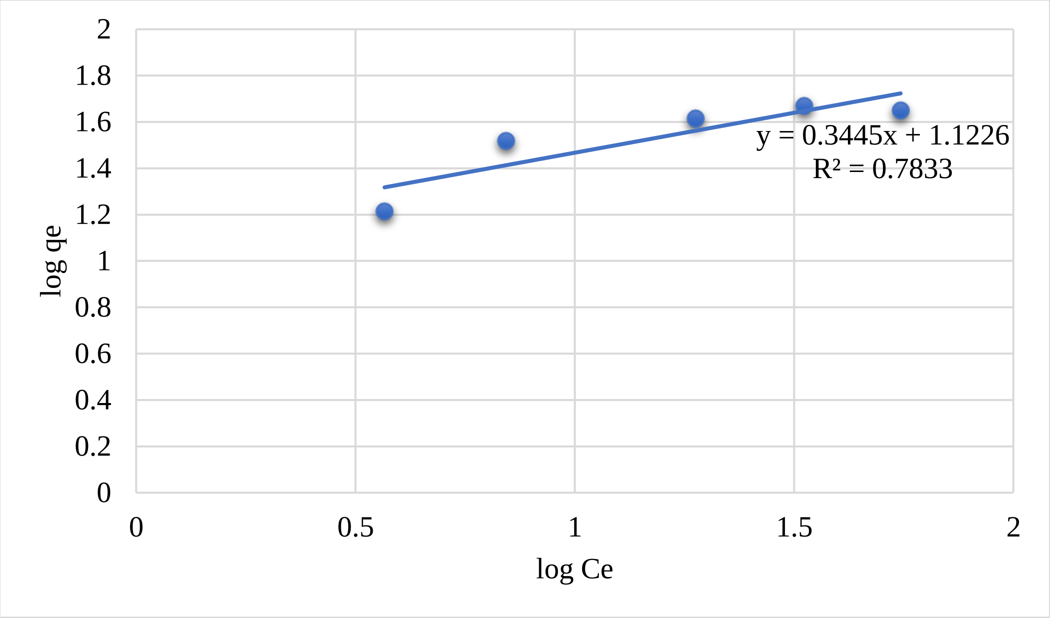


Figure 4.15: Plot of Linearized Freundlich Isotherm Model

The comparison between two isotherms models was summarized in Table 4.4, including respective isotherm constant and correlation coefficients, R^2. To find the most appropriate isotherm model, the experimental data had been fitted into both isotherm models was concluded that the Langmuir adsorption model with R^2 value of 0.9897 served as the best model for adsorption of Cu(II) ion onto iminodiacetate resin.

Table 4.4: Comparison of Isotherm Model

	Langmuir Isotherm	**Freundlich Isotherm**
Isotherm Constant, *K*	0.2066	13.26
Correlation coefficient, R^2	0.9897	0.7833

4.6 Adsorption Kinetics

The maximum uptake was found at shacking time of 330 minutes. The adsorption capacity of resin at different shaking time was shown in Figure 4.16. The initial adsorption rate was high due to large amount of vacant ion exchange sites available for adsorption, and most of the adsorption process took place on the resin surface.

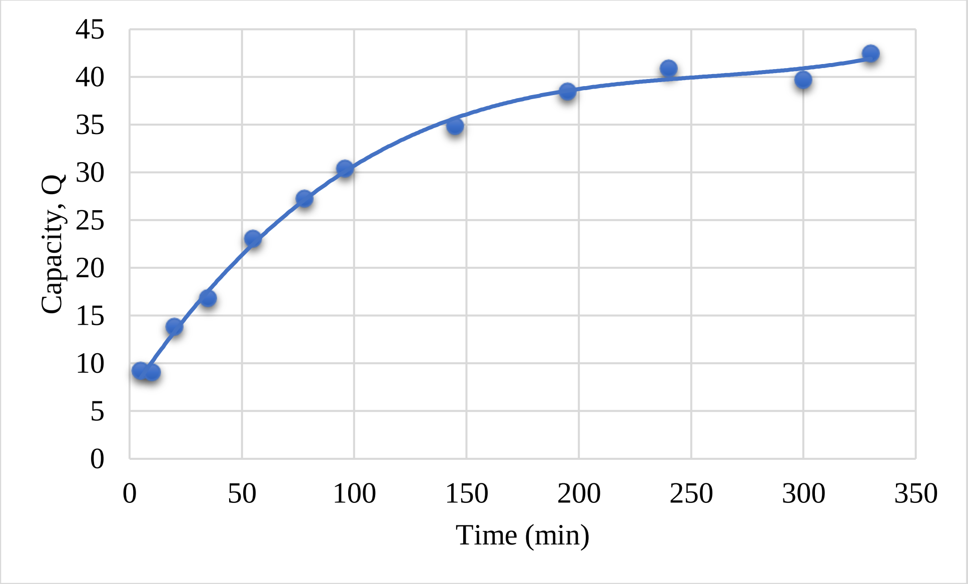


Figure 4.16: Adsorption Capacity at Different Shaking Time

4.6.1 Pesudo-first-order

Kinetic model such as Pseudo-first-order was used to assess the experimental data for adsorption capacity at different shaking time. The equation of pseudo-first-order kinetic can be expressed as follows:

$$\log(q_e - q_t) = log q_e - \left(\frac{K}{2.303}\right) t$$

where,

K : Overall rate constant

A graph was plotted taking log (q_e-q_t) as y-axis and time (min) as x-axis.

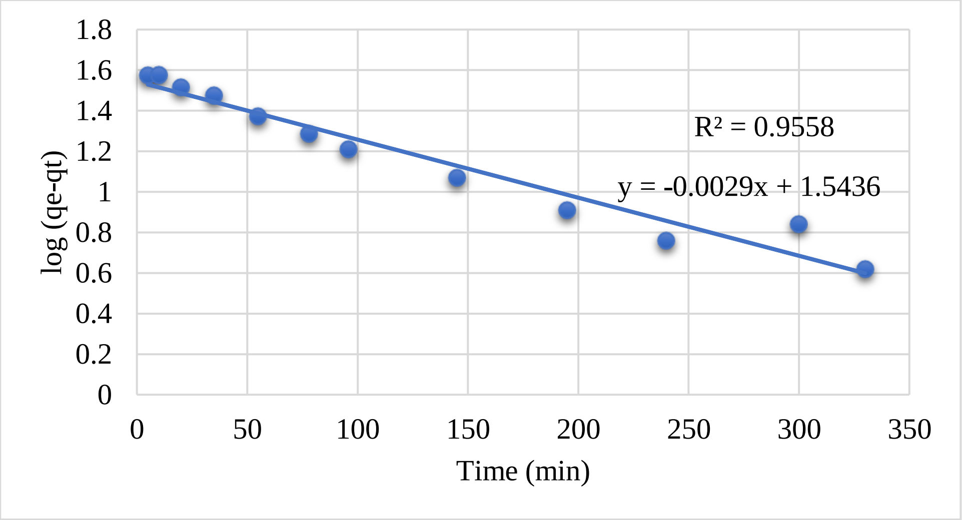


Figure 4.17: Plot of Pseudo-first-order

4.6.2 Pseudo-second-order

The kinetic model of pseudo-second-order equation can be formulated as follows,

$$\frac{t}{q_t} = \frac{1}{K_s q_e^2} + \left(\frac{1}{q_e}\right) t$$

where,

K_s : Overall rate constant

A graph was plotted taking t/q_t as y-axis and time (min) as x-axis in Figure 4.18. A nearly straight-line plot was obtained.

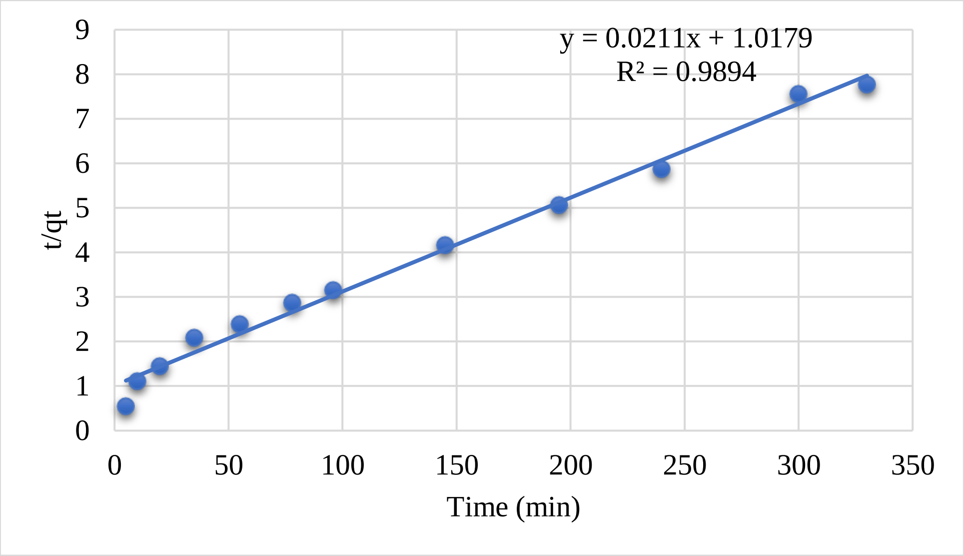


Figure 4.18: Plot of Pseudo-second-order

Both pseudo-first and second-order kinetic models showed approximately straight lines and high correlation coefficients. However, the pseudo-second-order had a correlation coefficient of 0.9894 which was slightly higher than pseudo-first-order of 0.9558. So, it was more appropriate to conclude that adsorption of Cu(II) by resin fulfiled the kinetic model of pseudo-second-order kinetic model.

4.6.3 Intraparticle Diffusion

The behaviour of resin adsorption was also investigated through intraparticle diffusion. The equation for intraparticle diffusion is expressed as follows:

$$q_t = k_{id} t^{0.5}$$

where,

k_{id} : Constant of intraparticle diffusion rate

If plotting a graph of q_t versus $t^{0.5}$ shows a straight line, it indicates that the adsorption is limited by intraparticle diffusion. However, from Figure 4.19, it did not show a near perfect straight line, suggesting that there were multiple factors affecting the adsorption process. Hence, it can be concluded that the adsorption process was rapid at initial stage due to high amount of binding site on the resin’s surface, followed by fair adsorption by intraparticle diffusion.

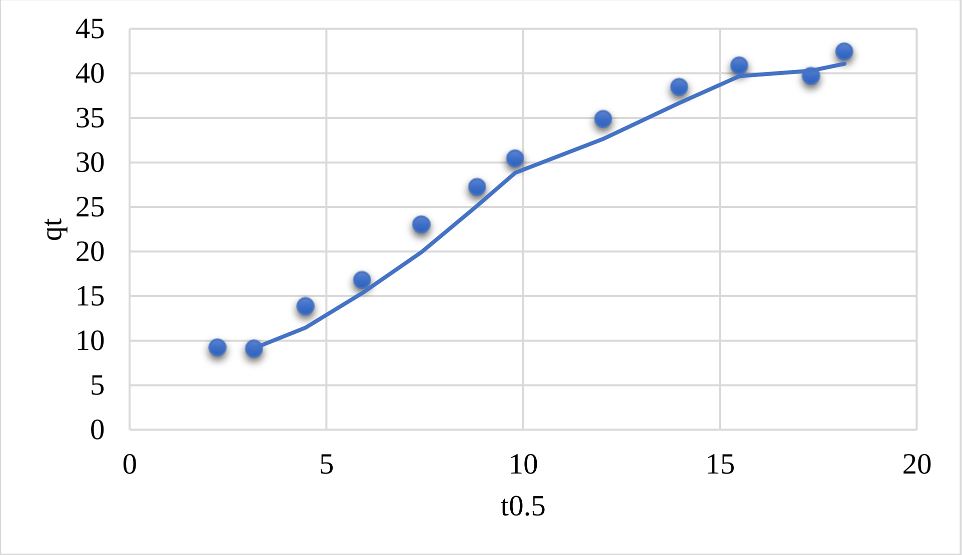


Figure 4.19: Plot of Intraparticle Diffusion

4.7 Durability Test

The resins were regenerated using 10% HCl after each servicing cycle. The percentage of adsorption capacity is a measure of durability of the iminodiacetate resin. The Cu(II) adsorption and HCl elution process were repeated 4 times to investigate the adsorption capacity percentage after each regeneration cycle. It was shown that the adsorption capacity of the resin decrease after each consecutive regeneration cycle (Figure 4.20). The decrease was possibly attributed to the to formation of stable copper-to-resin complex. It might be also due to insufficient HCl concentration to completely elute the exhausted resin. Based on the result, it was reasonable to conclude that iminodiacetate chelating resin demonstrated good durability and was suitable for use after multiple regeneration cycle without significantly compromising its adsorption capability.

However, these resins should have a higher durability according to the manufacturer. So, the adsorption capacity percentage of the resin should be higher than 80% after the fifth cycle. The main reason for the great decrease in adsorption capacity percentage in this study was due to the channelling of H^+ ions during the regeneration as the resin bed was very thin. It might also be due to insufficient concentration H^+ in the regenerant which was unable to knock-off the Cu(II) attached to the resin.

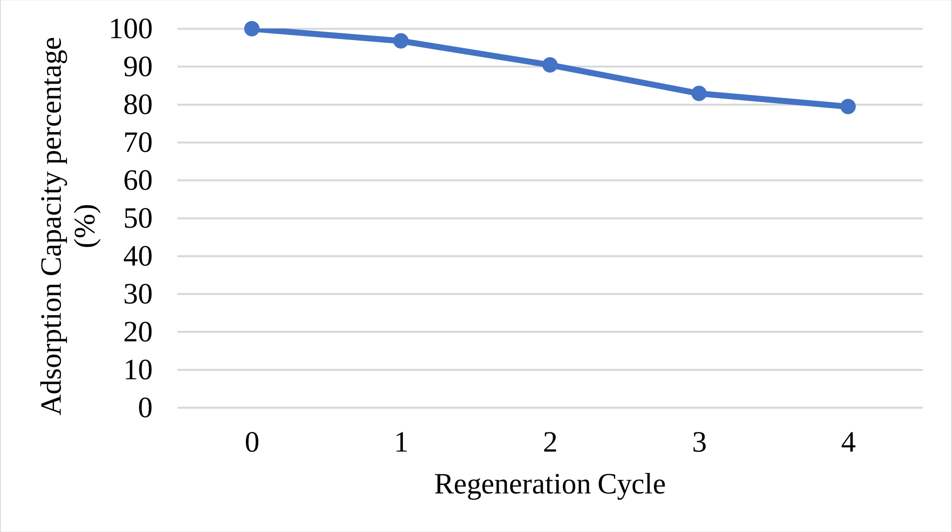


Figure 4.20: Adsorption Capacity Percentage After Several Regeneration Cycles

4.8 Industrial Wastewater Treatment under Optimal Conditions

The industrial wastewater was collected from a air-conditioner manufacturing company. It was found that the wastewater contained 0.48 mg/L of Cu(II). After adsorption by iminodiacetate chelating resin under optimal conditions, the concentration of Cu(II) was reduced to 0.077 mg/L in the first cycle and 0.064 mg/L in the second cycle.

4.9 Cost Analysis

Cost analysis was performed to determine the feasibility of using iminodiacetate resin for wastewater treatment in industrial scale.

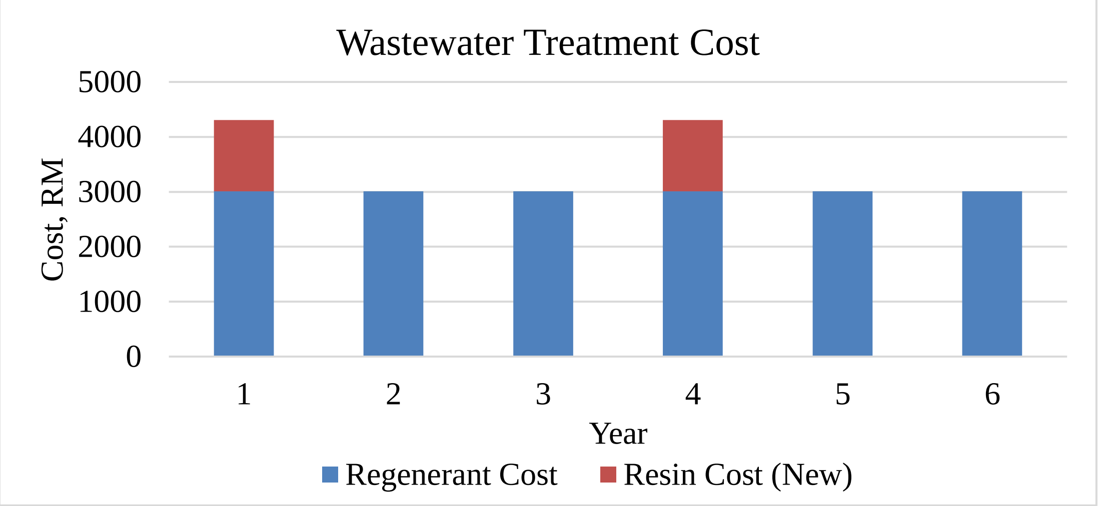
Table 4.5: General Information for Cost Analysis

	Unit	***Value***
Price of resin	RM/L	50.00
Price of Regenerant (HCl, Industrial Grade)	RM/ kg	2.50
Density of resin	g/mL	1.20
Wastewater production rate	m^3/day	20.00

Theoretically, considering only removing Cu(II) from industrial wastewater, the resin only need to be regenerated every 6 months. However, there were many other trace metal or elements present in the industrial wastewater which are not identified in this research and were not included and considered in this calculation. So, it is highly possible resin exhaustion will occur at an earlier duration (<< 6 months) due to adsorption of many other types of ion. Practically, in industrial practice, resin was regenerated as soon as once per day to ensure high removal quality, according to the wastewater treatment company. After calculations, the cost for the air-conditioner manufacturing factory was roughly at RM 3,000-RM 4,200. The higher cost during the first and fourth year was due to the extra cost for replacing the old resin with a new batch of resin. The remaining cost is contributed by the regenerant, HCl for resin regeneration.

Note: Detailed calculation shown in Appendix 1

Table 4.6: Summary of Wastewater Treatment Cost



CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

From this research, it is appropriate to conclude that iminodiacetate chelating resin is suitable for the removal of Cu(II) from synthetic and industrial wastewater. According to the batch method, the optimal pH for the adsorption of Cu(II) was found to be in the range of pH 5-7. Besides, the adsorption of Cu(II) by the resin increased with increasing initial concentration until it reached the saturation adsorption capacity. The total adsorption capacity increased with increasing bed height as a result of more ion exchange sites for the adsorption of Cu(II). The leakage of Cu(II) increased with increasing flowrate, or shorter contact time between Cu(II) and the resin.

Isotherm studies have been performed by fitting equilibrium data into both Langmuir and Freundlich isotherm models. The result indicated that Langmuir isotherm was the best isotherm model to be fitted to the experimental data, with higher correlation coefficient (R^2) of 0.9897. Furthermore, the pseudo-second-order served as the best kinetic model to explain the adsorption of Cu(II) using iminodiacetate chelating resin.

Durability test showed slight decrease in adsorption capacity percentage after multiple adsorption and regeneration cycle, probably due to the formation of stable copper-resin complex. In the nutshell, the results obtained through this research is decent and it is appropriate to confirm that iminodiacetate chelating resin is a highly efficient adsorbent to remove Cu(II) from wastewater.

5.2 Recommendations

Despite the finding that the iminodiacetate chelating resin demonstrated high Cu(II) removal efficiency, it can only be able to remove ions. Suspended solids such as precipitate, sludge, organic compound cannot be removed using ion exchange resin. So, it is highly recommended to perform pre-treatment such as filtration to remove suspended solid, then only proceed to heavy metal ion removal. Without the removal of suspended solids, the resin bed will likely be blocked by the suspended solid, resulting in low ion exchange adsorption performance.

Besides, flow rate meter can be installed to accurately control the flowrate of the wastewater during the column test, rather than depending solely on the degree of tap opening to control the flowrate which may be easily disorientated during the experiment.

Another recommendation is the addition of complexing agent Ethylenediaminetetraacetic acid (EDTA) into the synthetic wastewater. The addition of complexing agent will form Cu(II) complex and may affect the adsorption efficiency of the resin. So, it is worth to further study the behaviour of adsorption by the resin in the presence of complexing agent.

For advanced research, vessel design for wastewater treatment plant can be performed such as designing small or large-scale ion exchange column and the adsorption efficiency of the resin can be maximized through the column design. The height and internal diameter of the resin bed will affect the adsorption process, and thus the vessel design can be a part of extension from current study.

Last but not least, apart from Cu(II), iminodiacetate chelating resin can be further used to study the adsorption of other metal ions such as lead, chromium, nickel etc which are also commonly found in industrial wastewater. Iminodiacetate chelating resin has different affinity towards different types of metal ions, and different metal ions have different precipitation limit in terms of pH. So, the adsorption behaviour and optimal conditions using iminodiacetate chelating resin will be different for different types of metal ions.

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APPENDICES

Appendix 1: Sample Calculation

Sample calculation for Cost Analysis:

Several required values were obtained from the Resin's product specification and data provided by the wastewater treatment company's engineer:

	Unit	***Value***
Price of resin	RM/L	50.00
Price of Regenerant (HCl) Industrial Grade	RM/ kg	2.50
Density of resin	g/mL	1.20
Wastewater production rate	m^3/day	20.00

Assuming the concentration of Cu(II) in the industrial wastewater is constantly produced at 0.48 mg/L throughout the duration of service, and the concentration of Cu(II) for the treated wastewater is 0.064 mg/L.

We also assume all resin capable of achieving maximum adsorption capacity of 50 mg/g investigated during the research.

Computing the Bed Volume (BV) required:

According to product specification, suggested service flow rate is at 6-32 BV/hr. Assume 32 BV/hr,

Wastewater production rate:

$$20\,\frac{m^3}{day}\times\frac{1000\ L}{1\ m^3}\times\frac{1\ day}{24\ hrs}=833.33\,\frac{L}{hr}$$

Volume of resin required:

(Assume 32BV/hr)

$$\frac{833.33\ L}{hr}\times\frac{hr}{32BV}=26.04\ L\ of\ resin$$

Weight of resin required:

(Unit conversion)

$$26.04L \times \frac{1000\ mL}{L} \times \frac{1.2\ g}{mL} = 31{,}248\ g\ of\ resin$$

Adsorption of Cu(II) per litre wastewater:

$$0.48\frac{mg\ Cu(II)}{L} - 0.064\frac{mg\ Cu(II)}{L} = 0.416\frac{mg\ Cu(II)}{L}$$

Adsorption of Cu(II) per hour:

$$\frac{0.416\ mg\ Cu(II)}{L} \times \frac{833.33\ L}{hr} = 346.665\frac{mg\ Cu(II)}{hr}$$

Total capacity of resin for adsorption of Cu(II):

(Assume all resin achieved maximum capacity of 50 mg Cu(II)/ g resin)

$$31{,}248\ g\ resin \times \frac{50\ mg\ Cu(II)}{g\ resin} = 1562400\ mg\ Cu(II)$$

Time required upon resin exhaustion:

$$\frac{1{,}562{,}400\ mg\ Cu(II)}{346.665\ mg\ Cu(II)/hr} = 4{,}506\ hours = 187.78\ days \approx 6\ months$$

However, there are many other trace metal or elements present in the industrial wastewater which are not identified in this research and were not included and considered in this calculation. So, it is highly possible resin exhaustion will occur at an earlier duration (<< 6 months) due to adsorption of many other types of ion. Practically, in industrial practice, resin is regenerated as soon as once per day to ensure high removal quality, according to the wastewater treatment company.

According to product specification, regenerant required is 140 g of 33% HCl per L of resin.

Weight of HCl, regenerant required everyday:

(Assume resin regeneration is performed daily)

$$26.04\ L\ resin \times \frac{140\ g\ HCl}{L\ resin} = 3645.6\ g\ HCl = 3.6456\ kg\ HCl/day$$

Cost of regenerant daily:

$$\frac{RM2.50}{kg\ HCl} \times 3.6456\ kg\frac{HCl}{day} = RM\ 9.11/day$$

Cost of regenerant annually:

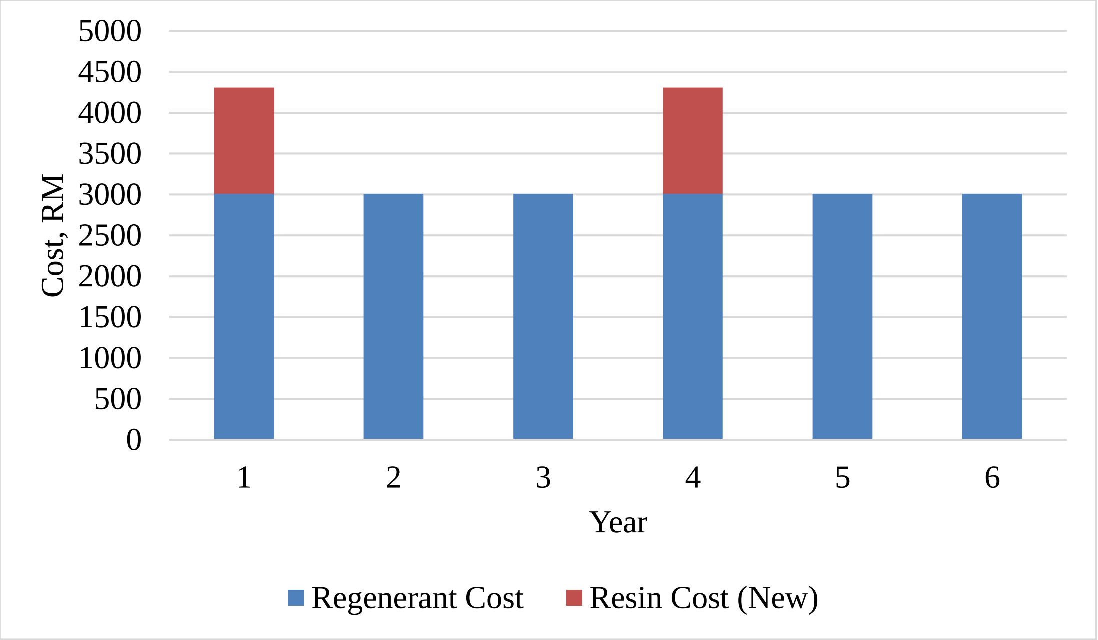
(Assume 330 working days)

$$\frac{RM\ 9.11}{day} \times \frac{330\ days}{year} = RM3006.30/year$$

Cost of resin per batch (subjected to adsorption and regeneration cycle of 900 cycles (approximate 3 years) before replacing with a new batch)

$$26.04\ L\ resin \times \frac{RM50.00}{L\ resin} = RM1302.00$$

Year	Type of cost	Cost, RM
1	New batch of resin + regenerant	RM 4308.30
2	Regenerant	RM3006.30
3	Regenerant	RM3006.30
4	New batch of resin + regenerant	RM 4308.30
5	Regenerant	RM3006.30
6	Regenerant	RM3006.30



Appendix 2: Photos of Laboratory Equipment Set Up

Photo 1: Set up using glassware provided from lab

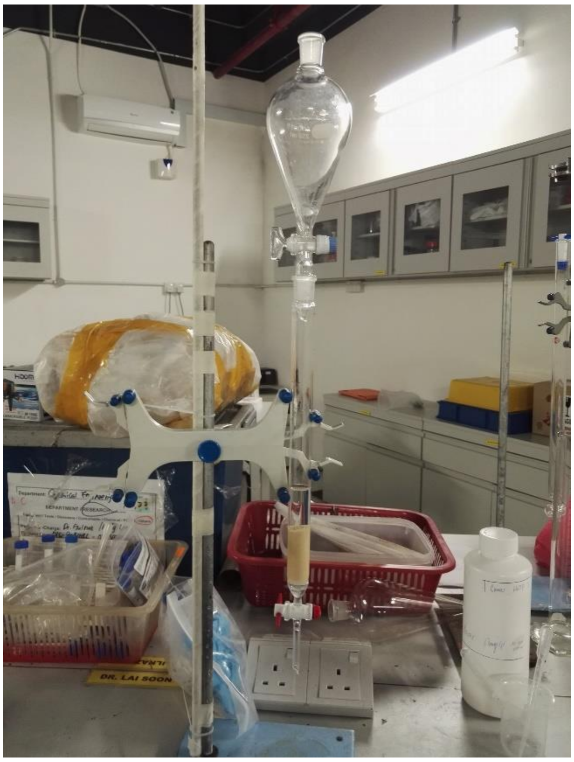


Photo 2: Set up using glassware provided by i-Chem Solution Sdn. Bhd

Photo 3: Chromatography column during adsorption of Cu(II)

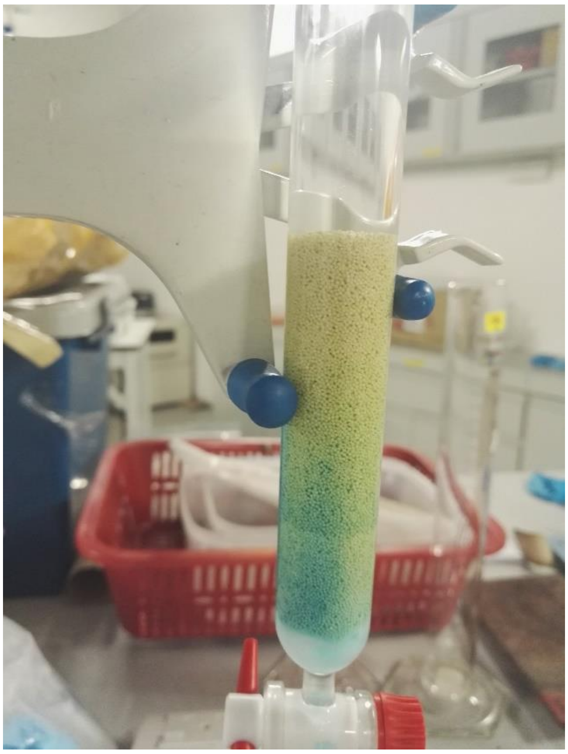


Photo 4: Chromatography column during regeneration

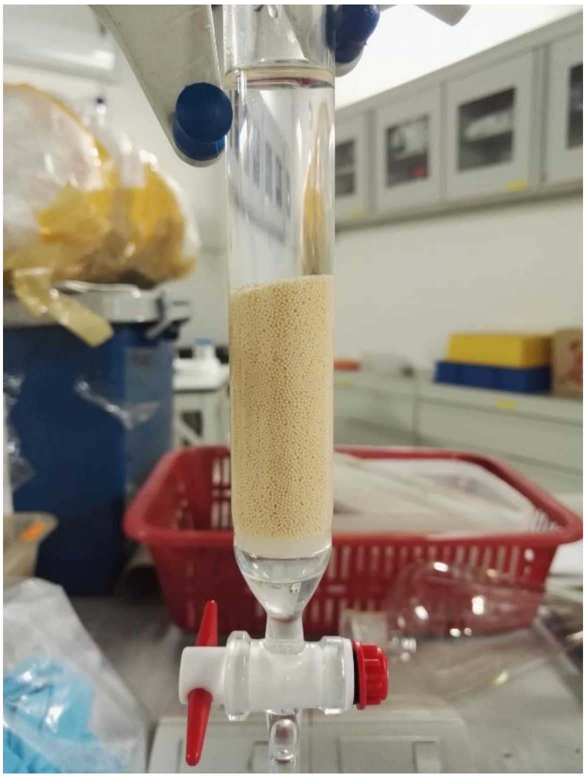


Photo 5: Freshly regenerated resin

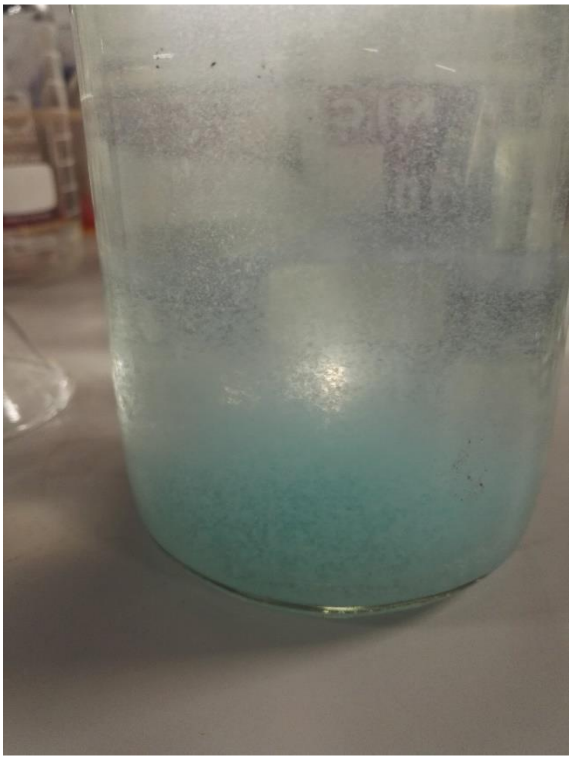


Photo 6: Formation of Copper (II) hydroxide precipitate after adding NaOH into synthetic wastewater

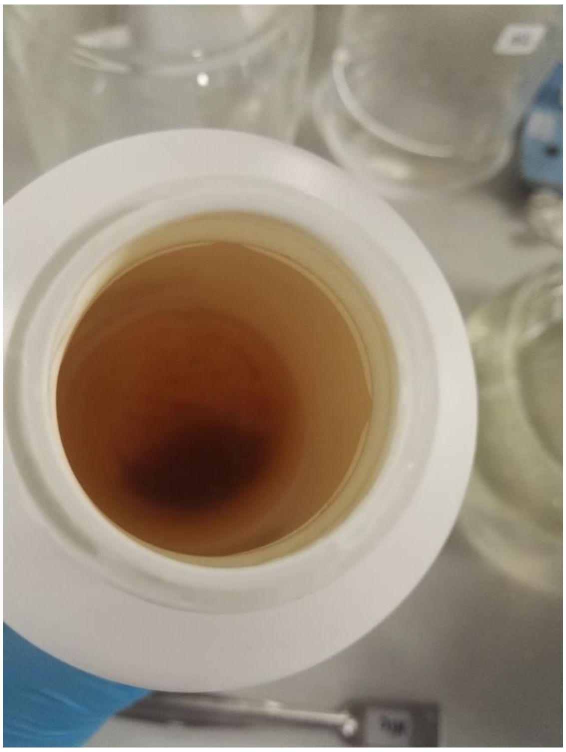


Photo 7: Suspended solids/ sediment present in industrial wastewater collected from air-conditioner manufacturing factory

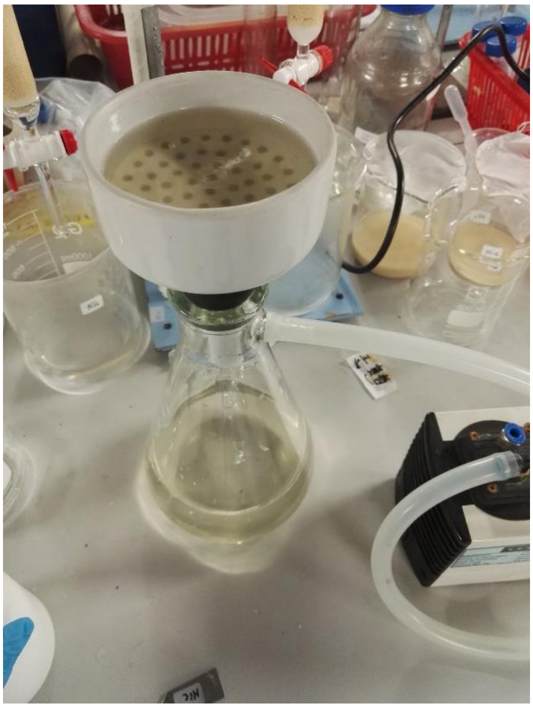


Photo 8: Filtration of sediment from industrial wastewater using vacuum pump

Appendix 3: SEM Image

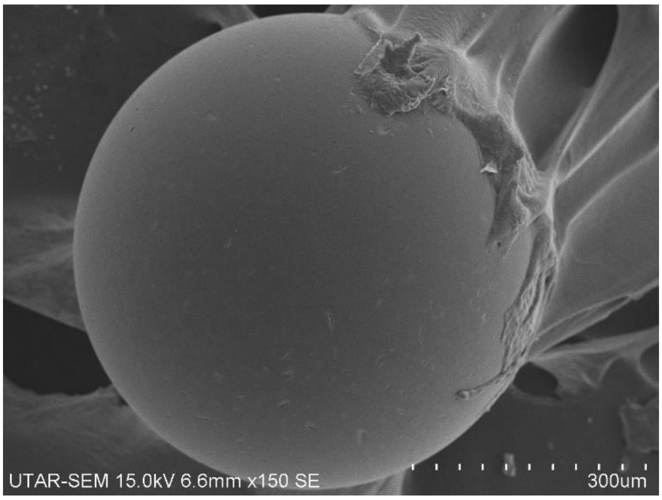


Photo 1: Before adsorption (x 150)

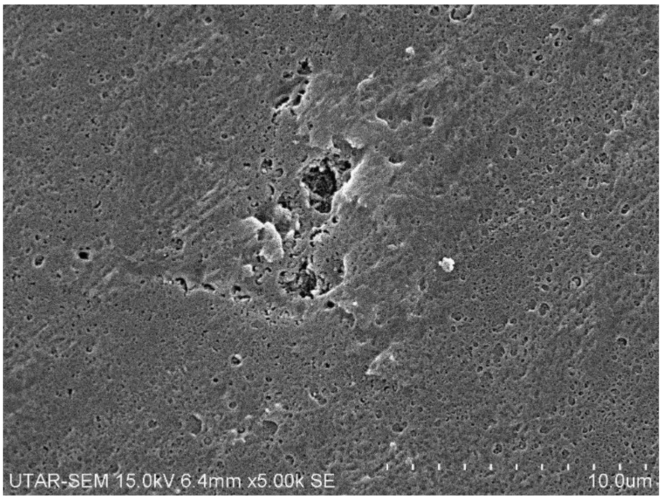


Photo 2: Before adsorption (x 5,000)

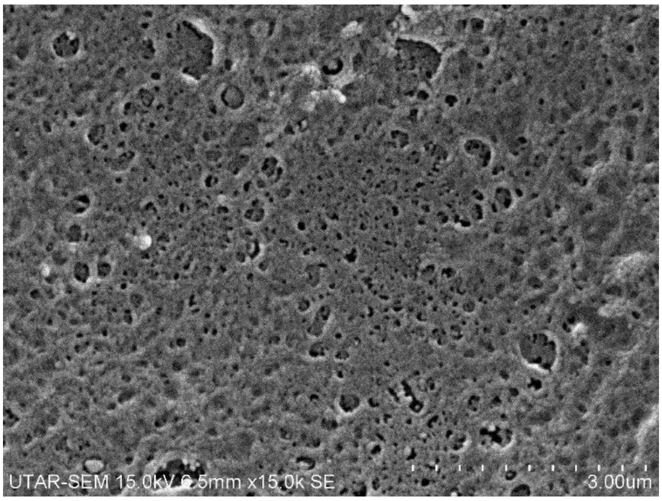


Photo 3: Before adsorption (x 15,000)

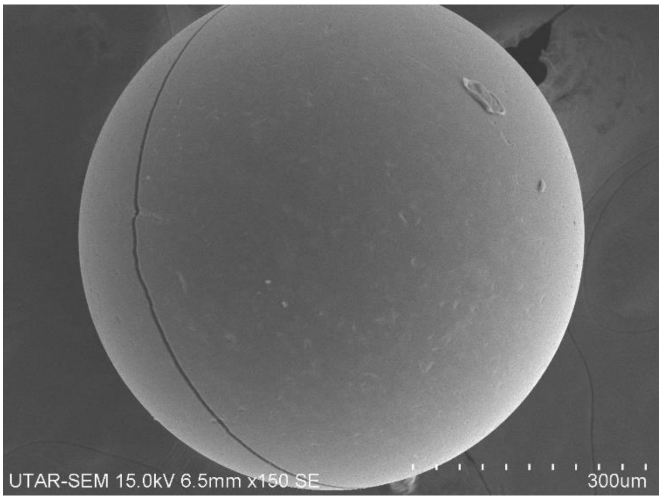


Photo 4: Before adsorption (x 150)

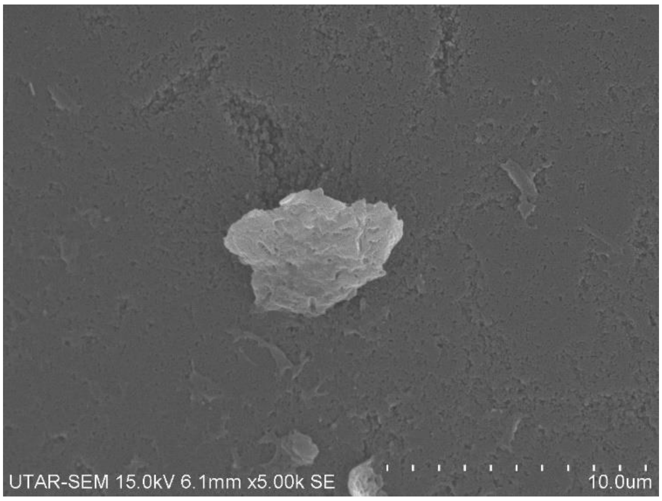


Photo 5: Before adsorption (x 5,000)

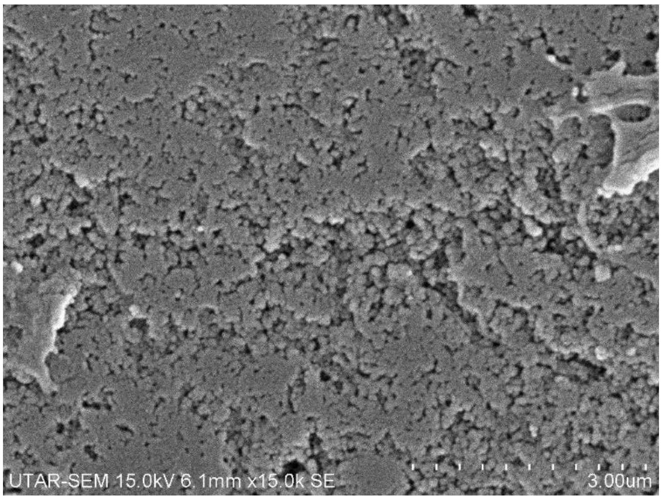


Photo 6: Before adsorption (x 15,000)

Appendix 4: EDX Results