Iron-copper Separation in Aqueous Solution Using Ion Exchange Resins

by

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ABSTRACT

Iron removal is an imperative process in hydrometallurgy processing of non-ferrous metallic ores as iron coexists with these non-ferrous metals in nature; e.g., the common copper mineral chalcopyrite is the sulfide of copper and iron. Precipitation methods and solvent extraction techniques are used to separate iron from copper leach solutions selectively. However, precipitation methods create a plethora of iron precipitates, making it not environment-friendly, and solvent extraction methods have the disadvantages of extractant's loss and potential fire accidents. Ion exchange resin technology is applied extensively in metal ion recovery or removal at low metal concentrations, e.g., ppm levels. This research studied the efficiency of 24 commercial resins in 14 different functional groups to remove Fe(III) from Cu(II) leach solutions at relatively high metal concentrations. The resin dosage ranged from 0.1 to 0.5 g / mL, to test the effect of resin type and dosage on the separation of iron from simulated copper leach solutions containing 45 g / L Cu(II) and 50 g / L Fe(III) at pH 1.5. The test results showed that resins with the amino-phosphonic functional group and a mixture of phosphonic and sulfonic groups showed the best percentage of Fe(III) removal, while the resin with bis-picolylamine groups obtained more than 92% Cu(II) loading with a moderate amount of Fe(III) removal. Resins with phosphoric, phosphinic acid, and amidoxime functional groups also favoured the loading of Fe(III) over Cu(II) but loaded less percentages of metals. Resins with the carboxylic, quaternary amine, and glucamine groups had the best potential to remove a significant amount of Fe(III), while keeping Cu(II) loading low using multiple adsorption stages. Resins with sulfonic groups, thiol, thiourea, and isothiourium groups did not obtain a notable loading of both metals from the leach solution. However, resins with the iminodiacetic acid group loaded a considerable percentage of both Fe(III) and Cu(II) at the highest resin dosage. After choosing selective resins based on better iron removal and copper recovery performance, single factor optimization tests were conducted by studying the effects of pH, adsorption time, and temperature on metal adsorption. Finally, elution experiments were performed with different acids for the resins having the most selective adsorption of Fe(III).

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CHAPTER 1
Introduction

1.1 Background and motivation

Iron is the fourth most abundant element in the earth's crust, and it is no wonder that the iron is ubiquitous in the structure of the common minerals of the base metals (Cu, Zn, Ni, and Co). It is found directly as an integral element of more than 600 minerals or as a replacement for an essential component of a significant number of other minerals.

Iron exists in different forms, such as oxide, silicate, sulphate, phosphate, arsenate, carbonate, sulphide, and arsenide minerals. Iron occurs in oxide ores, mainly as hematite, magnetite, goethite, and siderite, which are the main minerals for making steel, silicates, and valuable oxides like ilmenite and manganese minerals (James, 1966). Iron exists or coexists with other valuable metals in sulphide minerals like pyrite (FeS_2), pyrrhotite ($Fe_{(1-x)}S$ (x = 0 to 0.2)), chalcopyrite ($CuFeS_2$), sphalerite ((Zn,Fe)S), tetrahedrite ($(Cu,Fe)_{12}Sb_4S_{13}$), bravoite ($(Fe,Ni,Co)S_2$), and pentlandite ($(Fe,Ni)_9S_8$) (Kirk Nordstrom, 1982; Pradhan et al., 2008).

Iron is present with three different modes in non-ferrous ores: (1) ore minerals, (2) gangue minerals, (3) solid solutions. Ore minerals are those where iron works as an essential constituent of the mineral, which will be mined to extract valuable non-ferrous metals. The most common iron-containing ore minerals are Cu-Fe sulphide minerals, and Ni-Fe sulphides (Cabri, 1973). Gangue minerals are minerals for which iron acts as a necessary component or partial substitution of other elements, and it is not expected to recover from the ores. Pyrite and pyrrhotite are the most common iron-bearing gangue minerals found in sulphide ores (Chen & Petruk, 1980). Iron occurs in solid solutions means when iron replacement happens in the crystal structure of ore minerals or gangue minerals. Most iron is contained in sphalerite, a solid solution mineral which is the primary source of zinc in zinc sulphides ores (Wiggins & Craig, 1980). Other common minerals of this type are tetrahedrite (Cu-sulphide ores), cobaltite, and linnaeite (Co- and Ni- sulphide ores), and manganese oxide minerals (Jambor, 1981; Ostwald, 1978; W Petruk et al., 1971).

Despite the many iron-bearing mineral number, most iron in metallurgical concentrates can be accounted for by a few ore minerals or mineral gangue. In Brunswick mining and smelting (Canada) ores, for example, most of the iron in the copper concentrate is due to chalcopyrite, most of the iron in the lead concentrate is expected to be from pyrite and sphalerite, most of the iron zinc concentrate is present in sphalerite (PETRUK, 1981).

Different factors are directly involved with the extent of iron removal during beneficiation. First, the mode of occurrence of iron in ores has a significant impact, because iron existing in minerals of solid solution like sphalerite in a zinc concentrate, or iron acting as an essential constituent in ore minerals such as chalcopyrite in a copper concentrate, it is not possible to remove during mineral beneficiation (A. Baba et al., 2012). The degree of iron removed will depend on grain size and textures of Fe-bearing minerals present, in the case of gangue minerals. Grain size plays a vital role in iron removal. For large grain sizes, it is common to do mineral liberation by grinding and separation using physical methods such as floatation, magnetic, and gravity techniques. So, there should be a relation between the mineral size and degree of grinding for the successful separation of minerals (Chen & Petruk, 1980; William Petruk, 1976). Fine grinding requires more operational and capital costs, and for fine grinding (<5 μm), the cost is an issue; there is a chance of too much slimming, which will create poor separation. Textures of the minerals also have a significant effect on the efficiency of mineral processing. There are effects of inclusions, intimate intergrowths, fine exsolution blebs or lamellae, overgrowths, and thin rims in the ore minerals (Ramdohr, 1980). The iron containing minerals will be difficult to separate if the sizes of inclusions, exsolution blebs etc., are too small.

It is very well known that ferric iron acts as an oxidant during the acidic leaching of metal sulphides (John E Dutrizac & MacDonald, 1974). The chemical reactions for the sulphate leaching systems are shown below:

$$\mathrm{ZnS} + \mathrm{Fe_2}(SO_4)_3 = \mathrm{ZnSO_4} + 2\mathrm{FeSO_4} + \mathrm{S}$$

$$\mathrm{CuS} + \mathrm{Fe_2(SO_4)_3} = \mathrm{CuSO_4} + 2\mathrm{FeSO_4} + \mathrm{S}$$

The produced elemental sulphur, in all cases, has a direct impact on the kinetics of the reaction. For avoiding excessive use of iron concentrations in solutions, it is essential to regenerate the ferric iron. This can be done by the oxidation of ferrous iron using oxygen or air, but the reaction rate is very slow in acid media. So, better oxidation can be obtained using the mixtures of SO_2 and O_2 (Ferron, 2000; Tsugio Sato et al., 1984).

The chemical reaction of the regeneration of ferric iron can be written as:

$$2\mathrm{FeSO_4} + \mathrm{O_2} + \mathrm{SO_2} = \mathrm{Fe_2(SO_4)_3}$$

It can be seen that iron removal is an imperative process in the hydrometallurgy processing of non-ferrous metallic ores. The percentage of iron co-existing with the base metals is more than the metals of interest. Therefore, it is compulsory to remove iron from the process stream at the time of base metal production and purification (Kholkin et al., 2000; Meshram et al., 2019). Following the ore dressing, the concentrate may undergo a pressure leaching cycle leading to leach liquors (Whittington & Muir, 2000). The type of iron-bearing mineral species must be an essential factor during leaching. For example, between pyrite and pyrrhotite, the latter is more reactive as the former does not oxidize quickly in sulphuric acid media at a temperature below 170^0C with oxygen pressure, while pyrrhotite reacts readily under the same conditions. Hematite has a higher settling rate compared to goethite in sodium aluminate solution, so it is wise to convert goethite to hematite by maintaining a high temperature, and ultimately, it will increase the hematite concentration in the residue (red mud) (Basu, 1983; Brown & Tremblay, 1974). After pressure leaching, iron will be found in different forms through precipitation processes, such as insoluble hematite (Fe_2O_3), goethite (FeOOH), magnetite (Fe_3O_4), or jarosite ($MFe_3(SO_4)_2(OH)_6$), where M can be K^+, Na^+, or NH_4^+, etc. However, the precipitates will be discharged as solid waste, which will create environmental risk. Based on this necessity, other iron removal processes, e.g., solvent extraction and ion exchange, can be a better alternative. This research will study iron removal from the copper leach solution using ion-exchange resins before it is sent for copper electrowinning. There will be a direct comparison between the ion exchange resins with different functional groups and commercial brands based on adsorption performance towards iron and copper under specified experimental conditions. Last but not least, a promising elution strategy will be accomplished at the end to find out the potentiality of economic benefits.

1.2 Objectives

This research aims to remove the maximum percentage of iron using ion-exchange resins from the highly concentrated copper leach solution. The specific goals of this research are:

- To set up a direct comparison of different ion exchange resins' loading capabilities and selectivity to remove Fe (III) from the copper leach solution.
- To compare the loading efficiency of different commercial IEx-resins with analog functional groups
- To find the best ion-exchange resin-based on maximum adsorption of iron from a copper leach solution.
- To study the effect of different parameters, such as the effect of solution pH, temperature, and adsorption time, to maximize the percentage of Fe(III) adsorption.
- To perform elution tests for the resins with the most selective adsorption of Fe(III).

1.3 Outline of the thesis

This thesis is prepared in a traditional format. The outcome of the study is presented in five chapters. The outline is as follows:

- Chapter 1 will present the backgrounds, motivation, and objectives of the research work.

- Chapter 2 presents a brief review of different separation strategies for effective iron removal from leach solutions.

- Chapter 3 presents the materials and methods used in this study related to resin preparation and the preparation of synthetic leach solutions for conducting adsorption studies.

- Chapter 4 is divided into three sections. In the first section, this study will do the adsorption tests of different ion exchange resins with different functional groups under the same conditions and compare their performance. At the end of this section, the resins to be selected for further systematic study to get the best result will be confirmed. The second section will present the tests of different parameters on resins specified from section one, such as the effect of solution pH, temperature, and adsorption time for the adsorption experiment. In the last stage, the desorption process will be conducted on the loaded resin to recover the metals and recycle the resin.

- Chapter 5 will summarize the outcomes of the research and recommendations for future studies.

Co-Authorship: The research presented in this thesis has been performed by the author of this thesis, Mr. Shailen Saha, under the supervision of Dr. Yahui Zhang and Dr. Faisal Khan.

CHAPTER 2
Literature Review

Due to the close chemical properties of iron and non-ferrous metals, iron removal from impure leach solutions is not an easy task. For so many years, various hydrolysis–precipitation methods have been discovered for iron removal from hydrometallurgical solutions.

2.1 Precipitation method used in Hydrometallurgy

First, there were attempts to remove iron as a hydroxide, which is poorly filterable, voluminous, and precipitates as a gelatinous (Tainton & Leyson, 1924). The precipitates' size plays a significant role as the solid-liquid separation and washing thoroughly depend on this, and a dense deposit with crystalline character gives good results. The supersaturation of species at the time of precipitation determines the precipitate size. With the increase of the supersaturation level, the nucleation rate will increase, resulting in small particles' precipitation, which is not suitable for optimum solid-liquid separation. By using hot and dilute solutions, this problem is solved, and this principle is successfully applied in many precipitation processes developed for removing iron from different solutions (Claassen et al., 2002).

2.1.1 Jarosite precipitation

The first precipitation process is the Jarosite process, which solved the complexity of the initial treatment process. It made it possible to produce filterable iron precipitate on a commercial basis, for which it is still being used in many non-ferrous metal industries. The jarosite process usually entails the hydrolysis of ferric ions to build a solid compound and produce sufficient sulfuric acid (Schwertmann & Cornell, 2000).

The reaction of the jarosite process is illustrated below:

$$3Fe_2(SO_4)_3 + M_2SO_4 + 12H_2O = 2MFe_3(SO_4)_2(OH)_6 + 6H_2SO_4$$

Here, M can be a cation of K^+, $Na^{+,}$ and $NH_4^{+,}$ and the form $2MFe_3(SO_4)_2(OH)_6$ is a complex basic iron sulphate of jarosite. However, the extent of Fe precipitation in various synthetic jarosites is K> NH_4>Na (John E Dutrizac & Jambor, 2000). The jarosite process's stability zone is pH 1-3 with a temperature between 20^0C- 200^0C (Babcan, 1971; Ismael & Carvalho, 2003). Precipitation of jarosite becomes speedy when the temperature is about 80^0C and is nearly complete within several hours at 100^0C (Pammenter & Haigh, 1981). The most pH range for jarosite formation is 1.5-1.6 (Park & Park, 1978). The alkali sulphate concentration can also influence the extent of Fe precipitation because higher alkali sulphate concentrations (e.g.,> 1M Na_2SO_4) can make the precipitation of alkali-Fe^{3+} sulphates instead of jarosites (John E Dutrizac & Jambor, 2000). The advantage of the jarosite process is its characteristic of low capital and operating costs. The disadvantage is that it produces low iron contents, and the jarosite process requires a moderate acid concentration to confirm that only jarosite residue is present. For this reason, lime is used with ferric materials, but it results in the undesirable loss of metal values (J E Dutrizac, 1987). Additionally, there is an accumulation of hazardous waste in the jarosite process, which is against the rules and regulations for the management of hazardous waste introduced by the Basel convention in 1992 (Hsing et al., 2004; Leclerc et al., 2003).

2.1.2 Goethite (akaganeite) process

The Goethite process has also been practised in many metal industries as it can remove iron from solutions in a readily filterable form. The ferric iron in the solution obtained from the hot acid leaching stage containing 15-20 g/L Fe^{3+} and up to 50 g/L H_2SO_4 is reduced to the ferrous state by a concentration of close to 90^0C and of pH 2-3 (Posnjak & Merwin, 1922). The goethite precipitation follows the reaction shown below:

$$2Fe^{2+} + \frac{1}{2} O_2 + 3H_2O = 2FeO.OH + 4H^+$$

Then the reduced solution is neutralized with lime to 3-5 g/L H_2SO_4 to form goethite (FeO.OH). After the oxidation and neutralization, the solution's final ferric concentration becomes less than 1g/L, which is the primary condition of the goethite process (Allan et al., 1973; Davey & Scott, 1976). Normally α-FeO.OH (goethite) is formed from sulphate media but β-FeO.OH (Akaganeite) is precipitated from chloride solutions. The decisive matter is that the goethite process makes a residue more compact than the jarosite process, but it still contains some impurities which are not within an acceptable limit. Prolonged washing can remove most of these, but such activity will not be economical on a large-scale basis. Fe (III) concentration must be low for satisfactory goethite precipitation, which is accomplished in two ways, by slow oxidation or using dilution, which has developed the concept of the paragoethite process (Loan et al., 2006). It is termed as paragoethite because the residue of this process resembled goethite. In the paragoethite and similar zincor process, the leach liquor containing 16g/L Fe^{3+} and 160 g/L $ZnSO_4$ reacts continuously in a reactor at 85 °C temperature; the lime slurry is added to keep pH to 3.5. This process's advantage is that the residue obtained here has a high surface area, which provides a higher degree of anionic and cationic impurities removal. It runs with a low level of sulphate and operating cost. Adversely, this process results in more valuable metal losses than the jarosite process, which requires sufficient washing and de-watering. Also, the nature of the paragoethite and zincor process's complete reaction matrix produces a residue, which is not easy to determine (Dyer et al., 2012).

2.1.3 Hematite precipitation

Another precipitation process is hematite precipitation. Hematite is formed firstly by the reduction step of ferric to ferrous with neutralization; then the resulting ferrous iron is added with oxygen at a high temperature, in the range of 180- 200^{0}C, to make ferrous oxidation ferric, followed by hydrolysis to make hematite (M. C. Ruiz et al., 2007).

$$4Fe^{2+} + 2H_2O + O_2 = 2Fe^{3+} + 4H^+$$

Advantageously, hematite is iron-rich, a high-density compound having a moisture content of 10-20% compared to the 40-50% moisture content of jarosite or goethite (Onozaki et al., 1986). Further, hematite has high thermodynamic stability with a density of 4.9 to 5.3 g/cm^3 and almost 69% Fe content. In addition, hematite has a tremendous commercial value because it is extensively used in cement, pigment, steel, and ceramic industries (P A Riveros & Dutrizac, 1997). Despite its many advantages, it is not being used everywhere because it requires high temperatures and pressure applications, which are not easy. Major work on hematite precipitation in chloride media has been demonstrated by Riveros and Dutrizac (1997), Dutrizac and Riveros (1999), and Cohen et al. (2005).

2.1.4 Phosphate precipitation

The phosphate precipitation method is widely known for its rapid formation of ferric phosphate in acid media. It converts several grams per liter of iron to 0.1 g/L at room temperature, and it accomplishes this job within one hour or less. This system's principle is the same as removing phosphate from domestic water by introducing iron in the water (Jenkins et al., 1971). However, in hydrometallurgy, iron is the impurity that must be removed with the introduction of suitable phosphate to the solution. This process has the preferred selectivity of trivalent metals from divalent metals. So, this process is suggested to be used as iron removal during the purification of divalent metals such as nickel and copper (Twidwell et al., 1987). The reaction of iron phosphate precipitation is shown below:

$$Fe^{3+} + PO_4^{3-} + 2H_2O = FePO_4 . 2H_2O$$

Compared to the other precipitation methods occurring at high temperatures, the iron phosphate precipitation occurs at temperatures as low as 60^0 C and pH as low as 2 (Cruz et al., 1980). The phosphate precipitated solids become a sphere in shape that has the smallest surface area, decreasing the tendency to mix impure ions with phosphate precipitated solids (Twidwell et al., 1986).

2.1.5 Other available precipitation methods

Iron can also be precipitated as magnetite with the control of oxidation potential, pH value, and magnetic particles in the magnetite process. This process expresses better settle ability and filterability by magnetic flocculation and separation (Han et al., 2016). Cementation is another form of precipitation, a heterogeneous process in which ions at a solid metallic interface are reduced to zero valences. With the presence of solid iron, copper ions in the solution, mostly resulting from a leaching cycle, are displaced out of the solution. The chemical reaction occurring in copper cementation is shown below:

$$Cu^{2+}(aq) + Fe(s) = Cu(s) + Fe^{2+}(aq)$$

Then, the precipitated solid copper metal will be extracted from the scrap iron's surface as flakes or powder (Temur et al., 2016).

2.1.6 Comments on precipitation method

Based on the summary of different precipitation methods, the hematite process was recorded to produce precipitates of better quality. Precipitates of hematite are quickly extracted, and the chance of co-precipitation of other metals such as nickel and copper is lower than precipitates of jarosite and goethite. Phosphate precipitation has been proposed as highly selective of trivalent metals from divalent metals, making it less likely to co-precipitate nickel and copper during ferric phosphate precipitation. However, using the precipitation method in the hydrometallurgy of copper, iron is still being co-extracted or entrained to the electrowinning step at relatively low concentration, which creates many difficulties. Besides the disposal of the insoluble solid coming through this process is another serious factor related to adhering to the environmental rules and regulations. Thus, the use of the solvent extraction method later became the better pretreatment before the electrowinning of copper.

2.2 Solvent extraction method used in hydrometallurgy

In solvent extraction (SX), there will be a distribution of solute through the two phases of immiscible liquids, which contact each other (Rydberg et al., 2004). This process is one of the best alternatives for its ease, speed, and broad reach characteristics in metal recovery, besides using only simple equipment and requiring less time to perform, drawing chemists and engineers' attention to use this process thoroughly (Kislik, 2012). The organic phase of the SX process consists of extractant, diluent, and modifier. Extractants, which are typically viscous, are used to recover the desired metals from the leach solution. Therefore, diluents are used to make proper contact with the aqueous phase. A modifier is used to control the hydrodynamics of the system.

This process's basic idea is it requires multiple contacts for facilitating the suitable transfer of metal ions from the aqueous to the organic phase (Shibata, 1991). So, after extraction, there will be two more stages, named scrubbing and stripping. Scrubbing occurs by mixing the loaded organic phase with the aqueous phase to send back the solvent's impurities. Striping occurs when scrubbed organic phases are mixed with an aqueous solution to recycle the solvent after recovering the extracted species and sending it back to the aqueous phase for further use (C. K. Gupta & Krishnamurthy, 2005).

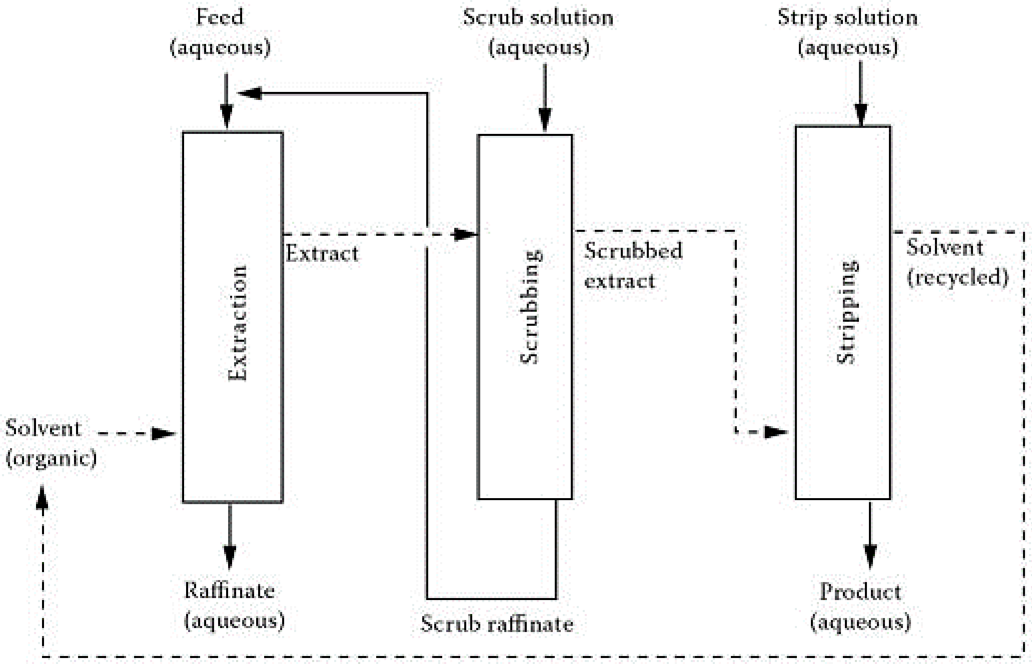


Figure 1. The schematic diagram of the solvent extraction process

2.2.1 Review of extractants and diluents used for iron extraction from the leach solution

As the primary purpose of solvent extraction is to extract and recover metals and acids from aqueous solutions, a number of extractants have been produced with significantly developed extraction properties, improved selectivity, and stability under very harsh conditions. Iron was extracted from a sulfuric acid solution with the mixtures of Kelex-100 and mono (2-ethylhexyl) phosphoric acid extractant (M2EPHA), but no significant result was found (Demopoulos et al., 1993). Fortes and Benedetto (1998) demonstrated that iron (III) could be effectively separated from acid solutions containing indium using di-(2-ethylhexyl) phosphoric acid (D2EHPA) diluted in isoparaffin. Suarez et al. (2002) also investigated the extraction of iron (III) from acid solutions using bis (2-ethylhexyl) phosphoric acid (HDEHP) and PENRECO$^{®\ 170}$ ES as a diluent. They explored significant advantages like decreasing the loss of diluent even more than 50% after one year, compared to using other diluents. Principe and Demopoulos (2004) investigated the extraction of iron (III) from a concentrated $ZnSO_4$ and H_2SO_4 solution, comparing the performance of the octyl phenyl acid phosphate (OPAP) and di-(2-ethylhexyl) phosphoric acid (D2EPHA), and they found that OPAP was a more suitable extractant to extract more iron from the acid solution. Alkylphosphonic acid monoalkyl esters such as 2-ethylhexyl 2-ethylhexyl-phosphonic acid (HEHEHP) are one of the solvent forms that can effectively remove Fe (III) from a sulphate solution (Gao et al., 1994; Majima et al., 1985; Taichi Sato et al., 1985; Sun et al., 1996). Deep et al. (2006) initially studied the use of a phosphinic acid extractant named bis (2,4,4-trimethylpentyl) phosphinic acid (i.e., Cyanex 272$^{®}$) for extraction of iron (III) from sulphate solution. They achieved good results with a dilute solution, with an iron content of up to 0.5 g/L. Later, they used a mixture of neutralized Cyanex 272 and tri-butyl phosphate (TBP) to extract iron (III) from the high iron content sulfuric acid medium. During this extraction, H^+ ions were generated, restricting mass transfer, and for this reason, a neutralized solvent was used to circumvent this problem (Deep et al., 2007). Also, iron can be separated from chloride and sulfate leach liquors produced by the acid leaching of aluminosilicate ore, using aliphatic monocarboxylic acid, a better alternative to the Bayer process for the manufacture of pure aluminium (Mühl et al., 1980). Van der Zeeuw, (1979) investigated the extraction of iron (III) with tertiary carboxylic acid / neodecanoic acid extractant (i.e., Versatic® 10). It is also possible to extract iron from base metal solutions at about pH 2, using a tertiary aliphatic carboxylic acid extractant named Versatic 911® (Fletcher et al., 1965). Rice (1978) also demonstrated the extraction of iron using the same extractant. Iron can be effectively and selectively extracted from sulphate solutions using PP'– di(2-ethylhexyl) methanediphosphonic acid (H2DEH[MDP]) extractant (Xue et al., 1999).

2.2.2 Review of extractants and diluents used for copper extraction from the leach solution

During the past 35 years, the use of solvent extraction for primary copper processing has dramatically increased. Production of high-purity copper through a combination of sulfuric acid leaching, upgrading, and copper purification by solvent extraction (SX), and metal recovery by electrowinning (EW), have gradually increased, now reaching 30% of total copper output. All the reagents produced commercially, in the beginning, were functionally based on Ketoxime. It was used solely for copper production for over a decade, following its first complete application by Bluebird Ranchers Mine, Arizona (Arbiter & Fletcher, 1994). Ketoximes are also widely used today to recover copper from dilute leach liquors and find applications in the extraction of nickel from ammonia solutions and in the processing of precious metals. While ketoximes typically do not permit copper extraction at pH values below 1.8 and have slow kinetics of removal, they exhibit around 300:1 copper selectivity over iron. Second-generation Aldoxime extractants were produced to resolve the ketoxime deficiencies (Dalton & Severs, 1986; Maes et al., 2003). Extractants of aldoxime have excellent kinetics of extraction, high selectivity, and high loading capacity. Since they extract at pH levels below 1, it is challenging to strip copper. Today, modified aldoximes and aldoxime – ketoxime mixtures are being used as extractants for copper removal. With developments in chemical and manufacturing methods, such reagents now have a high purity, and many of the drawbacks of earlier reagents have been overcome.

The first reagent developed by General Mills, named LIX 63 for this application, had many of the necessary properties to be successful as a copper solvent extraction reagent because it was copper-specific, stable, water-insoluble, inexpensive, and safe to use (Swanson & Agers, 1964). However, the reagent did not remove copper well below pH 3.5 and was therefore not an acceptable reagent. To improve metal transfer kinetics, LIX 64 reagent was composed of LIX 65 with a catalytic amount of LIX 63 added. Although LIX 64 had the properties needed to be commercially used as a copper extractant, the reagent had significant limitations regarding extractive power, the kinetics of metal transfer, copper/iron selectivity, viscosity, and separation of phases. As a result, LIX 64 could only be used under well-regulated conditions with a limited leach solution range. LIX 64N had dramatically improved properties over LIX 64, including increased extractive power, faster kinetics, faster phase separation, lower entrainment, increased selectivity of copper/iron, and lower viscosities. These enhanced properties expanded both the range of treatable copper leach solutions and the conditions under which these leach liquors could be treated. Calligaro et al. (1983) demonstrated the extraction of copper from a sulphate solution using LIX 64N in kerosene. Still, it had some drawbacks related to kinetics, the selectivity of copper/iron, and the pH and copper content of leach liquors that could be treated economically. Ashland Chemical Company launched Kelex 100 in 1968 as a reagent that would fulfill the perceived need for a copper solvent extraction reagent that could handle leach solutions with a lower pH and a higher copper content than LIX 64N more effectively. Although neither Kelex 100 nor Kelex 120 has ever been used commercially to recover copper from dilute sulfuric acid leach solutions, the concept of using modifiers to change a copper extractant's rate of extraction represented a significant advance in the production of reagents that has resulted in improved reagents still in use today. Shell International Chemicals put SME 529 onto the market in the mid-1970s as an alternative to LIX 64N (Van der Zeeuw, 1975).

The extraction of copper from sulphate and ammoniacal solutions using LIX 64N and SME 529 was also found in another study (Valdes et al., 1983). The Acorga company produced a series of reagents named P-1 and P-5000 (Tumilty et al., 1979). In implementing this series of reagents, Acorga not only applied to promote copper stripping with the strong copper extractant P–1, but Acorga also went one step further through the use of modifiers, by combining the strong copper extractant P–1 with varying quantities of nonylphenol to provide a series of reagents where the extractive strength could be adapted to any given leaching solution or collection of conditions. Unfortunately, the existence of nonylphenol in the reagent led to increased degradation of the reagent, higher organic phase viscosity, and higher entrainment; however, nonylphenol was not compatible with certain construction materials. Henkel announced in 1983 that patented mixtures of strong aldoxime extractants such as LIX 860-I with moderately strong ketoxime extractants such as LIX 64N and SME 529 provide reagents with fast kinetics and good aldoxime copper extraction characteristics, combined with stability and good ketoxime physical efficiency, and these have no hindering properties of modifiers (Kordosky et al., 1983). Copper extraction was found to be satisfactory when MSB-210 was used as a diluent with the mixtures of LIX 64N and SME 529 extractants (Valdes et al., 1983). Aldoxime/ketoxime mixtures have proved to be a significant advance in copper solvent extraction reagents, and these mixtures currently produce more copper than any other single reagent method. LIX 84I is another such kind of excellent aldoxime reagent used to extract copper from a sulphate solution (Reddy & Priya, 2004).

However, solvent extraction methods have the disadvantages of extractants and solvents loss and potential fire accident issues, due to the low auto-ignition temperatures of solvents such as kerosene.

2.3 Ion- Exchange technology in Hydrometallurgy

Modern copper hydrometallurgical flow sheets depend heavily on the use of SX for high pure cathode production. Nevertheless, IX is increasingly used to recover valuable metals from the processing of high-volume, low-concentration mine solutions, and from the primary output of dilute heap-leach solutions (Schlesinger et al., 2011). Selective chelating resins also provide opportunities for recovering useful trace impurities from electrolytes during copper cathode processing and mine wastewater copper (Ruiz et al., 2013). Chelating ion exchange resins vary from standard ion exchange resins, as here, the reactive portion of the resin binds ions by forming complexes, rather than involving only ionic bonding (Dorfner, 2011). Ion exchange is a phenomenon or cycle involving reversible ion exchange in solution with ions protected by solid ion exchange material, without any significant physical change taking place in its structure. The method of ion exchange typically involves either inorganic or organic ions, mainly in aqueous solutions, and it takes two steps to complete, i.e., the change of the solvent ions into the ion exchanger, and then the exchange of the ions from the ion exchanger (Wiegner & Jenny, 1927). The ion-exchange technology was initially explored with inorganic materials; these were found to be of some industrial value but were almost entirely replaced by synthetic resins (Adams & Holmes, 1935). Commercial applications of ion-exchange technology include water and wastewater treatments like water softening (Perlov & Legenchenko, 1990), removal of manganese or other organic matters from drinking water (Bolto et al., 2002; Heijman et al., 1999; White et al., 1995), recovery of valuable metals from hydrometallurgical leachates (Green, 2004; Kautzmann et al., 2002; Zhang et al., 2016), and decontamination and recuperation of waste streams (Dobrevsky et al., 1997; Hanine et al., 1992), etc.

2.3.1 Reasons for preferences of ion-exchange technology over solvent extraction

Like solvent extraction (SX), a specific/chelating ion-exchange (IX) resin is typically used to remove iron from copper electrowinning solutions. However, its use in extracting trace metallic impurities from hydrometallurgical process streams (with background metal concentrations varying from 50 g / l to 100 g / l) has dramatically increased over the last quarter-century (Sole et al., 2018). SX requires phase contact times of under 30 s to achieve equilibrium. Though IX kinetics are slow and need a high resin stock, the capital cost of a plant is adversely affected. The use of a countercurrent configuration will mitigate this (van Tonder, D., Lunt, D. and Donegan, 2010). Leach solution clarity is vital for both SX and IX. Liquid-solid separation can account for 25% of a plant's capital cost (van Tonder & Van Hege, 2007). Usually, thorough clarity, including countercurrent decantation (CCD) and belt filters, is used to minimize these problems. SX can handle up to 20 ppm total suspension solids (TSS). However, IX is more capable of handling solids, allowing IX to be used in systems with difficult liquid-solid separation characteristics by working in a countercurrent ion exchange (CCIX) or resin in pulp (RIP) system with uncertain solutions (Crane et al., 2009). Several authors suggested that such configurations may give substantial advantages, particularly for ores that contain clays or other hard-to-settle slimes (Baguelay, 2009; Crane et al., 2009). This solid-liquid extraction offers many advantages over liquid-liquid methods, since the latter ones allow additional mixing and settling before extractants are recovered and regenerated (Bachiller et al., 2004; Benamor et al., 2008). Resin durability is the main challenge in using the IX process, as resins have some limitations, including relatively low mechanical stability, the potential for chemical and physical fouling, and high water requirements associated with high-quality applications (Zontov, 2006). In recent years, significant manufacturing advancements have been made in improving the distribution of bead size and durability of strong-base resins. The real issue related to the ion-exchange process is that after the desorption process, the body of resins finds physical and chemical stability to use this again several times to separate metal ions (Akkaya & Ulusoy, 2008), and thus it decreases losses (Iglesias et al., 1999). Resin technologies have advanced to such an extent that resin failure costs in a RIP process are now small relative to solvent losses in an analogous SX system and are expected to contribute less than 0.02% of the annual operating costs in a typical plant (Yahorava et al., 2009).

2.3.2 Synthesis of ion exchangers and selection of materials for ion exchange technology

An ion exchanger may be any substance capable of removing ionic species from a solution by simultaneously releasing a chemically equivalent number of ions into this solution. Ion exchange is analogous to sorption because a solid takes up a dissolved material in both situations (Bolto et al., 2002). The functional distinction between these two processes is that the ion exchange is stoichiometric. Each ion removed from the solution is replaced by another equivalent ion of the same form. However, for sorption, a solvent is usually taken non-stoichiometrically without being substituted (Bolto et al., 2004). Ion exchange materials include organic and inorganic ion exchangers like cellulose, dextran and agarose derivatives, clays and clay minerals, zeolites, organic natural products, and synthetic liquid. However, the organic resins are by far the most effective ion exchangers for practical applications. High chemical and mechanical stability, high ion-exchange efficiency, and high exchange rates are their key advantages. Additionally, the choice of selecting the fixed ionogenic groups and the degree of cross-linking of the matrix in proportion to the intended applications makes them more feasible to use (Biswas & Packirisamy, 1985). Ion exchangers are insoluble materials consisting of ion exchange polymers and functional groups. Ion exchange polymers are generally cross-linked polymers attaching functional groups with them. Functional groups can be any kind of acidic, basic, or chelating groups attached to the polymers. Styrene is the primary starting material used in synthetic resin ion exchangers. The synthesis of polymers starts with the polymerization of styrene (or an acrylic monomer, usually methyl acrylate) and cross-linking agent (usually divinylbenzene, DVB) to form spherical beads in aqueous suspension (Biswas & Packirisamy, 1985). Unlike the irregular-shaped particles of the phenol-formaldehyde forms, the production of synthetic polystyrene and polyacrylic resins enabled these ion exchangers to be generated in spherical bead form (Vasilev, 1968). Here the monomers must be insoluble in water. Stabilizing ingredients are used to permanently disperse the monomer into spherical droplets. Monomer units will go towards the growing polymer chains, using an initiator on monomer mixtures producing free radicals (Golden, 2000). As a result, Styrene and Divinylbenzene will comprise a large number of unconnected chains and form an infinite single polymer chain network. Solvents will penetrate to the polymer chain network and swell the polymer. The extent of swell depends mainly on the percentage of DVB contained in a polymer network (Golden, 2000). The gel-type ion exchange resins typically carry a higher proportion of the cross-linking agent (>10% DVB) which creates less swelling in an aqueous solution. This type of polymer has no appreciable porosity. Porosity determines the size of the species, ion or molecule that can enter the structure. The gel ion exchange resin offers both high capacity and high chemical efficiency (Slagt, 2015). Cross-linking agents such as trimethylolpropane, trimethylacrylate, and trimethylolpropane triacrylate are more flexible than divinylbenzene, and may achieve a more accessible gel process (Alexandratos & Hussain, 1995). However, there is an effect on mechanical strength with the extent of cross-linking. The greater the cross-linking, the higher will be the mechanical strength of ion exchangers. Long cross-linking bridges can make the matrix more flexible. As a result, molecules of ions and water have less trouble penetrating inside the material (Kunin et al., 1962). Consequently, materials with long cross-links also offer the possibility of exchanging large organic molecules that cannot go into the traditional ion exchange materials. Materials of this type are macroporous or macroreticular ion exchange resins (Kun & Kunin, 1964). The capacity of macroporous ion exchange resin is less than gel, but it shows higher mechanical stability than gel and better resistance to oxidation (Bohling & Lundquist, 2012). The disadvantages of using this material is its limited capacity, and the resin regeneration cost is high. A uniform distribution of cross-linking bridges can be formed with the use of other synthetic polymers, for example, building methylene bridges during chloromethylation (Rempp et al., 1975). The objective of this process is to obtain polymers with a uniform pore size. The materials used in this structure are called isoporous. In practical application, these resins show maximum structural homogeneity. Higher resin capacity and regeneration efficiency than macroporous resins make this resin suitable from the economic point of view (Kressman, 1966). The structural models of gel type, macroporous and isoporous resins are shown in Figure 2.

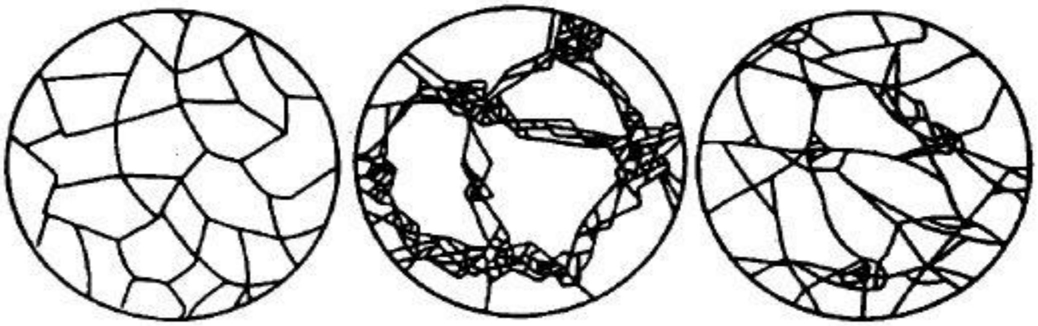
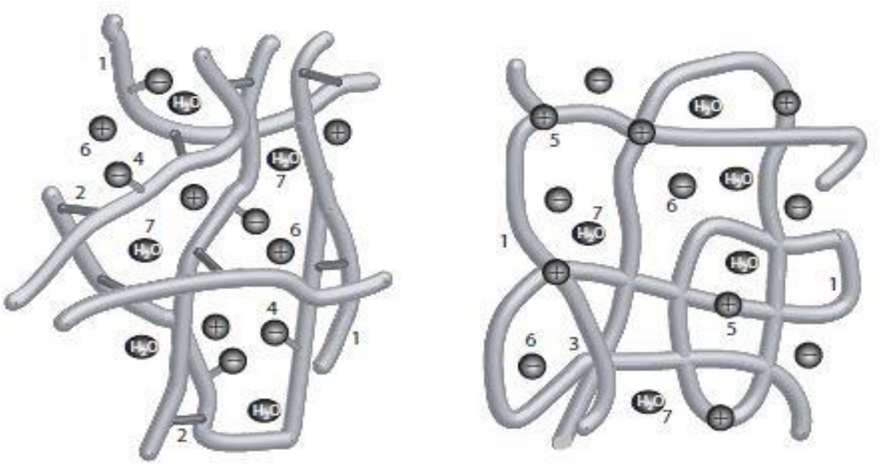


Figure 2. Structures of gel type, macroporous and isoporous ion exchangers (left to right) (Dorfner, 2011)

The second stage of synthesis is to add a functional group to the polymer. The functional group will contain a liable ion (cation or anion), exchanging ions in solution. Thus, the resin will be swollen by the water, but it will not be dissolved because of its polymer structure. The extent of swelling of resin is significant, as it controls the behaviour of resins in many applications.

From this review, it is clear that the degree of cross-linking and swelling ability of material has a significant effect on the rate of reaction and flexibility of the polymer network. So, selecting the correct material may be a compromise between desirable stability and reactivity for suitable practical applications.

The schematic diagram of the cross-linked polymer ion exchanger is shown in Figure 3.



(a) **(b)**

Figure 3. Schematic representation of polymeric cross-linked ion exchanger. (a) Cross-linked cation exchange material; (b) Unrecognisable cross linked anion exchange materials. 1 – Polymeric chain; 2 – cross-link; 3 – physical knot; 4 – negatively charged cation exchange group linked with the chain; 5– positively charged anion group attached to the chain; 6 – counterion; 7 – water (Zagorodni, 2006).

2.3.3 Reaction mechanism of ion exchange resins

Ion exchange is an equal number of ion exchanges between two or more ionized species in separate phases, of which at least one is an ion exchanger. The main exchange happens between mobile ions attached to functional groups on the polymer and target ionic species. The literature review found two main categories of interactions between them: (i) ion substitution of the resins mobile ion; (ii) the formation of coordination bonding between the electron donor of ion exchange resins and the target ion species.

2.3.3.1 Ion exchange resins based on ion substitution

An ion exchange resin is an insoluble matrix of polymers containing liable ions that can be exchanged with ions in the surrounding medium (Golden, 2000). The metal extraction in this process entirely depends on the charge pairing of ionized species. Polymeric support (Pol) with a functional group (Fg) exchanges its liable ion (L) with the ionized select species (T):

$$\text{Pol-Fg}^{\pm}\,\text{L}^{\pm} + \text{T}^{\pm} \leftrightarrow \text{Pol-Fg}^{\pm}\,\text{T}^{\pm} + \text{L}^{\pm}$$

There are two basic types, cation and anion exchange resins. Cation exchange resins are polymeric anions to which the labile cation is bound and will be exchanged in solution with other cations. Common examples of cationic exchange resins are polymers with sulfonic groups (e.g., $\text{R-SO}_3^-\ \text{H}^+$ or $\text{R-SO}_3^-\ \text{Na}^+$) and carboxylic groups (e.g., $\text{R-COO}^-\ \text{H}^+$ or $\text{R-COO}^-\ \text{K}^+$), which exchange positively charged hydrogen or others corresponding ions (Viallate, 2012). The exchange of cations occurs with an initial deprotonation or dissociation reaction to create negatively charged sites to attract appropriate target species following the reaction (Zagorodni, 2006):

$$\text{Pol-Fg}^-\,\text{H}^+ \leftrightarrow \text{Pol-Fg}^- + \text{H}^+$$

After being negatively charged, the resins will be attached with the free cation species in an aqueous solution:

$$\text{Pol-Fg}^- + \text{T}^+ \leftrightarrow \text{Pol-Fg}^-\,\text{T}^+$$

Cation exchange resins are mainly found in two forms. One is the H+ form, which is used for complete deionization. The other one is the salt (Na+) form used for water softening, removing the calcium and magnesium from hard water (Vaaramaa & Lehto, 2003). This reaction occurs as follows (Rodrigues, 2012):

$$\text{Pol-Fg}^{-}\ \text{Na}^{+} + \text{T}^{+} \leftrightarrow \text{Pol-Fg}^{-}\ \text{T}^{+} + \text{Na}^{+}$$

After exhaustion, the resin is converted back into the form of hydrogen (regenerated) by contact with an acid solution, or into the form of sodium with a solution of sodium chloride.

Anion exchange resins are polymer cations to which the labile anion is bound and are exchanged with other anions in solution. Common examples of anionic exchange resins are resins with amino groups (e.g., $R\text{-}NH_3^{+}OH^{-}$) and quaternary ammonium groups (e.g., $R\text{-}N(CH_3)_3^{+}\ OH^{-}$), which exchange negatively charged hydroxyl ions (Viallate, 2012). Initially, anion exchange resins will make a dissociation reaction to create positively charged sites to attract negative target species (Wachinski, 2016).

The dissociation reactions occur as follows:

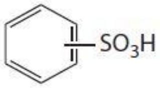
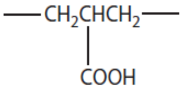
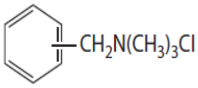
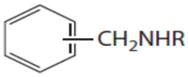
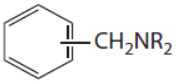
$$\text{Pol-Fg}^{+}\ \text{OH}^{-} \leftrightarrow \text{Pol-Fg}^{+} + \text{OH}^{-}$$

When the resin is positively charged, it will be adsorbed by the negatively charged metal complexes (represented as CplxT^{-}) following the reaction:

$$\text{Pol-Fg}^{+} + \text{CplxT}^{-} \leftrightarrow \text{Pol-Fg}^{+}\ \text{CplxT}^{-}$$

Both anion and cation resins can be made from the same organic base polymers. They vary in the ionizable group to which the hydrocarbon network is connected. It is this functional group that defines the resin's chemical actions. Since the functional groups in polymer networks are the forms of acids, salts, and bases, the resin's characterization is entirely pH-dependent. The terms strong and weak are used to completely differentiate the function of resins. As the cation and anion exchangers are identified as acids and bases, they are subdivided into strong and weak cation/anion exchangers. The classification of ion exchange resins is shown in Table 1. Both strong acidic or basic resins can be easily ionized and exchanged with ions in dissolved salts. However, weak resins cannot be ionized to split the salts (Frisch & Kunin, 1957), but they remove cations/anions from solutions according to their characteristics. Strong cation resins (SCR) typically replace one ion with another, depending on the resin's selectivity, and work at all pH values. This type of resin has rapid exchange rates and stability, and its capacity will remain almost the same, even after several years. However, weak cation resin (WCR) has a stronger affinity for hydrogen to be used at a pH over 4. The WCR resin is prepared by copolymerization of acrylic or methacrylic acid with DVB (Stránská et al., 2018). Because of its higher affinity for hydrogen, it shows higher regeneration efficiencies. Examples of strong and weak cation exchange resins are functional groups containing sulfonic acid and carboxylic acid, respectively (Schwellenbach et al., 2016).

Table 1. Classification of major ion exchange resins (Wachinski, 2016)

Type		**Active group**	**General configuration**
Cation Exchange Resins	Strong acid	Sulfonic acid	
	Weak acid	Carboxylic acid	 $-CH_2\underset{\mathrm{COOH}}{\underset{\vert}{C}}HCH_2-$
Anion Exchange Resins	Strong base	Quaternary ammonium	
	Weak base	Secondary amine	
	Weak base	Tertiary amine	

Strong anion resins (SAR) are strongly ionized like strong acid resins and can be used across the entire pH range. SAR resins are usually used to demineralize, dealkalize, and extract total organic carbon (TOC) or other organic substances (Wheaton and Bauman 1951). However, the degree of ionization of weak anion resins (WAR) is strongly influenced by pH, as they exhibit lower exchange capacity at a pH higher than 7. This type of resin is produced based on phenol-formaldehyde or epoxy matrices instead of polystyrene-DVB (Vasilev, 1968). In most cases, WAR resins are used jointly with SAR to perform a complete demineralization process.

2.3.3.2 Formation of ion Exchange resins related to coordination bonding

Many ions of transition metals appear to have a lone pair of electrons surrounding themselves with molecules or ions. These surrounding species (ligands) donate to the central ion their electron pairs, forming covalent-like bonds, called coordination bonds. Nitrogen, sulphur, and oxygen are among the atoms capable of contributing electron pairs. Molecules or ions that contain such atoms may serve as ligands. Coordination number or coordination valence, which is a property of the central ion, represents the number of ligands being coordinated around the central atoms (Yoshida et al., 2000). The most common number is six, while more than one coordination number may be shown by the same central atom, depending on the ligands and conditions. The ligand is called monodentate, bidentate, or polydentate, depending on the number of coordinating bonds which the ligand may form. In Figure 4, the coordination of a metal ion with hexadentate ligand Ethylenediaminetetraacetic acid (EDTA) is presented.

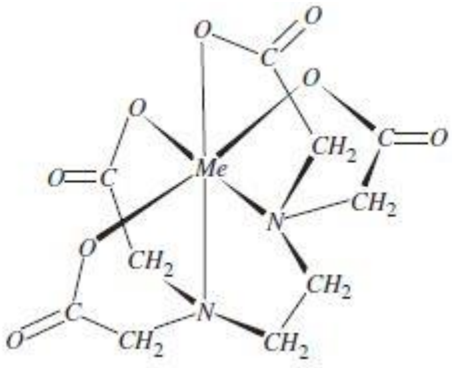


Figure 4. Ethylenediaminetetraacetic acid (EDTA) as an example of a hexadentate ligand (Zagorodni, 2006)

Various combinations of electron-donor elements and organic structures allow for the design of a wide range of coordinating groups. Nonetheless, there is only a small range of available chelating products because of some groups' low stability and for commercial reasons, such as a high synthesizing cost (Sahni & Reedijk, 1984). Significant physicochemical properties such as stability or the solubility constant of the built complex, the charge of ligand and metal ion, electronegativity, geometry, and ionic diameter, determine the proper selection of metal-ligand bonding and the stability (Martell & Hancock, 2013). Most of the properties mentioned above can be explained by the Pearson Hard and Soft Acids and Bases (HSAB) theory. Lewis acids and bases are classified as hard and soft to define chemical hardness, and Pearson has proposed the HSAB Principle (Pearson, 1963). The HSAB Principle states that hard acids tend to bind to hard bases and soft acids tend to bind soft bases. The term 'hard' is used to define the low polarizability of chemical species, whereas 'soft' is used to represent the high polarizability of chemical species. Lewis’s theory of acids and bases, and the classification of ions by hardness, is shown in Table 2. The interaction between hard acid and bases is due to electrostatic interaction, but the interaction between soft acid and bases occurs for covalent interaction. Hard acids are ions with low electronegativity, and are non-polarizable, highly chargeable, attracted to hard bases with high electronegativity, and low polarizability, and hard to reduce. By comparison, soft acids are polarizable ions with low charge and relatively high electronegativity, which suit the relatively soft bases of high polarizability, low electronegativity, and are readily oxidized (Pearson, 1987). However, intermediate acids can be attracted with either hard or soft bases following the HSAB theory (Zaganiaris, 2016). For example, soft base ion exchange resins containing a thiourea group or thiol group are both used to recover palladium(II) (soft acid) from chloride and chloride–nitrate solutions or copper(II) and zinc(II) base metal ions solutions (Birinci et al., 2009; Hubicki et al., 2007).

Table 2. The grouping of ions based on chemical Hardness following Lewis theory of acids and bases as suggested by Pearson (1997) and Zaganiaris (2016)

	Acids	**Bases**
Hard	H^+, Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Sn^{2+}, Al^{3+}, Se^{3+}, Ga^{3+}, In^{3+}, La^{3+}, Cr^{3+}, Co^{3+}, Fe^{3+}, As^{3+}, Ir^{3+}, Si^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+}	H_2O, OH^-, F^-, $CH_3CO_2^-$, PO_43^- SO_4^{2-}, Cl^-, CO_3^{2-}, ClO_4^-, NO_3^-ROH, RO^-, R_2O, NH_3, RNH_2, N_2H_4
Intermediate	Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Mn^{2+}, Bi^{2+}, In^{3+}	NO_2^-, SO_3^{2-}, SCN^-, Aromatic Amines, Pyridine, Aniline
Soft	Cu^+, Ag^+, Au^+, Hg^+, Cs^+, Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}, Tl^+	R_2S, RSH, RS^-, I^-, SCN^-, $S_2O_3^{2-}$, R_3P, R_3As, $(RO)_3P$, CN^-, RCN, CO, C_2H_4, C_6H_6, H^-, R^-

Additionally, chromium ions (hard acid) can be removed from wastewater using hard base ion exchange resins containing an amino group (Gode & Pehlivan, 2005). When the metal ions which have to be removed are between two hard or soft acids, a base group that contains the same number of donor atoms compared to the oxidation state of the target acid ion has to be found (Stöhr et al., 2001; Zhao et al., 2002). For example, ion exchange resins of carboxylic acid groups containing two oxygen donor atoms prefer the interaction of metal ions with a valence of two (II) over three (III) electrons (Wachinski, 2016).

2.3.4 Major functional groups of polymeric resins used in hydrometallurgy

Ion exchange resins are composed of different functional groups consisting of nitrogen, oxygen, phosphorous, or sulfur. For metal adsorption, the functional groups will be ionized so that resins can exchange their mobile ions with metal ions for the desired adsorption. As mentioned, the most common commercial polymer materials used for ion exchange technology are polystyrene crosslinked with divinylbenzene (PS-DVB), polyacrylic divinylbenzene (PA-DVB), polystyrene (PS), and divinylbenzene (DVB). Despite so many combinations, the main extraction characteristic depends on the active element of the functional group. The literature review found that major functional groups based on nitrogen as an active element used in the metal recovery process are quaternary ammonium groups, amino groups, picolylamine groups, pyridine groups, and guanidine groups (Grosse et al., 2003; Kramer et al., 2006; Van Deventer, 2011). Sulfonic groups, thiol groups, and thiourea groups are the most common functional groups based on sulfur as an active element (Hubicki & Wołowicz, 2009; Moosavirad et al., 2015; Nikoloski & Ang, 2014) and the main functional groups produced based on phosphorous as an active element are phosphonic, phosphoric, phosphinic and phosphine groups (Bari et al., 2009; Drozdzak et al., 2015; Navarro et al., 2009). Carboxylic group resins are the only type of resins that use oxygen exclusively as the active atom and are the most popular WCR available on the market (V. K. Gupta et al., 2004). The ion exchange mechanism can involve a combination of counterions and functional groups, causing a high affinity of the material to the ion or group of ions. Sometimes, it may create two unfavorable scenarios (Zagorodni, 2006). Firstly, one or more ions want to associate with one functional group. Thus, there will be a dense region of materials around the functional groups, which hinders the desired ions from associating with a functional group.

Secondly, more complications can happen when two or more functional groups are not correctly distributed in the bulk of the materials but are associated with one ion.

For this reason, associating two or more groups demands that the groups be brought into certain geometrical positions. Fabrication of functional polymers with appropriate functional group structures will provide materials explicitly designed for certain forms of complex formation (Yoshida et al., 2000). This approach, called imprinting, was initially suggested for silica gels (Polyakov et al., 1937). Iminodiacetic, aminophosphonic, oxime, thiocarbamate, and glucamine are such kinds of functional groups of resins manufactured using more than one functional group (Kiefer & Höll, 2001; Lee & Lee, 2016).

2.4 Summary

The following conclusions of different separation strategies can be drawn from this literature review:

I. The precipitation method used in the hydrometallurgy of copper makes iron partially co-existent with copper in the electrowinning step and results in insoluble solid disposal, which is against the environmental rules. Thus, metallic values must be recovered to comply with the strict environmental regulations and to conserve natural resources.
II. Emulsification is a general problem with solvent extraction and causes the loss of extractants and electrolyte contamination.
III. In the ion-exchange process, resins can be used several times for the separation of metal ions, as it becomes stable after the desorption process.
IV. The advantage of ion exchange resins lies in the flexibility of adding functional groups for particular metals under fixed process conditions.

V. Loading efficiency of different commercial resins but made with analogue functional groups can show different extraction characteristics.

VI. There was no adequate research comparing different functional groups' performance for specific metal separation from highly concentrated pregnant leach solution and under specified pH conditions.

VII. Therefore, this research studied the adsorption properties and selectivity between Fe(III) and Cu(II) at high concentrations using 24 different commercial resins with 14 kinds of functional groups.

CHAPTER 3
Materials and methods

3.1 Materials

Simulated copper leach solution was prepared with 45 g/L of copper and 50 g/L of iron in proportion to the heap leaching of copper ore from the Disele deposit investigated by Lwambiyi et al. (2009) to find the adsorption selectivity of Fe(III) over Cu(II) by selected ion exchange resins. The determined metal concentration was prepared using chemicals of analytical grade, including $CuSO_4$. $5H_2O$ and Fe_2 $(SO_4)_3.5H_2O$ with deionized water. Commercial resin brands like Purolite, Amberlite, Lewatit, Resintech with different functional groups were used. Different concentrations of dilute HCL and NaOH solutions were used to adjust the pH of the solution. Different acid concentration solutions and complexing agent solutions were prepared for the desorption test.

3.2 Resin Preparation

In the experiment, the resin for testing was initially washed with deionized water and kept on a reciprocating platform shaker (Promax 2020, Heidolph Instruments GmbH & Co.KG) for 1 h. Then it was activated with a 15% (v/v) HCl solution with the agitation of 150 rpm for 24 h. Next, the resin was washed two times with DI water at room temperature for 1 h and dried at room temperature for 72 h. At that point, before every adsorption test, the resin's corresponding amount was weighed and kept in a separate 125 mL Erlenmeyer flask with 50 ml DI water for 1 h to allow initial swelling. Lastly, the resin was filtered and made ready to mix with 20 ml simulated copper leach solution for the adsorption test. Table 3 illustrates the summary of ion-exchange resins based on their properties such as functional group, the order of selectivity, particle size, and ion exchange capacity.

3.3 Experimental procedures

The adsorption test of resins was divided into two sets of experiments. In the first set, the main aim was to explore the suitable resins for the adsorption of Fe(III). For this purpose, various amounts of resins with different functional groups were interacted with 20 mL simulated copper leach solution at room temperature and natural pH (i.e., 1.5) for 2 h (René A. Silva et al., 2019). After 2 hours, there were minor changes in adsorption percentages of resins. The resin dosages chosen for the adsorption test were 0.1, 0.2, 0.3, 0.4, and 0.5 g/mL. Initially, the effect of resin dosage was done beyond the maximum limit of 0.5 g/mL. But after 0.5 g/mL, the adsorption percentage of desired metal became slow, and the undesired metals were increasing. The metal concentration before and after the adsorption test was measured using wavelength dispersive X-ray fluorescence spectroscopy (XRF Supermini200, Rigaku Co.). For each point of the adsorption curves, the metal concentrations were measured three times, and then the average results were taken into consideration to get accurate results. The effect of SO_4^- alone on the adsorption test was not examined. The adsorption percentage of a metal by resin was calculated using the following formula:

$$\eta = \frac{Co-C}{Co} \times 100\ \%$$

The ion exchange resin capacity or metals loading per gram of dry resins, Q, can be measured using the following equation:

$$Q = \frac{(Co*Vo)-(C*V)}{m}$$

Where Co and C are the initial and final concentration of iron or copper in adsorption, respectively (g/L); V_0 and V are the initial and final volume of solution respectively (L), usually $V_0 = V$; m is the amount of resin used for adsorption (g). From this result, it was easy to select a suitable resin to use in the second set of experiments. In the second set of experiments, efficient resins with functional groups were systematically tested to find the best iron adsorption conditions under i) different solutions pH, ii) different temperatures, and iii) different adsorption time. For different pH values, 15% (v/v) NaOH and 10% (v/v) HCL were used as the solution pH modifier before contact with resins. The temperature tests were conducted by doing the adsorption test using different temperatures (i.e., 20^o C, 30^o C, 40^o C, 50^o C, and 60^o C). Lastly, the adsorption time test was accomplished by doing adsorption experiments for different adsorption time (i.e., 20 min, 40 min, 60 min, 90 min, and 120 min).

In the elution tests, the loaded resin was rinsed with acid solution using a shaker in a conical flask for a certain period of time (Zhang et al., 2016).

Table 3. Different commercial ion-exchange resins used in this research based on various properties according to technical data provided by manufacturers and as illustrated by Silva et al. (2018)

	Functional group (ionic form)	**Order of selectivity**	**Resin brand**		**Producer**	**Polymeric matrix**	**Particle size [mm]**
1	Amino-phosphonic (Na+)	$Fe^{3+} > Pb^{2+} > Cu^{2+} > Zn^{2+} > Al^{3+} > Mg^{2+} > Ca^{2+} > Cd^{2+} > Ni^{2+} > Co^{2+} > Sr^{2+} > Ba^{2+}$	1	IRC747	Amberlite®	Styrene DVB copolymer	0.52–0.66
			2	TP 260	Lewatit®	Macroporous Crosslinked PS	0.50–0.60
			3	MTS9500 (S950)	Purolite®	Macroporous Crosslinked polymer	0.60–0.85
			4	MTS9400 (S940)	Purolite®	Macroporous PS Crosslinked DVB	0.42–0.85
			5	SIR-500	Resintech	Macroporous styrene with DVB	0.30–1.18
2	Phosphoric acid (Di-2-ethylhexyl-phosphoric acid; D2EHPA)	$Ti^{4+} > Fe^{3+} > In^{3+} > Sn^{2+/4+} > Sb^{3+} > Bi^{3+} > Vo^{2+} > Be^{2+} > Al^{3+} > Zn^{2+} > Pb^{2+} > Cd^{2+} > Ca^{2+} > Mn^{2+} > Cu^{2+} > Fe^{2+} > Co^{2+} > Ni^{2+} > Mg^{2+} > Cr^{3+}$	6	VP OC 1026	Lewatit®	Macroporous styrene with DVB	0.30–1.20
3	Phosphinic acid (Bis-(2,4,4-trimethylpentyl-) phosphinic acid)	$Fe^{3+} > Zn^{2+} > Al^{3+} > Cu^{2+} > Co^{2+} > Mg^{2+} > Ca^{2+} > Ni^{2+}$	7	TP272	Lewatit®	Macroporous Crosslinked PS	0.30–1.60
4	Phosphonic & Sulfonic (H^+)	Selectivity order not reported	8	MTS9570 (S957)	Purolite®	Macroporous Crosslinked polymer	0.55–0.75
5	Iminodiacetic (Na^+)	$Fe^{3+} > Cu^{2+} > Ni^{2+} > Zn^{2+} > Co^{2+} > Cd^{2+} > Fe^{2+} > Mn^{2+} > Ca^{2+} > Mg^{2+}$	9	TP 207	Lewatit®	Macroporous Crosslinked PS	0.40–1.25
			10	TP 208	Lewatit®	Macroporous Crosslinked PS	0.50–0.60
			11	MTS9300 (S930)	Purolite®	Macroporous crosslinked polymer	0.60–0.85
6	Sulfonic (H^+)	Too strong to show specific selectivity	12	IR120	Amberlite®	Styrene DVB copolymer	0.60–0.80
			13	G-26	Dowex®	Styrene with DVB	0.60–0.70

7	Carboxylic (H^+)	$Fe^{2+} > Cu^{2+} > Zn^{2+} > Pb^{2+} > Ti^{2+} > Mn^{2+} > Cd^{2+}$	14	Mac-3	Dowex®	Polymeric, macroporous	0.30–1.20
			15	WACG-HP	Resintech	Acrylic/DVB	0.3–1.20
8	Thiol	Selectivity order not reported	16	MTS9240	Puromet®	Macroporous Crosslinked PS	0.30-1.00
9	Bis-pycolilamine	$Cu^{2+} > Ni^{2+} > Fe^{3+} > Zn^{2+} > Co^{2+} > Cd^{2+} > Fe^{2+} > Mn^{2+}$	17	TP 220	Lewatit®	Macroporous, Styrene DVB copolymer	0.57–0.67
10	Thiourea	$Hg^{2+} > Ag^{+} > Au^{1+/3+} > Pt^{2+/4+} > Cu^{2+} > Pb^{2+/4+} > Bi^{2+} > Sn^{2+} > Zn^{2+} > Cd^{2+} > Ni^{2+}$	18	TP 214	Lewatit®	Macroporous Crosslinked PS	0.50-0.60
			19	MTS9140	Puromet®	Macroporous PS Crosslinked DVB	0.30-1.20
11	Isothiouronium	Selectivity order not reported	20	MTS9200	Puromet®	Macroporous PS Crosslinked DVB	0.30-1.20
12	N-methylglucamine	Selectivity order not reported	21	S108	Purolite®	Macroporous PS Crosslinked DVB	0.42-0.63
13	Amidoxime	Selectivity order not reported	22	MTS9100	Puromet®	Polyacrylic crosslinked with divinylbenzene	0.30-1.20
14	Quaternary Ammonium	Selectivity order not reported	23	4400 Cl	Amberjet®	Styrene DVB copolymer	0.53-0.63
			24	21K XLT	Dowex®	Styrene DVB, gel	0.6-1.2

*PS-polystyrene, DVB- divinylbenzene

CHAPTER 4
Resin adsorption and desorption study

4.1 Resin exploration

Chelating resins containing functional groups of electron donor atoms (e.g., N, P, O, and S) are capable of forming coordination bonds with the targeted metal ions. The selectivity of a resin to a specific metal ion depends on the stability constant of the complex they form. Commercial resins with different functional groups or resins with the same functional groups but from different brands were tested to determine their adsorption selectivity to Fe(III) and Cu(II).

4.1.1 Resins with aminophosphonic groups

Amino-phosphonic resins (also known as amino-methylenephosphonic resins) consist of groups containing phosphorous and nitrogen atoms, which are used in the purification process for copper-nickel sulfate solution. These resins were first synthesized by Kennedy and Ficken in 1956 and then by Manecke and Heller in 1960 (Kennedy & Ficken, 1958; Manecke & Heller, 1960). The significant advantage of these resins is their capability of adsorbing alkaline earth ions from both high concentrated brine solutions and solutions of low concentration, such as less than 0.02 mg/L. Some of the commercial applications of these resins include removing gallium from acidic leach liquors of zinc ores (Jacquin et al., 1987), elimination of zinc and nickel from wastewaters of the plating industry (Leinonen et al., 1994), and separation of antimony from copper electrolytes (Patricio A. Riveros, 2010). Five different commercial ion exchange resins containing aminophosphonic functional groups were tested, that is, Puromet MTS9500 and MTS9400 (previously known as Purolite S950 and S940), Amberlite IRC747, Lewatit TP260, and Resintech SIR-500. All resin brands showed maximum Fe(III) removal at a resin dosage of 0.5 g/mL (see

Figure 5). Excluding Resintech SIR-500, the other four resins brands removed more than 82% of Fe(III). Lewatit TP260 removed the highest amount of Fe(III), 92%.

Although all of these resins have the same functional groups, they showed different Fe(III) loading behaviours. This might be due to unknown structural properties like the synthesis process, cross-linking degree, and average pore size.

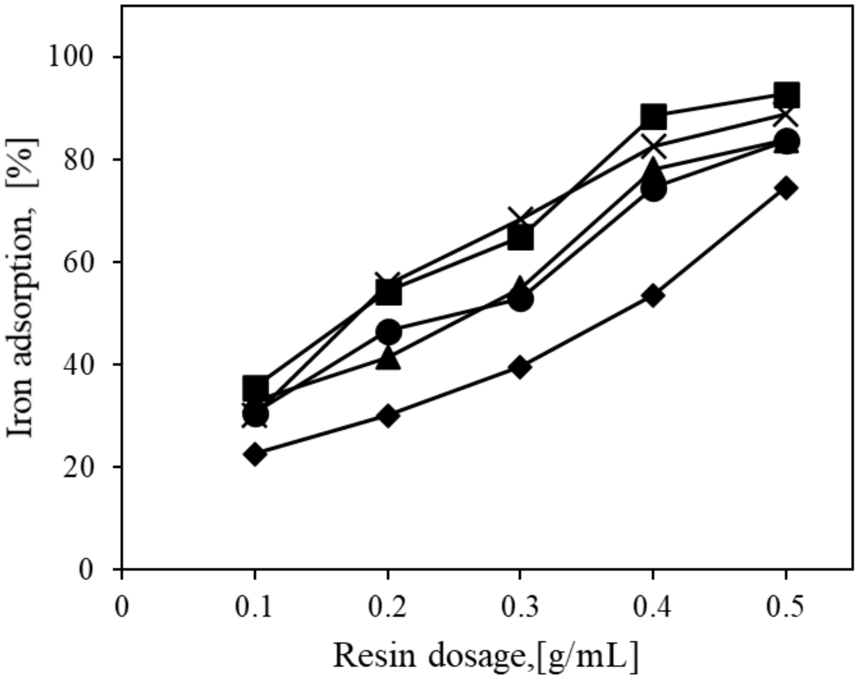


Figure 5. Percentage of (■) Fe adsorption with Lewatit TP260, (●) Fe adsorption with Puromet MTS9500, (▲) Fe adsorption with Puromet MTS9400, (×) Fe adsorption with Amberlite IRC747, and (◆) Fe adsorption with Resintech SIR-500 from simulated copper leach solution.

At the maximum resin dosage of 0.5 g/mL, Resintech SIR-500 obtained the least percentage of Fe(III) removal, 75%. The average loading of Fe(III) was 79.14 mg per gram of dry resin. Both Lewatit TP260 and Amberlite IRC747 obtained around 90% of Fe(III) removal with the highest average loading of 125 mg per gram of dry resin. The other two resins, Puromet MTS9400 and Puromet MTS9500, both achieved 82% of Fe (III) loading.

Compared to the percentage of Fe(III) removal, the resins showed moderate adsorption preferences to Cu(II) (see Figure 6). Maximum Cu(II) recovery was achieved, 60%, using both Lewatit TP260 and Puromet MTS9500 at the resin dosage of 0.5 g/mL, and the highest average loading of Cu(II) was 74 mg per gram of dry resin. Amberlite IRC 747showed 48% Cu(II) recovery and 91% Fe(III) removal at the highest resin dosage. The other two resins, Puromet MTS9400 and Resintech SIR500, both loaded 47% of Cu(II) at the maximum resin dosage of 0.5 g/mL, with the average loading of 78 mg and 62 mg per gram of dry resin, respectively.

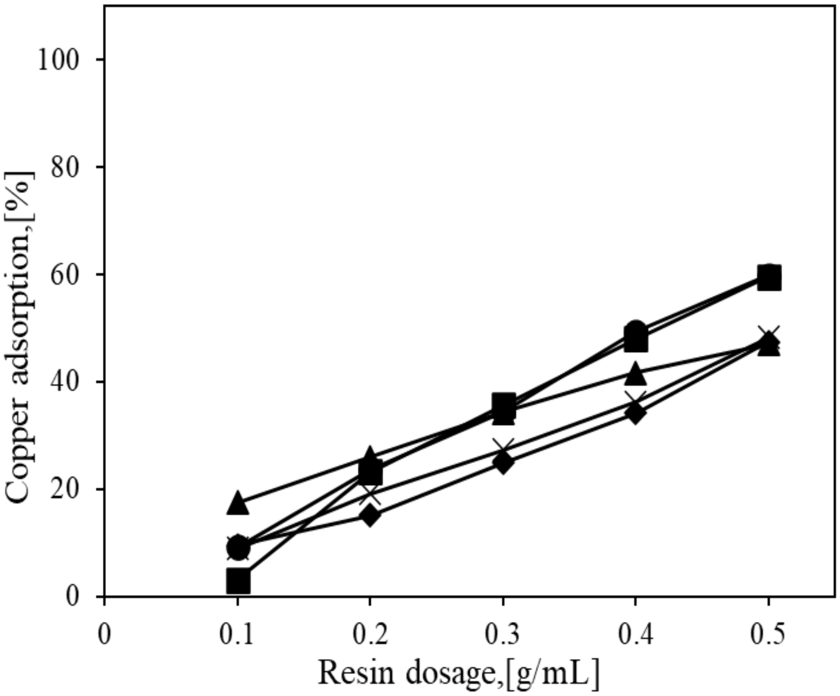


Figure 6. Percentage of (■) Cu adsorption with Lewatit TP260, (●) Cu adsorption with Puromet MTS9500, (▲) Cu adsorption with Puromet MTS9400, (×) Cu adsorption with Amberlite IRC747, and (◆) Cu adsorption with Resintech SIR-500 from simulated copper leach solution.

4.1.2 Resins with phosphoric groups

Solvent Impregnated Resins (SIR) containing Di-2-ethylhexyl-phosphoric acid (a.k.a., D2EHPA) can be produced with the adsorption of organophosphorus extractant into, polymeric macroporous adsorbent Amberlite XAD 2 (Cortina et al., 1994). Generally, the phosphoric acid group shows good selectivity toward metal ions with high oxidation states (Jyo et al., 1996). Therefore, Lewatit VPOC 1026 resin containing D2EHPA extractant was used to separate Fe(III) selectively from the leaching solutions. This resin's total exchange capacity is 13 g Zn/L, which is equivalent to 0.40 eq/L (see Table 3). The Fe(III) removal slowly increased with the increment of resin dosage from 0.1g/mL to 0.5 g/mL. Thus, this resin removed around 15% Fe(III) at the minimum dosage and 45% Fe(III) at the resin's maximum dosage (see Figure 7).

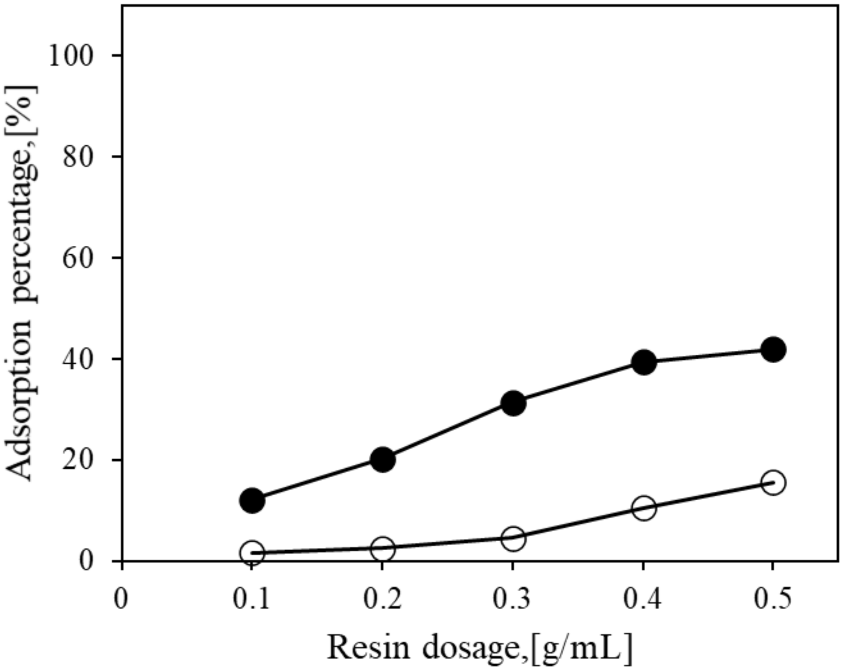


Figure 7. Percentage of (●) Fe and (○) Cu adsorption with Lewatit VPOC1026 containing a phosphoric acid group

However, the Cu(II) loading was very low with the variety of resin dosages. Cu(II) loading was below 10% before the resin dosage of 0.3 g/mL. Maximum Cu(II) loading of only 15% was obtained at the highest resin dosage (see Figure 7). From the observation of this experiment, it was found that the specific gravity of Lewatit VPOC 1026 resin is low. The resin beads tended to come to the surface of the leaching solution. Thus, due to the buoyant characteristic of this resin, there was not adequate resin solution contact at the rated agitation speed. Immersing the resin beads under the solution's surface may help improve the percentage of metal loading.

4.1.3 Resins with phosphinic acid groups

Macroreticular chelating resins containing phosphinic acid groups have high capacity and selectivity for hard Lewis acid cations (see Table 2). The phosphinic acid group containing resins can be used to extract Fe^{3+} from high chloride concentration solutions (Navarro et al., 2009) and Zn^{2+} from solutions containing ions like Cu^{2+}, Cd^{2+}, and Cl^- (Cortina et al., 1995). Lewatit TP 272 is another commercial SIR resin coming from phosphinic acid groups and was used in this experiment. The resin beads of Lewatit TP 272 are microporous cross-linked, containing the extractant bis-(2,4,4-trimethylpentyl-) phosphinate, and are impregnated with the solvent named C 272 (Egawa et al., 1994). Although the beads' density is initially lower than water, the density increases after contacting the leach solution.

The resin loading capacity is specified at 12.5 g Zn/L or 0.40 eq/L (see Table 3). This resin also did not show significant Fe(III) removal with increased resin dosages, like the resins in the phosphoric acid functional group. The percentage of Fe(III) removal started with 12 % at minimum resin dosage, and a maximum of around 42% of Fe(III) removal was obtained at maximum resin dosage (see Figure 8).

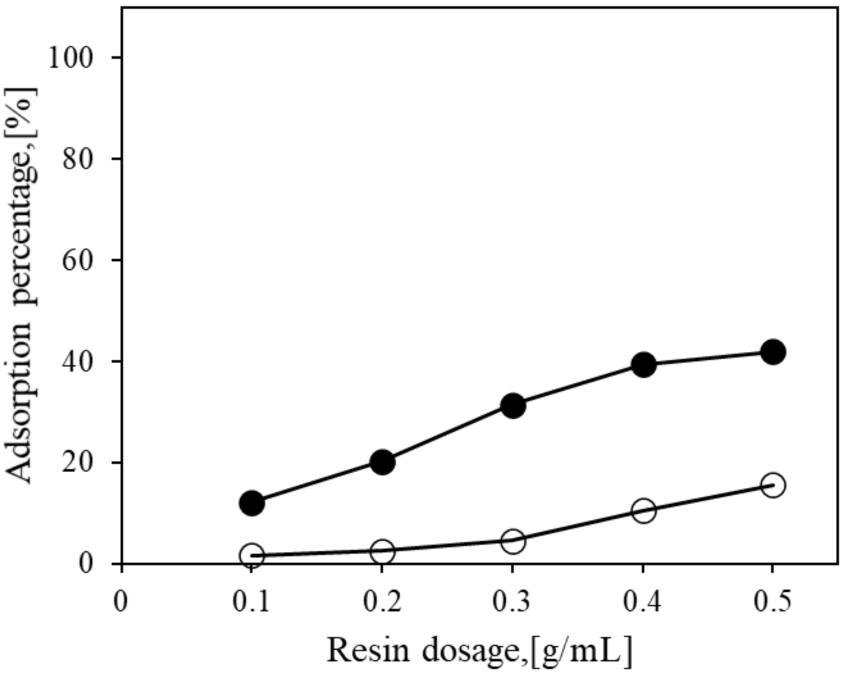


Figure 8. Percentage of (●) Fe and (○) Cu adsorption with Lewatit TP272 containing a phosphinic acid group.

The Cu(II) recovery percentages were almost the same for all resin dosages tested. The maximum Cu(II) loading rate was only around 15% at the resin dosage of 0.5g/mL (see Figure 8). The experiment shows that Lewatit TP 272 is also similar to Lewatit VPOC 1026, as it has a low specific gravity (<1), and its buoyant aspect makes it difficult to have proper contact with a leach solution at the rated agitation speed. Increasing the agitation speed can improve contact between resin and solution, and the percentage of metal loads may increase.

4.1.4 Resins with sulfonic groups

Resins containing sulfonic groups are the strongest cation exchanger resins used for the adsorptions of cations from high concentration solutions. However, their high strength shows no apparent adsorption preference between cations and results in low metal selectivity. The literature review found studies on using resins of these groups in recovering the heavy metals from wastewater (Kocaoba, 2007), and copper recovery from a waste solution (Van Nguyen et al., 2009). The ion exchange capacity of this resin is 2 eq/L (see Table 3). Two commercial ion exchange resins containing sulfonic groups were selected in this research. One is Amberlite IR 120 (Na^+ form), and the other is Dowex G 26 (H^+ form). Both resins showed almost the same percentage of iron removal with the variation of resin dosage, but at the maximum resin dosage, Amberlite IR 120 resin attained 10% more iron reduction than Dowex G 26 (see Figure 9). This result satisfied the findings conducted by Mensah-Biney et al. (1995), who compared the capacity of gold metal loading in ferric sulfate solutions with two forms (Na^+ and H^+) of sulfonic group resins and found that the sulfonic acid groups containing resins with Na^+ form show almost 10% more adsorption than sulfonic acid groups of resins with H^+ form. The reason can be related to the better ionization properties exhibited by the Na^+ form. The same trend was found in the percentage of copper recovery. Amberlite IR 120 resin showed a maximum of 55% copper loading, where Dowex G 26 obtained 47% of copper (see Figure 9).

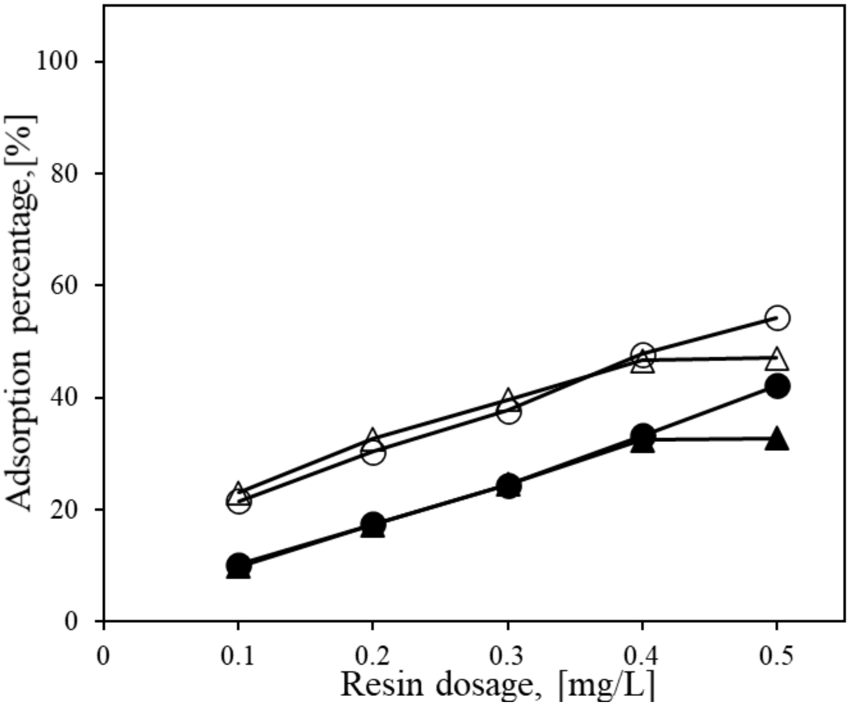


Figure 9. Percentage of (●) Fe and (○) Cu adsorption with Amberlite IR120, (▲) Fe and (△) Cu adsorption with Dowex G26 containing a sulfonic functional group.

Both resins were more selective (i.e., more percentage of metal removal) of copper than iron. On average, 1 g of dry sulfonic groups containing resins can load a maximum of 43 mg of Fe(III) and 62 mg of Cu(II).

4.1.5 Resins with mixtures of phosphonic and sulfonic groups

Resins containing both sulfonic and phosphonic acid groups bonded in a styrene-divinylbenzene polymer network usually show a high attraction for extraction of actinide ions (Horwitz et al., 1993). These resins can also be used to extract Fe (III) and Cr (III) from very acidic solutions (Chiarizia et al., 1993). Compared to other phosphorous based resins, these resins have a dual adsorption mechanism. Sulfonic groups in these resins improve the resin's hydrophilic characteristics and permit the easy access of ions into the polymer network. However, phosphonic acid functional groups in the resins determine the specific selectivity towards targeted metal ions (Horwitz et al., 1992). This hydrophilic characteristic overcomes the buoyancy problems related to other phosphorus-based resins (Chiarizia et al., 1997). Thus, it will make adequate resin electrolyte contact, allowing high percentages of metal removal at a suitable agitation speed. As there are few commercial resins available for this group, only Purolite MTS 9570 (previously known as Purolite S957) resin, containing both phosphonic and sulfonic groups, has been tested in this research. The percentage of iron removal rapidly increased with resin dosage increase, like resins with aminophosphonic functional groups. Iron removal percentage started with 69% at minimum resin dosage and exceeded 80% after the resin dosage of 0.2 g/mL (see Figure 10). A maximum of 99% of Fe(III) was removed with the maximum resin dosage of 0.5g/mL. On average, 1 gram of dry resin loaded 132 mg of Fe(III).

However, the adsorption behaviour of Cu(II) with this resin was not significant. The increment of the percentage of copper loading was slow with the changes of resin dosages. The copper loading rate was 30% at the lowest resin dosage and around 54% at the highest resin dosage, when 51 mg Cu(II) was loaded with 1g of dry resin (see Figure 10).

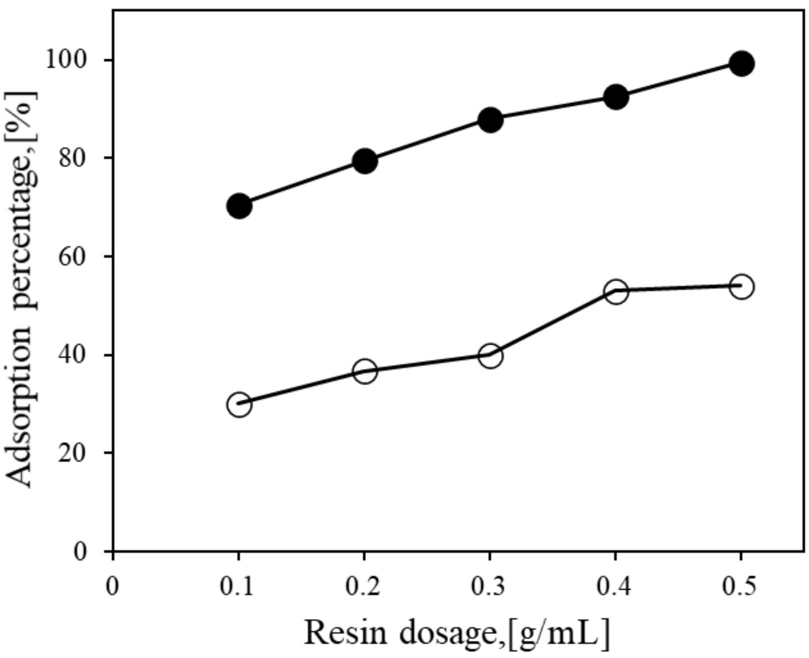


Figure 10. Percentage of (●) Fe and (○) Cu adsorption with Puromet MTS9570 containing mixtures of a phosphonic and a sulfonic acid group.

4.1.6 Resins with iminodiacetic groups

Iminodiacetate resins are chelating resins with functional groups consisting of two carboxylic groups and one nitrogen as the central atom. Iminodiacetic acid acts as a tridentate chelating species in the complexation reactions. It is used to form acid-based cation exchange resin, introduced as chloromethylated styrene–DVB co-polymeric resin. Major commercial applications of these resins include heavy metals removal from industrial wastewater (Ling et al., 2010; Misra et al., 2011) and recovery of Ni(II) and Cr(III) from aqueous solutions (Gode & Pehlivan, 2003; Leinonen & Lehto, 2000). Three different commercial ion exchange resins containing the iminodiacetic acid functional group were tested: Lewatit MP TP 207, Lewatit MDS TP 208, and Puromet MTS 9300 (previously known as Purolite S 930). This resin's ion exchange capacity varies from 0.9 to 2.9 eq/L (see Table 3). The percentage of Fe(III) removal achieved using two resins (Lewatit MP TP 207 and Lewatit MDS TP 208) with the resin dosage variation was similar. Lewatit MP TP 207 and Lewatit MDS TP 208 removed 18% and 19 % Fe(III), respectively, with the minimum resin dosage, and the maximum removal percentage of Fe(III) was 71 % by Lewatit MP TP 207 (see Figure 11). The average Fe(III) loading was 84 mg for Lewatit MP TP 207 and 81 mg for Lewatit MDS TP. Puromet MTS 9300 achieved the highest percentage of Fe(III) removal among these three resins. The maximum Fe(III) removal percentage was 78% with 0.5 g/mL resin dosage, where the average loading was 86 mg per gram of dry resin.

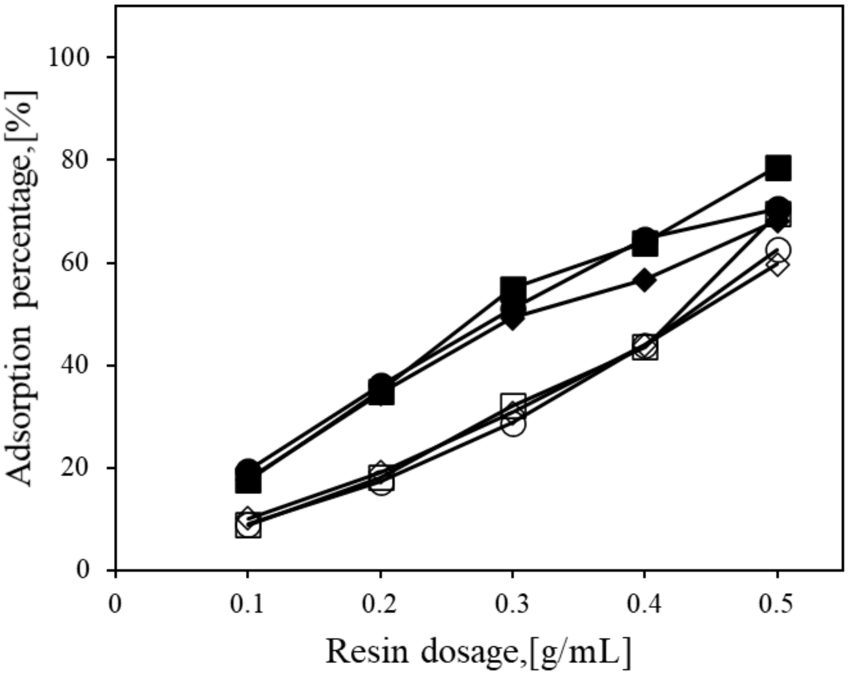


Figure 11. Percentage of (●) Fe and (○) Cu adsorption with Lewatit TP207, (■) Fe and (□) Cu adorption with Puromet MTS9300, and (◆) Fe and (◇) Cu adsorption with Lewatit TP208 containing iminodiacetic acid groups.

The Cu(II) adsorption behaviour was very similar to that of iron. All three resins showed a good percentage of copper recovery with the variation of resin dosage. The maximum Cu(II) co-loading by Lewatit MP TP 207 and Lewatit MDS TP 208 was 63%, and 60% at the highest condition tested, with an average loading of 45 mg and 47 mg of Cu(II) per gram of dry resin, respectively (see Figure 11). The maximum percentage of Cu(II) recovery was 69 %, with the average loading of 48 mg Cu(II) per gram of dry resin using Puromet MTS 9300.

4.1.7 Resins with carboxylic acid groups

There are only a few resins available based on oxygen-containing carboxylic groups. Resins with carboxylic groups are one of the common WCR used in different commercial applications. Major applications include water softening and treatment and recovery of metals from wastewater (Dąbrowski et al., 2004). Other applications include the removal of heavy metals from industrial wastewater (Kaušpėdienė et al., 1998). Two commercial resins, containing carboxylic groups, Dowex Mac 3 and Resintech WACG, are tested in this research. Both these resins have an ion exchange capacity between 3.8 and 4 eq/L (see Table 3). The Fe(III) removal proportionally increased with the increment of resin dosage from 0.1 g/mL to 0.5 g/mL.

Dowex Mac 3 removed a maximum of 46% Fe(III) with the highest resin dosage and 15 % Fe(III) with a minimum resin dosage (see Figure 12). Resintach WACG showed a little more percentage of Fe(III) removal, and at the highest resin dosage, it showed a maximum of 50% Fe(III) removal.

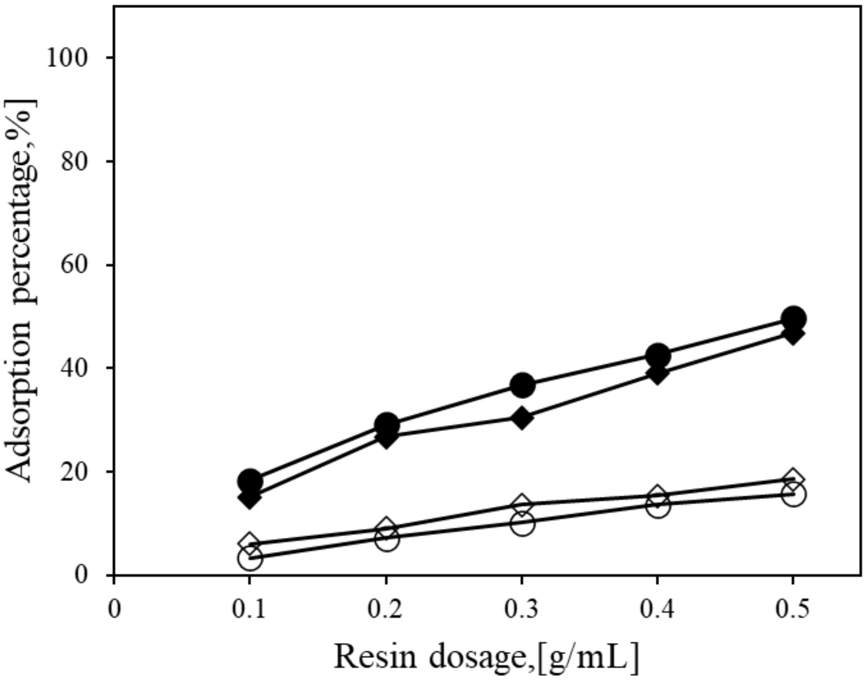


Figure 12. Percentage of (●) Fe and (○) Cu adsorption with Resintech WACG, (▲) Fe and (△) Cu adsorption with Dowex Mac 3 containing a Carboxylic acid functional group.

Conversely, a slight variation of the percentage of Cu(II) recovery occurred with resin dosage changes. Only 18% and 15% Cu(II) were recovered using Dowex Mac 3 and Resintach WACG, respectively (see Figure 12). On average, resins with carboxylic acids loaded around 65 mg of Fe(III) and 43 mg of Cu(II) per gram of dry resin. Multiple adsorption stages with the highest resin dosage can be an excellent strategy to achieve more percentage of Fe(III) removal.

4.1.8 Resins with thiol groups

Metal ions of soft Lewis acids have a high affinity towards soft Lewis bases like thiol groups. This soft acid-base interaction creates the opportunity to form coordinate covalent bonds that eliminate the risk of mixing polluted metals into purified water. Thiol groups can be incorporated into different substrates, such as ceramics, biomagnetic particles, poly(methyl methacrylate), silica, alumina, and carbon nanotubes (Xia et al., 2017). The literature review found significant amounts of heavy metals such as Hg^{2+}, Pb^{2+}, and Ag^{+} can be removed from aqueous solutions using resins containing thiol groups (Li et al., 2011). Additionally, thiol groups can be used for base metals production following the order of selectivity. However, after the adsorption process of precious metals, the recuperation of adsorbed metals becomes difficult, which leads to the use of a sufficient amount of organic diluent (Iglesias et al., 1999).

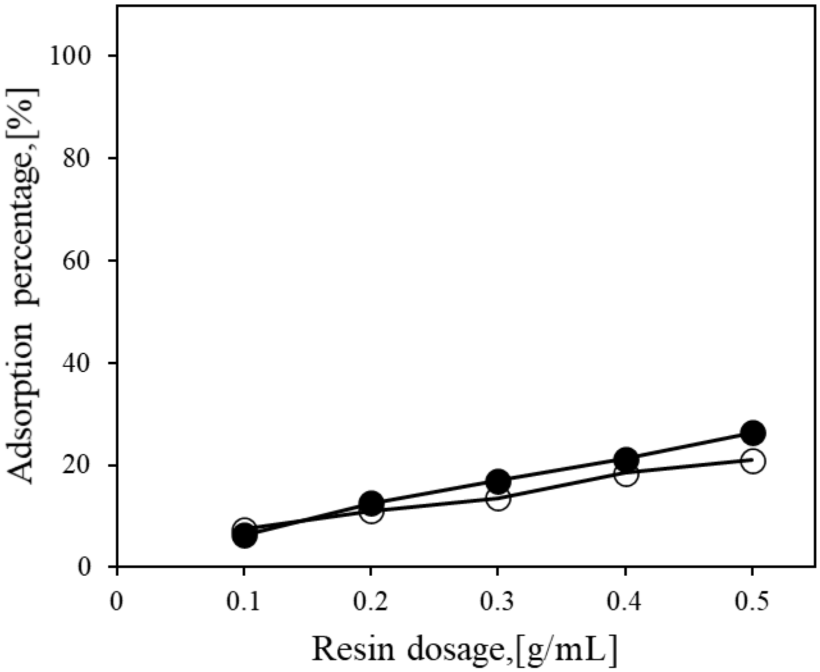


Figure 13. Percentage of (●) Fe and (○) Cu adsorption with Puromet MTS9240 resins containing Thiol groups.

Puromet MTS9240 (previously known as Purolite S924) resin containing thiol groups was used in this experiment. It loaded a maximum of only 26% Fe(III) at the highest resin dosage, i.e., 0.5g/mL (see Figure 13). There was small changes in the percentage of Fe(III) removal with the variation of resin dosage from 0.1 g/mL to 0.5g/mL. On average, Puromet MTS9240 loaded 28 mg of Fe(III) per gram of dry resin.

Similarly, the scenario of Cu(II) recovery with the resin dosage was similar, and a maximum of 21% Cu(II) was loaded with the use of Puromet MTS 9240 resin (see Figure 13). On average, 23 mg of Cu(II) was loaded by 1 gram of dry resin.

4.1.9 Resins with bis-pycolylamine or 2- (aminomethyl) pyridine groups

Chelating resins of WARs with nitrogen donor atoms exhibit much better properties than other commonly used chelating groups. They provide significant opportunities related to metal removal, separation, preconcentration, and purification from solid waste, wastewater, etc. Most significantly, this type of resin has a high exchange of loading capabilities at very low pH, i.e., highly acidic conditions (pH < 2) compared to other commercial resins (Sengupta et al., 1991). Wołowicz and Hubicki (2012) studied the selective recovery of noble and base metals from acidic solutions using resins with this group, and noble metals showed better results than base metals. Among base metals, copper showed more selectivity.

Lewatit TP 220 resin, containing bis-pycolylamine groups, was tested in this research. Results showed that this is one of the resins which led to significant adsorption preferences to Cu(II) over Fe(III). Lewatit TP 220 resin did not obtain more significant Fe(III) removal from the solution than other resins containing aminophosphonic and iminodiacetic acid groups. Maximum 48% Fe(III) removal was possible at the highest resin dosage (see Figure 14), at which Lewatit TP 220 loaded 66 mg of Fe(III) per gram of dry resin.

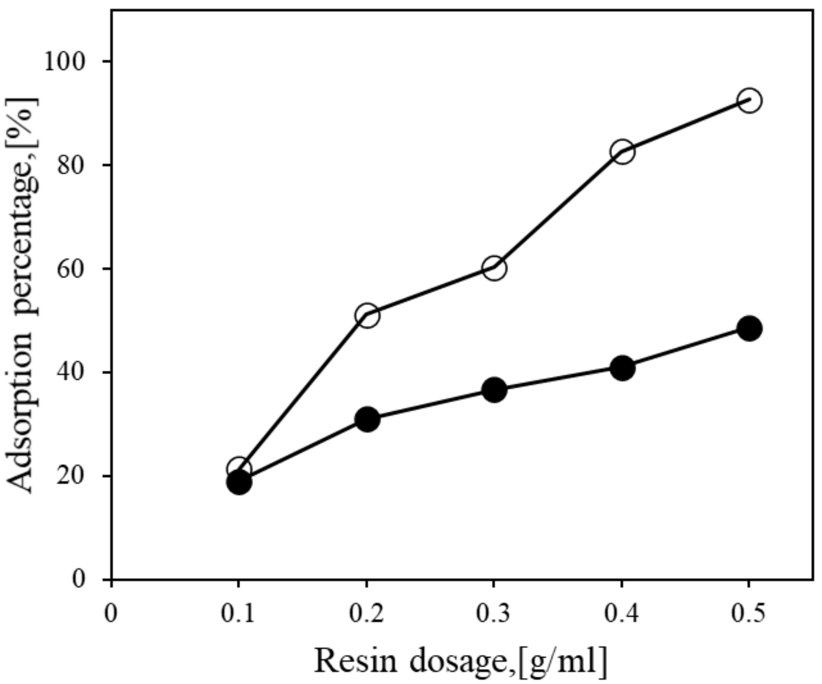


Figure 14. Percentage of (●) Fe and (○) Cu adsorption with Lewatit TP220 resins containing bis-pycolylamine groups.

Conversely, copper loading accelerated with a resin dosage increment from 0.1 g/mL to 0.5 g/mL. Lewatit TP 220 showed a minimum of 21% Cu(II) recovery with the lowest resin dosage and a maximum of 92% Cu(II) recovery with the highest resin dosage (see Figure 14)), when the resin showed 96 mg of Cu(II) recovery per gram of dry resin used in the solution.

4.1.10 Resins with thiourea and isothiouronium groups

According to the hard and soft acids and bases theory (HSAB), functional groups containing S and N donor atoms prefer to interact with soft bases, which was the basis to develop such chelating resins bearing S and N atoms. Chelating resins containing thiourea and its conjugate thiouronium groups are anion exchangers with S and N donor atoms, which have been used to separate platinum group metals (PGMs) from mixtures of base metals (Birinci et al., 2009; Fieberg et al., 1980).

These groups show better selectivity than thiol groups to mercury, gold, silver, and other PGM ions.

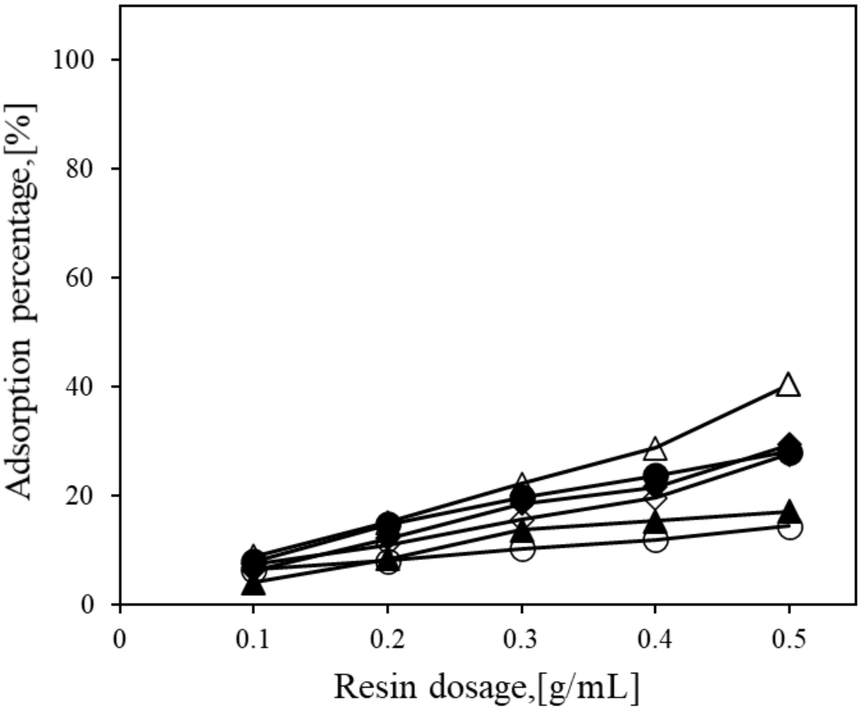


Figure 15. Percentage of (●) Fe and (○) Cu adsorption with Puromet MTS9200, (▲) Fe and (△) Cu adsorption with Puromet MTS9140, (◆) Fe and (◇) Cu adsorption with Lewatit MP TP214 containing thiourea and isothiouronium groups.

Lewatit MP TP214 and Puromet MTS9140 are two resins containing thiourea functional groups that were employed in this research. Neither of these resins showed significant Fe(III) removal from the synthetic solution. Lewatit MP TP214 loaded only 29% of Fe(III), and Puromet MTS9140 achieved less than 20% of Fe(III) removal from the solution. Also, Puromet MTS9200 resin with isothiouronium groups showed a similar low percentage of Fe(III) removal (see Figure 15). Resins with thiourea groups loaded less than 30 mg of Fe(III), while resin with isothouronium groups loaded 34 mg of Fe(III) per gram of dry resin.

The loading of Cu(II) with the variation of resin dosage demonstrated a similar trend. Lewatit MP TP214 resin obtained only 28% of Cu(II), and Puromet MTS9200 loaded less than 15% of Cu(II) at the highest resin dosage. Nevertheless, Puromet MTS9140 resin loaded a maximum of 40% of Cu(II) at the resin dosage of 0.5g/mL, which was a little higher than the percentage of Fe(III) removal (see Figure 15). On average, a maximum of 58 mg of Cu(II) per gram of dry resin was loaded by resins with thiourea configurations,40 mg of Cu(II) was loaded per gram of dry resin by isothiouronium groups.

4.1.11 Resins with glucamine groups

Resins containing glucamine groups are classified as weak anion exchangers, and are used in many commercial applications. These resins are used mainly for boron removal from drinking water and industrial wastewater treatment (Kabay et al., 2007). Studies showed that ion-exchange resins containing glucamine groups enhance arsenate retention as $H_2AsO_4^-$ at pH 4–6, showing increased arsenate selectivity, even in the presence of sulfate ions, relative to strong base anion-exchange resins (Dambies et al., 2004). They can also be used for the adsorption and recovery of molybdenum and vanadium (Polowczyk et al., 2017).

In contrast, this resin removed more than 75% of Fe(III) at the highest resin dosage condition (see Figure 16). On average, the resin loaded 64 mg of Fe(III) per gram of dry resin. The percentage of Cu(II) loading with the variation of resin dosage was negligible, i.e., less than 10% until the resin dosage of 0.3 g/mL was reached (see Figure 16). A maximum of 31% of Cu(II) was loaded from the solution using the highest resin dosage. On average, Cu(II) loading was two times less than for Fe(III), i.e., 25 mg per gram of dry resin.

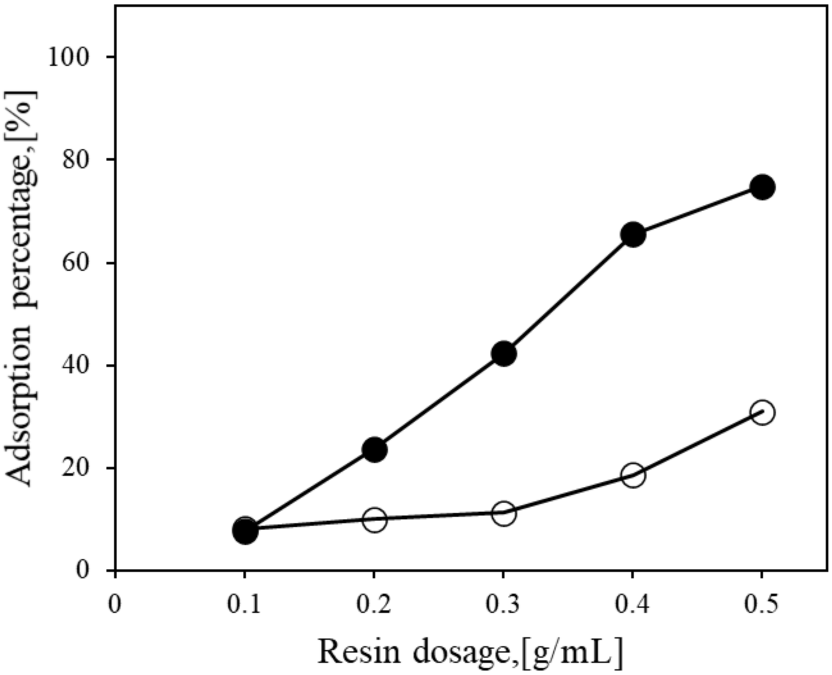


Figure 16. Percentage of (●) Fe and (○) Cu adsorption with Purolite S108 resins containing glucamine groups.

4.1.12 Resins with amidoxime groups

Oximes, an essential class of chelating agents, are extensively used for the separation and spectrophotometric determination of various metal ions. Many forms of oximes have been produced experimentally and commercially, such as hydroxy, ketoxime and aldoxime, etc. The relative selectivity and capacity of different types of oximes are mainly related to the nature of the polymer backbone (Ebraheem & Hamdi, 1997). It is understood that amidoxime groups form stable bidentate complexes with trivalent cations such as Ga, Cr, Fe, and other bivalent cations like Cu, Pb, and U(VI). Besides, they are efficient extractants for REE (rare earth elements) from solutions for their ability to make the most substantial complexes with oxygen donor ligands (Wood & Williams-Jones, 1994). The number of commercial resins containing amidoxime functional groups is scarce. Duolite ES-346 is a very familiar resin containing this group used in the market earlier. While alkali and alkali earth metals show low selectivity to this resin, other metals represent different selectivity patterns. The literature review says that chelating resins containing amidoxime groups can be used to recover uranium from seawater (Lieser et al., 1987) and adsorption of copper, zinc, and lead from the aqueous solutions (Ferreira et al., 1998).

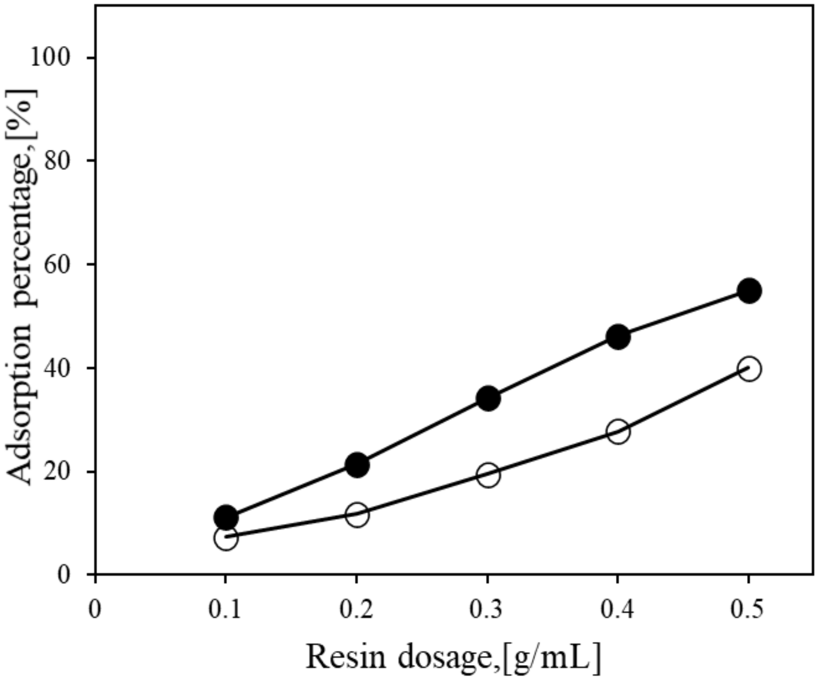


Figure 17. Percentage of (●) Fe and (○) Cu adsorption with Purolite MTS9100 resin containing amidoxime groups.

In this research, Purolite MTS9100 (the industrial equivalent to Duolite ES 346 and Dianion CR-50) resin containing amidoxime groups with an ion exchange capacity of 1.26 eq/L(see Table 3) was tested. The results showed consistency in the increment of Fe(III) removal with a resin dosage increase. The maximum 54% Fe(III) loading was obtained with the maximum resin dosage of 0.5g/mL (see Figure 17). The loading trend of Cu(II) was similar, but a bit slower, and the maximum of 40% of Cu(II) was obtained with the use of the highest resin dosage (see Figure 17).

On average, Puromet MTS9100 loaded 56 mg of Fe(III) and 31.22 mg of Cu(II) per gram of dry resin.

4.1.13 Resins with quaternary ammonium groups

Resin with quaternary ammonium groups is one of the most common ion exchange resins. It is mostly used as SAR in commercial applications. Mainly, it is used to extract precious and base metals in cyanide forms from alkaline leach solutions. The characteristics of a higher amount of metal removal, a high percentage of elution, and physicochemical stability can mitigate the high cost of resins (Breguncci et al., 2001). Resins containing quaternary ammonium groups are advised to be used for purification from the liquid solution. Otherwise, the selectivity of resins to target metal ions in a multi-ionic metal solution is reduced because of their high strength (Dai et al., 2010). Commercial application of these resins includes selective adsorption of the gold-cyanide complex ion ($Au(CN)_2^-$), silver-cyanide complex ion ($Ag(CN)_2^-$), and other base metal cyanide species (Kotze et al., 2005; Ok & Jeon, 2014).

Amberjet 4400 Cl and Dowex 21K XLT are the two resins containing quaternary ammonium functional groups tested in this research. Both resins have an ion-exchange capacity of around 1.40 eq/L (see Table 3). The variation of Fe(III) removal with the resin dosage change was almost the same for the two resins tested. A maximum of 40% Fe(III) was removed using the highest resin dosage of 0.5 g/mL(see Figure 18). A maximum of 54 mg of Fe(III) was loaded per gram of dry resin for these two resins on average.

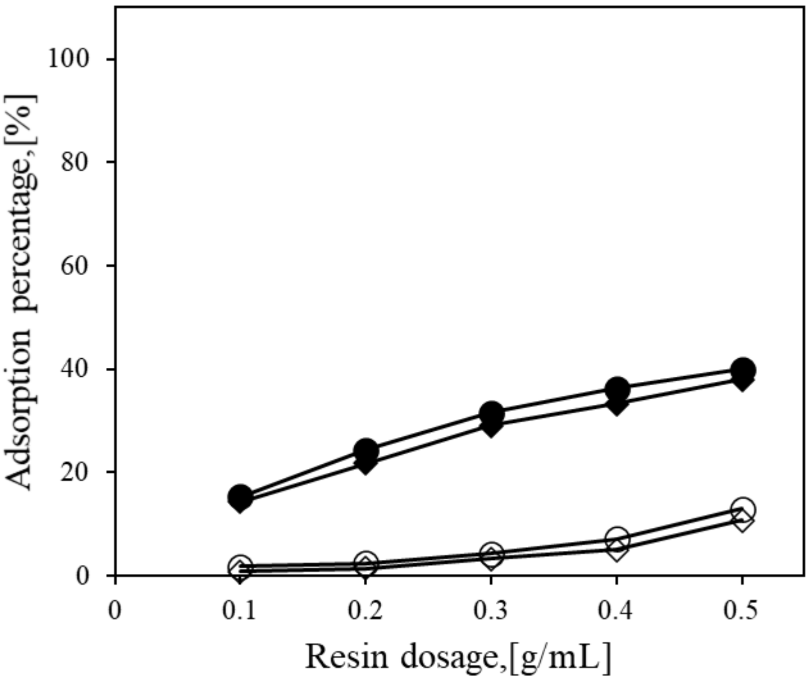


Figure 18. Percentage of (●) Fe and (○) Cu adsorption with Dowex 21K XLT, (▲) Fe and (△) Cu loaded on Amberjet 4400 Cl containing a Carboxylic acid functional group.

Similarly, the percentage of Cu(II) loading change with resin dosage was also close for these two resins. The Cu(II) recovery was almost negligible for all resin dosages (see Figure 18). A maximum of 13% Cu(II) was recovered using the highest resin concentration, i.e., 0.5 g/mL. On average, only 8 mg of Cu(II) was loaded per gram of dry resin using these two resins. As the Cu(II) recovery was negligible at maximum resin dosage, compared to Fe(III) removal, multiple stages of adsorption may realize the possibility of obtaining a good percentage of Fe(III) removal.

4.2 Selection of resins for the single factor optimization tests

Both iron and copper loading percentages increased with the increasing dosage of the resins. High resin dosage means more area is available on the resin surface for the adsorption of metal ions. When limited availability exists, one metal may be preferentially adsorbed. Based on these exploration tests, Puromet MTS9400, Puromet MTS9500, and Lewatit MP TP260 resins containing aminophosphonic groups and Puromet MTS9570 resin containing a combination of phosphonic and sulfonic acid groups were selected for single factor optimization tests to selectively adsorb Fe(III) over Cu(II) from solution. However, Lewatit MP TP220 resin with bis-picolylamine groups was chosen to recover Cu(II) from the leach solution.

4.2.1 Effect of pH on metal loading

The pH value is one of the significant impact factors during the adsorption process, affecting the metal ions binding to the resin surface. Variation in pH can affect metals' adsorption or selectivity with metals' activation/deactivation to resins’ surface. The difference in pH can change the solubility of metal species and precipitates form to allow a pH of solution of more than the maximum limit, which creates uncertainty about the resin performance's reliability. Fig. 19 and Fig. 20 demonstrate the influence of solution pH on resin adsorption efficiency under the experimental conditions of a resin dosage of 0.5 g/mL, temperature of 20^0 C, and adsorption time of 2.0 h. The solution pH effect showed fluctuation in Fe(III) loading and Cu(II) loading. Our objective in this research is to obtain either the highest Fe(III) removal with lowest Cu(II) recovery or highest Cu(II) recovery with lowest Fe(III) removal, using resins from the synthetic leach solution.

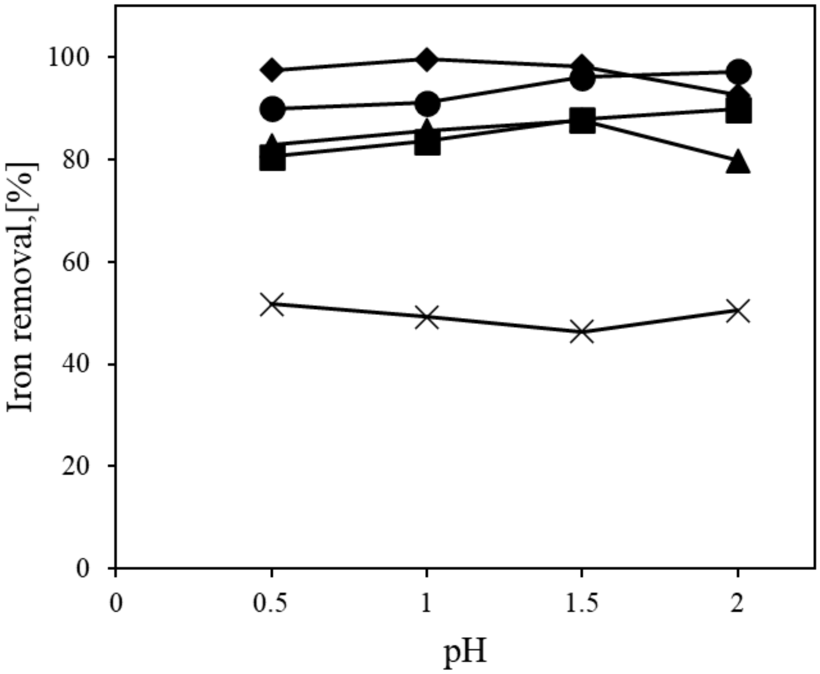


Figure 19. Effect of pH on the loading of Iron by IEx resins with (■) Fe loaded on Puromet MTS9400, (▲) Fe loaded on Puromet MTS9500, (◆) Fe loaded on Lewatit TP260, (●) Fe loaded on Puromet MTS9570, and (×) Fe loaded on Lewatit TP220.

Resins with aminophosphonic groups and mixtures of phosphonic and sulfonic groups showed the best scenario at pH 1.5, except for Lewatit TP260 and Puromet MTS9400(see Figure 19 and Figure 20). Lewatit TP260 obtained 97% of Fe(III) and 49% of Cu(II) at pH 1.0, which gave the best combination of metals loading. At pH 1.5, Puromet MTS9570 loaded 99.5 % of Fe(III) with 50% of Cu(II), and Puromet MTS9500 achieved 88% loading of Fe(III) with 57% of Cu(II) recovery. Puromet MTS9400 achieved the best result at pH 2.0 with 87% of Fe(III) removal and 43% Cu(II) recovery. The copper selective resin Lewatit TP220 containing bis-picolylamine groups showed 94% of Cu(II) and 46% of Fe(III) loading at pH 1.5, which is the most expected result among the pH values tested here.

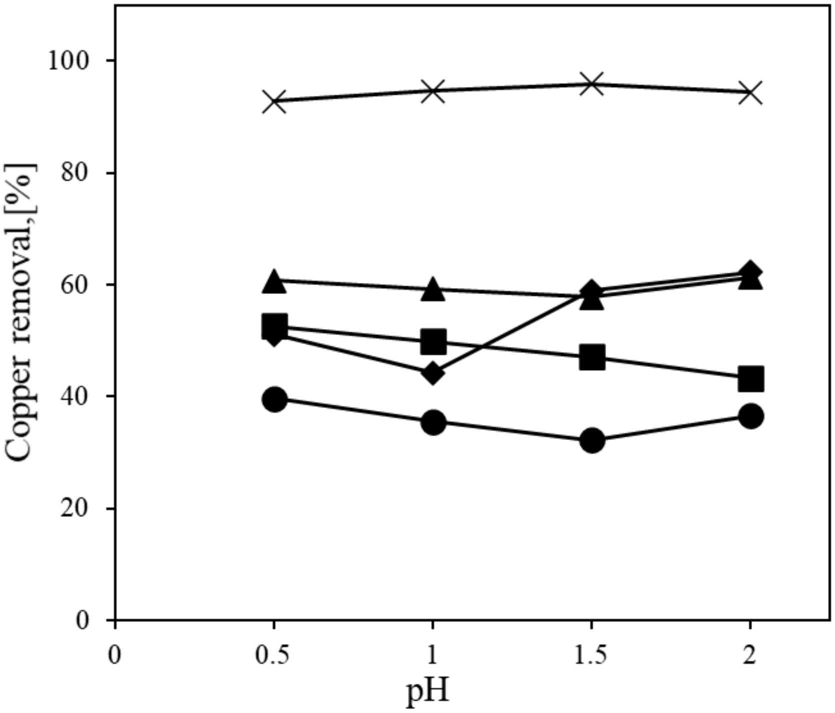


Figure 20. Effect of pH on the loading of Copper by IEx resins with (■) Cu loaded on Puromet MTS9400, (▲) Cu loaded on Puromet MTS9500, (◆) Cu loaded on Lewatit TP260, (●) Cu loaded on Puromet MTS9570, and (×) Cu loaded on Lewatit TP220.

4.2.2 Effect of adsorption time on metal loading

Experiments were carried out under the conditions of resin dosage of 0.5g/mL, pH of 1.5, and a temperature of 20^0 C. With the increase of adsorption time, the loading of both Fe(III) and Cu(II) increased (see Figure 21 and Figure 22). However, there was not much change in Fe(III) and Cu(II) loading with time variation. Puromet MTS9570 resin with a combination of phosphonic and sulfonic functional groups loaded a maximum of 99% of Fe(III) and 51% of Cu(II) at an adsorption time of 2 h. The rate of increase of Cu(II) loading was more than Fe(III) loading with the change of time using resins of aminophosphonic functional groups, except for Puromet MTS9400.

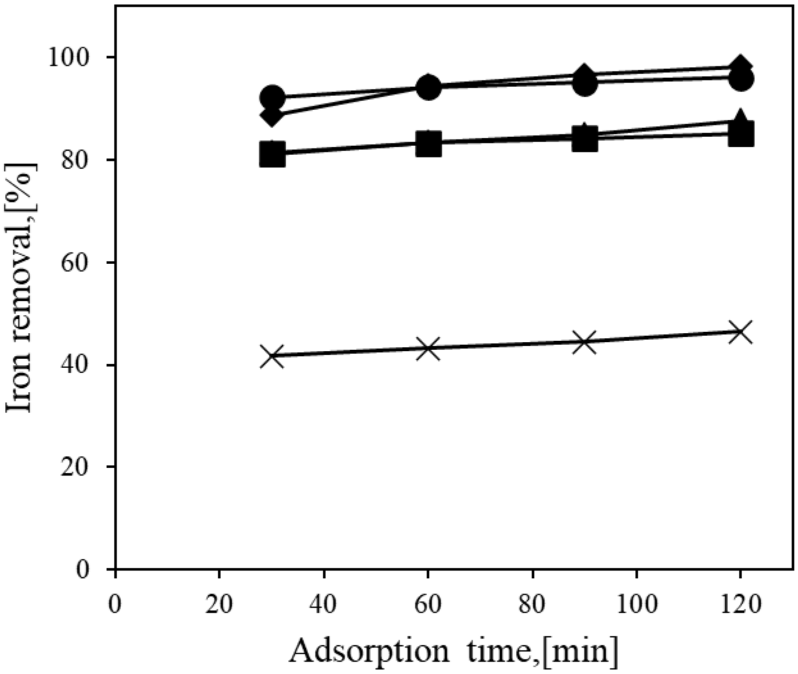


Figure 21. Effect of adsorption time on the loading of Iron by IEx resins with (■) Fe loaded on Puromet MTS9400, (▲) Fe loaded on Puromet MTS9500, (◆) Fe loaded on Lewatit TP260, (●) Fe loaded on Puromet MTS9570, and (×) Fe loaded on Lewatit TP220.

Puromet MTS9400 showed almost the same behaviour for the loading of Cu(II) and Fe(III) with the increment of adsorption time. The removal percentage of Fe(III) was increased by 6% using Puromet MTS9500 with the change of adsorption time from 30 min to 120 min, when the Cu(II) recovery percentage increased by 10%. Similarly, the Fe(III) removal and Cu(II) recovery percentages were increased by 6% and 12%, respectively, with the increment of adsorption time from 30 min to 120 min, using Lewatit TP260. The only copper selective resin, Lewatit TP220, showed almost consistent behaviour to Fe(III) and Cu(II) loading with time variation. Preliminary experiments were conducted for up to 24 h, but the adsorption efficiency after 2 h was negligible. Therefore, it was assumed that the resin and solution had reached equilibrium in 2 h.

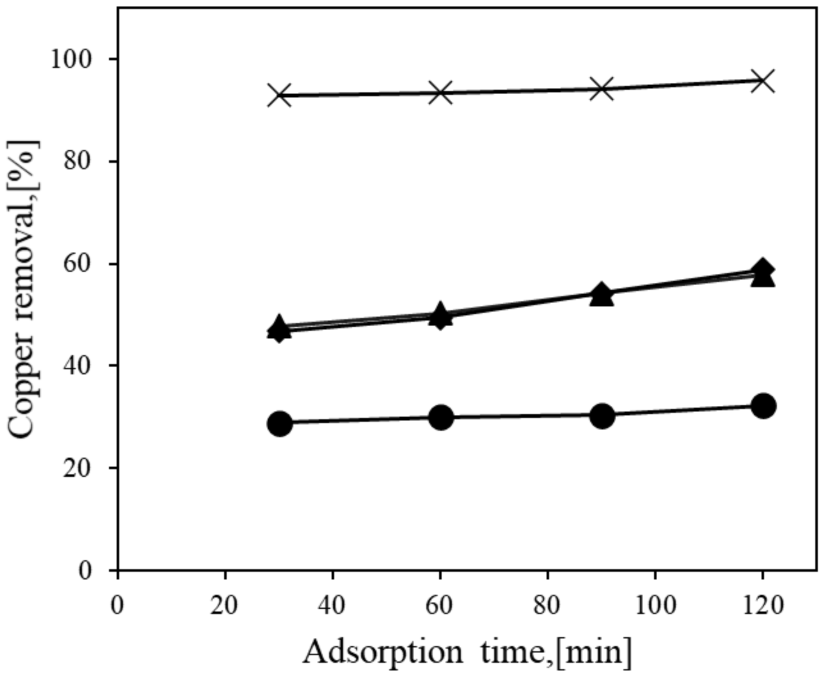


Figure 22. Effect of adsorption time on the loading of Copper by IEx resins with (■) Cu loaded on Puromet MTS9400, (▲) Cu loaded on Puromet MTS9500, (◆) Cu loaded on Lewatit TP260, (●) Cu loaded on Puromet MTS9570, and (×) Cu loaded on Lewatit TP220.

4.2.3 Effect of temperature on metal loading

Experiments were carried out under the conditions of resin dosage of 0.5 g/mL, pH 1.5, and an adsorption time of 2 h. Different resin brands showed different behaviour with temperature variation (see Figure 23 and Figure 24). Puromet MTS9570 resin with a mixture of phosphonic and sulfonic functional groups showed the same action for Fe(III) and Cu(II) loading with the temperature change. There is a constant line to the adsorption curve of both Fe(III) and Cu(II) for this resin. Except for Lewatit TP260, the other two brands of resins with aminophosphonic functional groups showed the same behaviour. Puromet MTS9500 and Puromet MTS9400 presented the same tendency as for both Fe(III) and Cu(II) loading with temperature variation. In these two resins, with the increase of temperature, the Fe(III) loading increased, and the loading of Cu(II) decreased. Puromet MTS9500 achieved 90% of Fe(III) and 48% of Cu(II) loading; Puromet MTS9400 loaded 90% of Fe(III) and 41% of Cu(II) at the adsorption temperature of 60^0C.

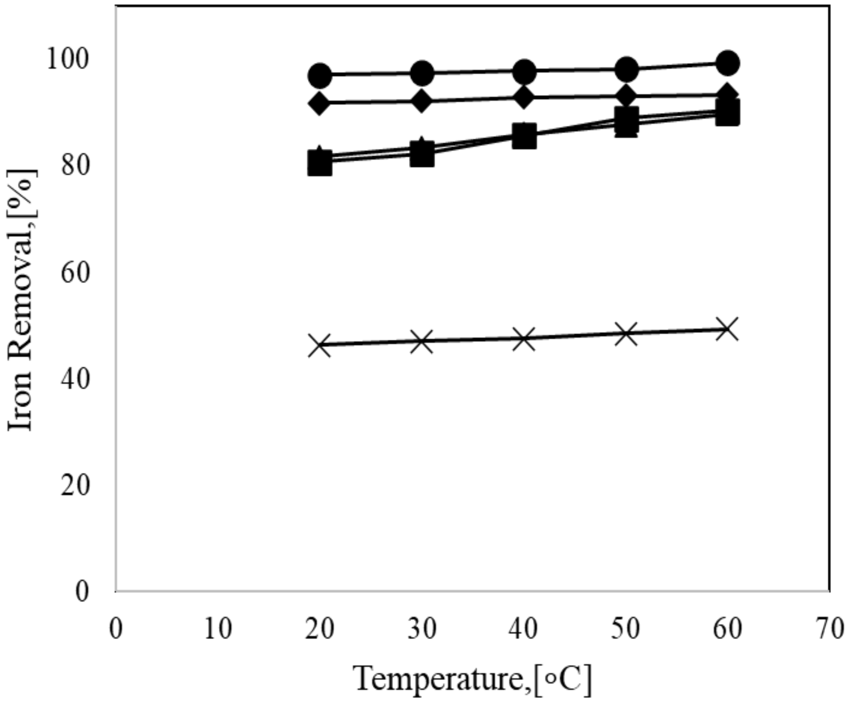


Figure 23. Effect of temperature on the loading of Iron by IEx resins with (■) Fe loaded on Puromet MTS9400, (▲) Fe loaded on Puromet MTS9500, (◆) Fe loaded on Lewatit TP260, (●) Fe loaded on Puromet MTS9570, and (×) Fe loaded on Lewatit TP220.

Lewatit TP260 did not show a significant difference in Fe(III) and Cu(II) loading with the change of adsorption temperature. Lewatit TP220 resin with bis-pycolylamine groups also showed the same tendency as Fe(III) and Cu(II) loading with the temperature variation.

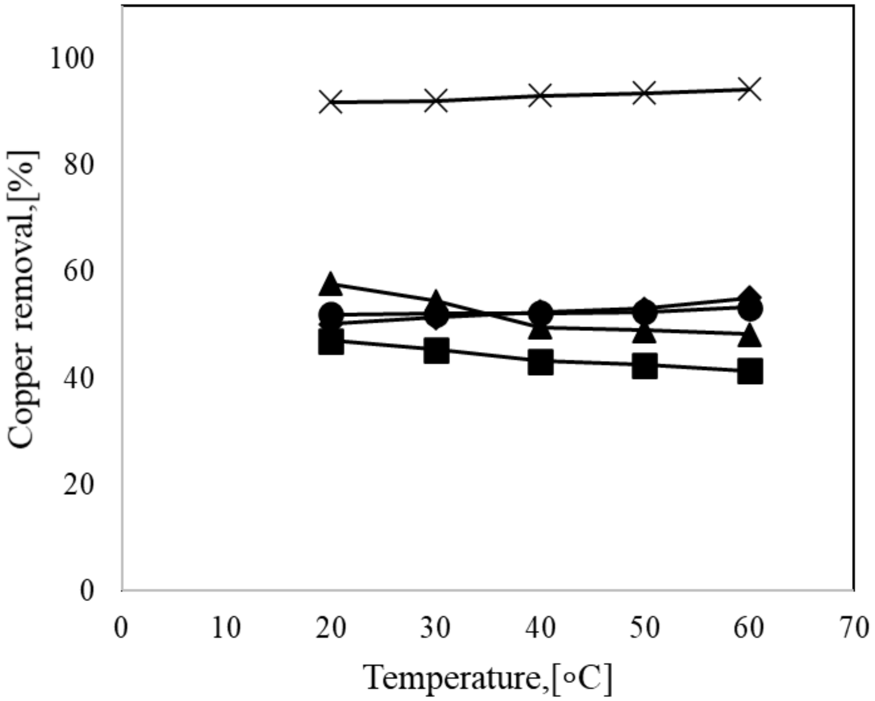


Figure 24. Effect of temperature on the loading of Copper by IEx resins with (■) Cu loaded on Puromet MTS9400, (▲) Cu loaded on Puromet MTS9500, (◆) Cu loaded on Lewatit TP260, (●) Cu loaded on Puromet MTS9570, and (×) Cu loaded on Lewatit TP220.

4.3 Elution test

Based on the adsorption test results, resins with an aminophosphonic functional group and a mixture of phosphonic and sulfonic functional groups showed better results regarding the highest Fe(III) removal with less Cu(II) loading. However, only resin Puromet MTS9570, with a mixture of the phosphonic and sulfonic groups, was selected to do further desorption study, as it showed around 90% Fe(III) removal with 40% Cu(II) loading at the resin dosage of 0.3 g/mL, compared with 92% of Fe(III) removal with 60% of Cu(II) loading by the resin with aminophosphonic functional group at maximum resin dosage. For this iteration, two-stage elution was conducted.

4.3.1 First stage elution-unloading of copper from resin

In the first elution stage, 15 g of loaded resin Puromet MTS 9570 with 88 mg/g iron and 36 mg/g copper was rinsed with sulfuric acid solutions of different concentrations to strip copper from loaded resin. As a result, 40 mL of 10%, 1%, 0.5%, and 0.1% sulfuric acid solutions were used each time to rinse the resin for 1 hour. Based on the analyses of iron and copper concentrations in rinsed solution, the desorption extent of iron and copper was calculated. Table 4 shows the result of desorption tests.

Table 4. Iron and Copper desorption percentage using sulfuric acid solutions of different concentrations

Percentage of H_2SO_4 solution used	**Iron desorption rate (%)**	**Copper desorption rate (%)**
10 %	13	33
1%	7	28
0.5%	6	24
0.1%	10	24

From Table 4, it is understandable that the low concentration of the sulfuric acid solution was not enough to strip copper from the resin. Thus, a 40% sulfuric acid solution was further used after rinsing the resin with 10% sulfuric acid solution, and it achieved an overall 27 % of Fe (III) and 65 % of Cu(II) desorption.

4.3.1 Second stage elution-unloading of iron from resin

After unloading the maximum possible amount of copper from the resin using different concentrations of sulfuric acid in the first stage of elution, the second stage of elution was performed, using a high concentration of hydrochloric acid to strip off the iron from the loaded resin containing 64.24 mg/g Fe(III) and 12.6 mg/g copper. 40 mL of 50% HCl was used to rinse the resin, and it desorbed overall 47.25 % of Fe(III) with an insignificant percentage of copper. As it was too difficult to unload Fe(III) from the resin using HCl, different complexing agents such as oxalic acid, citric acid, and EDTA (Ethylenediamine tetra acetic acid) were tried to elute the resin (Zhang et al., 2016). For every complexing agent, different concentrations such as 1.12%, 2.25%, 4.55%, and 9% were explored, and each time the resin loading 64.24 mg/g Fe(III) and 12.6 mg/g copper was rinsed using 40 mL of different concentrated rinsing solutions for 1 hour.

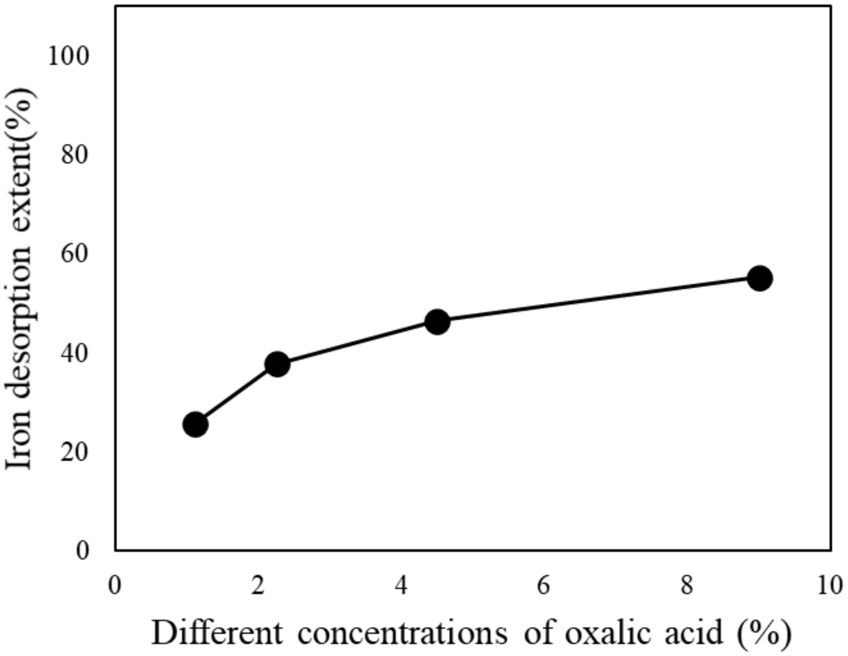


Figure 25. Percentage of iron desorbed in second stage elution using oxalic acid solutions of different concentrations.

Figure 25 illustrates the performance of oxalic acid solutions of different concentrations to desorb iron from loaded resin. The percentage of desorption of iron increased with the increment of the concentrations of oxalic acid solution. However, variations of acid concentrations did not make remarkable differences to the unloading of copper, achieving less than 3% of copper desorption, which was not represented in the figure. The highest 53% of iron was possible to desorb using 9% oxalic acid solution.

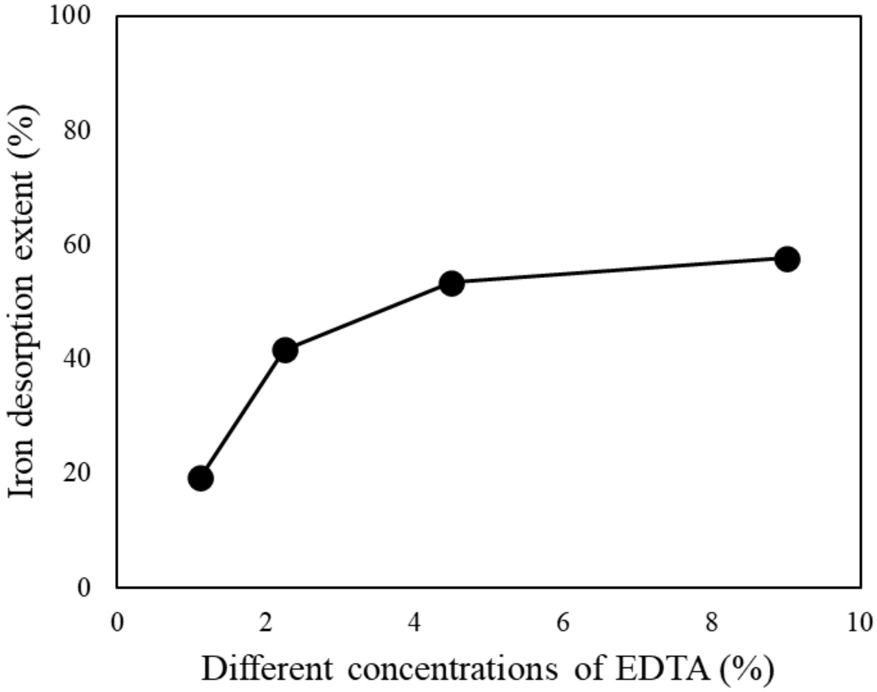


Figure 26. Percentage of iron desorbed in second stage elution using EDTA solutions of different concentrations.

The desorption scenario of iron and copper using different EDTA concentrations was very similar to the oxalic acid solution results (Figure 26). The percentage of iron desorption increased with the increment of EDTA solution concentration and achieved 57% of iron desorption using a 9%

EDTA solution. The copper desorption percentage was very insignificant, unloading only 3% of copper, with the changes of EDTA concentration.

The iron desorption pattern using citric acid was different from those using oxalic acid and EDTA. Negligible unloading of both iron and copper was observed using different concentrations of citric acid in this stage.

4.4 Discussion

The results showed that most of the resins tested here showed a preference for Fe(III) loading over Cu(II) from the leach solution. Throughout the experiment, the characteristic of resins followed the HSAB principle. According to the HSAB principle, resins containing hard bases strongly prefer to load metals of hard acid-like Fe(III). Resins with borderline or soft bases groups prefer metal loading to intermediate acid Cu(II) or show low metal loadings for Fe(III). Our findings from this experiment followed the same trend. It was possible to achieve high Fe(III) loading from high metal concentration and acidic pH fixed to 1.5. Our research showed Also, resins showing good behaviour in high metal concentration conditions will follow the same trend at low metal concentration, i.e., high Fe(III) loading from low Cu(II) concentrated solution. However, resins showing a significant percentage of Fe(III) removal from low Cu(II) solution in the first set of the test might not offer the same results in the second set of the test, i.e., in a high Cu(II) solution. Of all of the tested resins, the resins showing the best results for the removal of Fe(III) are amino-phosphonic groups and resins with a mixture of phosphonic and sulfonic groups (see Table 5 and Table 6). All brands of resins of amino-phosphonic groups loaded a significant amount of Fe(III). Lewatit TP260 showed the best results between them, achieving 92% of Fe(III) with 60% of Cu(II) at a resin dosage of 0.5 g/ml.

Table 5. Adsorption percentage of Fe(III) and Cu(II) obtained at maximum resin dosage from the adsorption test of commercial resin brands of different functional groups.

	Functional group (ionic form)	**Resin brand**		**Producer**	**Adsorption of Fe(III) obtained (%)**	**Adsorption of Cu(II) obtained (%)**
1	Amino-phosphonic (Na+)	1	IRC747	Amberlite®	88.95	48.25
		2	TP 260	Lewatit®	92.78	59.56
		3	MTS9500 (S950)	Purolite®	83.74	59.77
		4	MTS9400 (S940)	Purolite®	83.84	47.08
		5	SIR-500	Resintech	74.56	47.44
2	Phosphoric acid (Di-2-ethylhexyl-phosphoric acid; D2EHPA)	6	VP OC 1026	Lewatit®	44.5	24.1
3	Phosphinic acid (Bis-(2,4,4-trimethylpentyl-) phosphinic acid)	7	TP272	Lewatit®	42	15.55
4	Phosphonic & Sulfonic (H$^+$)	8	MTS9570 (S957)	Purolite®	99.45	53.55
5	Iminodiacetic (Na$^+$)	9	TP 207	Lewatit®	70.5	62.56
		10	TP 208	Lewatit®	68.15	59.65
		11	MTS9300 (S930)	Purolite®	78.73	69.56
6	Sulfonic (H$^+$)	12	IR120	Amberlite®	42.2	54.32
		13	G-26	Dowex®	32.8	47.1
7	Carboxylic (H$^+$)	14	Mac-3	Dowex®	46.78	18.55
		15	WACG-HP	Resintech	49.7	15.77
8	Thiol	16	MTS9240	Puromet®	26.3	21.03
9	Bis-pycolilamine	17	TP 220	Lewatit®	48.64	92.68
10	Thiourea	18	TP 214	Lewatit®	29.44	27.66
		19	MTS9140	Puromet®	17.25	40.52
11	Isothiouronium	20	MTS9200	Puromet®	28.14	14.49
12	N-methylglucamine	21	S108	Purolite®	74.88	31
13	Amidoxime	22	MTS9100	Puromet®	55	40
14	Quaternary Ammonium	23	4400 Cl	Amberjet®	37.96	10.77
		24	21K XLT	Dowex®	40.02	12

The only brand of resin tested for a mixture of phosphonic and sulfonic groups, Puromet MTS9570, achieved 99.5% of Fe(III) against 54% of Cu(II) at a 0.5 g/mL resin dosage. Both resins of phosphoric and phosphinic groups (phosphorous-containing groups) showed almost the same behaviour.

Table 6. Summary of the results obtained in the experiment based on the commercial brands of resins classified by functional groups, selectivity comparison between literature, and experimentally achieved in relation with the best percentage of metal loading.

Functional group	**Fe(III)/Cu(II) selectivity found in the literature**	**Selectivity obtained**	**Best results obtained**
Amino-phosphonic	$Fe^{3+} > Cu^{2+}$	$Fe^{3+} > Cu^{2+}$	92% Fe(III) 60% Cu(II) TP260, 0.5 g/mL
Phosphoric	$Fe^{3+} > Cu^{2+}$	$Fe^{3+} > Cu^{2+}$	45% Fe(III) 24% Cu(II) VPOC1026, 0.5g/mL
Phosphinic	$Fe^{3+} > Cu^{2+}$	$Fe^{3+} > Cu^{2+}$	42% Fe(III) 16% Cu(II) TP272, 0.5g/mL
Sulfonic	Not found	$Cu^{2+} > Fe^{3+}$	54% Cu(II) 42% Fe(III) IR120, 0.5 g/mL
Phosphonic & Sulfonic	$Fe^{3+} > Cu^{2+}$	$Fe^{3+} > Cu^{2+}$	99.5% Fe(III) 54% Cu(II) MTS9570,0.5 g/mL
Iminodiacetic	$Fe^{3+} > Cu^{2+}$	$Fe^{3+} > Cu^{2+}$	78% Fe(III) 68% Cu(II) MTS9300, 0.5g/mL
Carboxylic	Not found	$Fe^{3+} > Cu^{2+}$	50% Fe(III) 15% Cu(II) WACG-HP, 0.5g/mL
Thiol	Not found	$Fe^{3+} \approx Cu^{2+}$	26% Fe(III) 21% Cu(II) MTS9240, 0.5g/mL
Bis-pycolilamine	$Cu^{2+} > Fe^{3+}$	$Cu^{2+} > Fe^{3+}$	92% Cu(II) 48% Fe(III) TP220, 0.5g/mL

Thiourea and Isothiouronium	Not found	$Cu^{2+} > Fe^{3+}$	40% Cu(II) 17% Fe(III) MTS9140,0.5 g/mL
Glucamine	Not found	$Fe^{3+} > Cu^{2+}$	71% Fe(III) 18% Cu(II) S108, 0.4 g/mL
Amidoxime	Not found	$Fe^{3+} > Cu^{2+}$	55% Fe(III) 40% Cu(II) MTS9100,0.5 g/mL
Quaternary amine	$Fe^{3+} > Cu^{2+}$	$Fe^{3+} > Cu^{2+}$	40% Fe(III) 13% Cu(II) 21K XLT, 0.5g/mL

A maximum of 45% of Fe(III) and 24% of Cu(II) was possible to be removed and recovered. The unsatisfactory loading result was related to the resin's low specific gravity and improper resin solution contact at the rated agitation speed for its buoyant characteristic. Resins with sulfonic groups did not show significant adsorption because of their high strength. Two forms (Na+ and H+) of resins were tested, and the Na+ type showed better results than the H+ type. However, these resins showed more Cu(II) loading than Fe(III) (achieving a maximum of 54% of Cu(II) against 42 % of Fe(III) at the highest resin dosage) from the leach solution. The difficulties associated with resins of phosphorous groups and sulfonic groups can be solved using resins with a mixture of phosphonic and sulfonic acid groups, because sulfonic groups provide hydrophilic characteristics, allowing easy access of ions into the polymer network, and phosphonic groups show specific selectivity towards targeted metal ions. For example, Puromet MTS9570 (resin containing a mixture of phosphonic and sulfonic acid groups) showed very satisfactory Fe(III) removal from a pregnant leach solution. Resins with the carboxylic acid group and quaternary amine groups showed the same behaviour towards metal selectivity. Both resin groups showed moderate adsorption preference to Fe(III) and negligible preference to Cu(II). Resins with carboxylic groups removed 50% of Fe(III) and only 15% of Cu(II), and resins with quaternary amine groups obtained 40% of Fe(III) and less than 13% of Cu(II). Multiple adsorption stages with maximum resin dosage can maximize the Fe(III) removal while retaining less Cu(II) adsorption. Resins with glucamine groups also exhibited significant Fe(III) removal (achieving 75% of Fe(III) removal with 31% of Cu(II) recovery) at maximum resin dosage. However, this resin showed less than 20% of Cu(II) replacement with more than 65% of Fe(III) loading at a resin dosage of 0.4 g/mL, so multiple adsorption stages with this rate of resin dosage will enable more satisfactory Fe(III) removal. Resins with thiol groups achieved almost the same percentages of Fe(III) and Cu(II) loading, but resins with amidoxime groups indicated different adsorption preferences with an unsatisfactory result (achieving a maximum 55% of Fe(III) against 40% of Cu(II) at maximum resin dosage). Resins with thiourea and isothiourium groups exhibited mixture behaviours for metal adsorption. One particular brand of resins extracted more Fe(III) than Cu(II), but another brand of resins showed the opposite result. In contrast, resins with iminodiacetic acid groups and bis-pycolilamine groups displayed notable adsorption of Cu(II) compared to all other resins tested here. Iminodiacetic acid group loaded a maximum of 69% of Cu(II) with more than 80% of Fe(III) loading, but resin with bis-pycolilamine groups was the only group of resin that achieved more than 92% of Cu(II) against 46% of Fe(III). Therefore, relatively simple elution can recover Cu(II) successfully from concentrated Fe(III) solutions.

Based on the findings of successful metals adsorption (high Fe(III) removal with less Cu(II) loading or high Cu(II) recovery with less Fe(III) loading) from a leach solution using multiple commercial brands of resins, some particular brands of resins from different groups were selected to study the effects of various parameters on the results of adsorption. Throughout this research, the removal or recovery of the metal of more than 70% was considered high and low for less than 70%. Amino-phosphonic resins, a mixture of the phosphonic and sulfonic acid group, and bis-pycolilamine were tested for this purpose. From the pH test observation, it was found that Puromet MTS9500 presented the highest Fe(III) removal with the lowest Cu(II) recovery at pH 1.5, and Puromet MTS9400 and Lewatit TP260 showed the best scenario at pH 2 and pH 1, respectively. Resins with a mixture of phosphonic and sulphonic functional groups and bis-pycolylamine groups obtained good results at pH 1.5. The effect of adsorption time on adsorption performance was the same with all brands of resins. All resins satisfied the best condition of metals adsorption with an adsorption time of 2 h (120 min). The temperature effect was evident in the loading of both Fe(III) and Cu(II). Puromet MTS9500 and Puromet MTS9400 resins with aminophosphonic groups removed more Fe(III) with less Cu(II) recovery with the increase of temperature. Both showed the best results at an adsorption temperature of 60^0 C, but the other resin of this group, Lewatit TP260, did not show a significant difference with the change of temperature. Puromet MTS9570 resin with a mixture of phosphonic and sulphonic functional groups and Lewatit TP220 resin with a bis-pycolylamine group showed almost the same percentage loading for Fe(III) and Cu(II) with the temperature variation. The resins selected for testing the temperature effect followed both exothermic and endothermic adsorption processes.

Lastly, desorption studies were performed on the Puromet MTS 9570 resin containing a mixture of phosphonic and sulfonic acid groups. At the beginning of the desorption process, stripping the copper from the resin was attempted, using multi-time rinsing with different sulfuric acid concentrations. The resulting 65% of copper along with 27% of iron was desorbed using 10% sulfuric acid rinsing first, followed by 40% sulfuric acid rinsing. In the last stage of the desorption process, a 50% of hydrochloric acid concentration solution was tested in an attempt to desorb iron from the loaded resin, but it did not provide the expected result. Afterward, different complexing agents such as oxalic acid, EDTA, and citric acid were investigated to get the desired iron desorption performance. The oxalic acid and EDTA presented indistinguishable manners towards the iron desorption and obtained around 55% of iron unloading from the resin. Conversely, citric acid exhibited unfavorable iron desorption performance than the other two complexing agents used here. In summary, 65% of copper and 62% of iron were possible to desorb from this process which is not ideal. As the metal desorption percentage is much lower than 90%, it does not follow the resin recycling condition. So, more powerful eluents can be tried for more successful results. Besides, a more in-depth analysis of resin's adsorption selectivity to iron and copper is required to find the best resin. Consequently, studying the elution strategy for that specific resin will satisfy our ultimate goal.

CHAPTER 5
Conclusions and Future Work Scopes

5.1 Conclusions

The ion exchange process using resins with different functional groups as an alternative to other separation processes has been investigated to obtain Fe(III) from Cu(II) solutions at high metal concentrations. The direct comparison between 14 different functional groups using 24 different commercial brands of resins was made based on the metals loading capabilities and selectivity. Metals loading tests revealed that resins with amino-phosphonic groups and a mixture of phosphonic and sulfonic groups removed more than 90% of Fe(III) from the leach solution. However, resin with a combination of phosphonic and sulfonic groups performed less Cu(II) loading with high Fe(III) loading than did with aminophosphonic groups, signifying that it can be an effective adsorbent for the selective removal of iron from highly concentrated copper solutions. Resins with bis-pycolilamine groups showed the best percentage of Cu(II) recovery. That is why resins containing these functional groups were selected to study the effects of different parameters on metal adsorption. Resins containing other functional groups like thiol, amidoxime groups did not show a preference to remove Fe(III) and recover Cu(II) from the leach solution. Resins with phosphonic and phosphinic groups showed unsatisfactory loading, because their buoyant characteristics made improper resin-solution contact. Sulfonic groups have high strength, which did not allow apparent cation preference in high metal concentration solutions. Carboxylic acid and quaternary amine groups showed an average percentage of Fe(III) removal against the least amount of Cu(II) recovery. Still, a significant amount of Fe(III) can be removed using multiple adsorption stages. However, resins with the glucamine group also have the potentiality to achieve a higher percentage of Fe(III) using several adsorption stages as this group removed 75 % of Fe(III) at a single adsorption stage. Resins with thiol groups showed almost the same preference for loading Fe(III) and Cu(II). Unlike other functional groups except for bis-pycolylamine groups, resins with thiourea and isothiourium groups showed more selectivity to Cu(II) than Fe(III). Resins with iminodiacetic acid groups showed notable adsorption preference for both Fe(III) and Cu(II), which did not allow the choice of this functional group to test the effect of the single factors on adsorption results. The elution process was done using sulfuric acid rinsing for copper desorption and rinsing of complexing agents for stripping off iron from loaded resin. However, the results were not satisfactory, which needs more study in the future.

5.2 Future work scopes and recommendations

From this research, it can be concluded that most of the resins studied favoured Fe(III) adsorption over Cu(II), and the ion exchange process can be suitably used to remove Fe(III) from Cu(II) solutions spontaneously. Resins with the same functional groups from different commercial brands showed varying degrees of Fe(III) removal and Cu(II) recovery, which will provide better options to select a particular resin in specific applications. Additionally, it will be an alternative to attain co-production of high purity Fe-subproduct, which will offer economic opportunities. The elution process conducted here did not obtain the outcome level needed, but it is a promising operation. Therefore, more in-depth adsorption studies to find the best selectivity of resins for iron and copper are required. Then we can apply a similar elution strategy accomplished here on that specific resin. When these prospective adsorption and desorption studies are successful, the key advantages of using the ion exchange resin process in hydrometallurgy will be manifested. Finally, economic studies of that specific resin are needed to certify it as the best resin for Fe(III)- Cu(II) separation, making it suitable for industrial application.

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