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Research paper

Copper recovery from chalcopyrite flotation plant tailings acid leach using ion exchange resin dowtm XUS 43578.00

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Abstract

This study examined the feasibility of recovering copper from a sulphuric acid leach solution of chalcopyrite flotation plant tailings assaying 0.18 % copper and 0.19 % zinc using DOWTM XUS 43578.00 ion exchange resin. Zn2+cations are counter ionsto Cu2+cations during the ion exchange process. Adsorption and desorption tests were conducted on the resin with a leach solution containing26 mg Cu/L and 225 mg Zn/L,under various conditions of pH, DOWTM XUS 43578.00resin dosage, agitation time and eluant(ammonium hydroxide solution) concentration. The DOWTM XUS 43578.00resindemonstrated a high selectivity for copper over zinc, with a separation factor of 30.26 mg/g. The highcopper distribution coefficient of65L2/g2suggeststhe resin can effectively concentrate copper in leach solutions of these particular tailings.A 4M ammonium hydroxide solution yielded the highest copper recoveryat pH 3and0.6gresin dosageafter3hours of agitation. These results can be improved by a pre-treatment step to remove the zinc before the copper ion exchange process, and modifying the experiments to simulate industrial practice by having multi-stage sorption and desorption phases.

Keywords: *Acid Leach; Copper Tailings; Distribution Coefficient; DOWTM XUS 43578.00ion Exchange Resin; Separation Factor.*

1. Introduction

Dwindling copper reserves and stricter environmental protection laws across the globe have caused copper producers to turn to secondary ore sources like tailings dams. While most copper hydrometallurgical extraction plants use a leach – solvent extraction – electrowinning process, ion exchange offers an alternative to the solvent extraction circuit, especially in situations where the metal concentrations in solution are extremely low.Mining activities pollute the environment in several ways. There are gaseous emissions from mine machinery, dust, particulate matter, noise, acid mine drainage, tailings dumps and tailings dams. Modern mining practice requires that mining companies have environmental protection and remediation strategies for all phases of the mine life. The tailings dam considered for this study is for a copper mine where the predominantly chalcopyrite ($CuFeS_2$) ore is mined underground and concentrated through several mineral processing techniques which include, crushing, grinding, flotation, thickening and filtration. The copper concentrate contains about 27% copper [1] and the waste material, sent to the tailings dam, contains about 0.18% copper on average. Currently mine personnel are conducting metallurgical test work for recovering copper from the tailings dump in order to maximize on returns.

Ion exchange (IX) has proven to be an environmentally friendly technology with extensive applications in hydrometallurgical operations. The exchange procedure in ion exchange produces no precipitation and no inorganic pollution [2].Ion exchange reactions involve the interchange of ions between an aqueous solution and insoluble solid resin. It is one of the unit operations used in hydrometallurgy to purify and concentrate the metal values from leach liquors. The use of ion exchange is especially prevalent in the uranium industries. Although solvent extraction (SX) is used now more than ever, there are problems in its use, e.g. emulsion formation, and solvent loss in the operation circuit can be costly and troublesome. The ion exchange technique has been proven to be an economic process for recovering low concentrations of uranium from mine waste streams. In addition, the resin-in-pump process can be used to recover metal ions from uranium containing slimy pulp (from which the separation of clear liquor is difficult). IX technology is considered a complementing technology, and sometimes a substitute technology, for SX.

Ion exchange technology that has been adapted to hydrometallurgical processes can be described by a two-stage sequence:

i) Adsorption – utilization of an anionic or cationic organic resin to remove metal ions from an aqueous solution when that solution is passed through a bed of resin.
ii) Elution – the recovery of metal ions in a concentrated and purified form (aqueous solution) by passing a small volume of suitable solution (eluent) through the loaded bed.

The reactions can be performed in fixed bed, moving bed or resin-in-pulp reactors.Resins, based on the bis-picolylamine (BPA) functionality have been specially established for extracting copper. Dowex M4195 formerly known as Dow XFS-4195 is one of those resins, which can take up ions from $3M H_2SO_4$ but requires a concentrated acid (10M) for regeneration while the other resin Dow XFS-4196 can be regenerated with sulphuric acid of concentration 100 g/L. The consumption of H_2SO_4 amounts to 1.7g/g Cu which is 10% greater than the stoichiometric amount of 1.54 g/L [3]. DOW^{TM} XUS 43578.00 is another copper selective resin which can be eluted with 2M ammonium hydroxide, where the cycle of the eluant can minimize waste generation and can result in ammonia/copper waste streams having very high copper content (in excess of 100g/L) [4].

Ion exchange involves the reaction between a solid material and a solution. The principle is that ions are exchanged between the ion exchanger and the ions in solution such that every ion removed from the solution is replaced by an equivalent amount of ionic species of the same sign [5]. Exchange processes can be characterised into cationic or anionic exchange and are represented by the following equations described by [6]:

$$M^-A^+ + B^+ \leftrightarrow M^-B^+ + A^+ \quad (1)$$

Equation 1 is a cationic exchange reaction and Equation 2 is an anionic exchange reaction.

$$M^+A^- + B^- \leftrightarrow M^+B^- + A^- \quad (1)$$

Where M^-/M^+ are the fixed anionic and cationic component of the ion exchanger and A^+/A^- are the exchangeable ions carried on the resin.

The ion exchange process is reversible and therefore the ion exchange resin can be re-used many times.In hydrometallurgy the reverse ion exchange process is used to reclaimthe ions exchanged onto the resin. This process is referred to as elution. Elution is the opposite of sorption in the sense that the sorbed ions are recovered for further purification. According to [7] the efficiency of elution can be characterised by the following factors: required amount (volume and concentration) of the eluant; degree of the exchanger conversion i.e. which part of the sorbed substances is recovered from the material and which of the sorbent is converted to the new ionic form; and concentration of effluent.

Zagorodni[8] reportedon the adsorption of copper using various ion exchange resins such as Amberlite IR-120, 252H and 1500H;Dowex 50W;and Chelex 100.Ina related study by[9] the recovery of copper from a bioleach solution by ion exchange involved usage of the developmental chelating resin Dow XUS 43605. In that study, resin screening tests were conducted at a pH of 3 and 4 to determine which resins had a higher selectivity for copper. The study compared resins such as Dowex M4195, Amberlite IRC-748, Purolite S930 Plus and Purolite S991 and concluded Dow XUS 43605 to be the ultimate resin for copper adsorption from the bioleach solution although resin screening results showed Dowex M4195 resin to have a higher separation factor for copper over other ions that were present in the solution.However, Dowex M4195 was disregarded because of its high affinity for copper, poor iron rejection and problems of elution using H_2SO_4. Other authors [10, 11] have reported the use of ammonium hydroxide to efficiently solubilize the copper from Dowex M4195instead of eluting with H_2SO_4. According to [4], DOW^{TM} XUS 43578.00can also be eluted with ammonium hydroxide because of its similarchemistry to Dowex M4195.

A study by [10] evaluated three chelating resins Dowex M4195, Amberlite IR120 and Amberlite IRC748 for the selective recovery of chromium and copper in leachate from chromated copper arsenate treated wood. In that study, screening tests revealed Dowex M4195 to be copper selective and Amberlite IR120 to be chromium selective. Copper was eluted from the resins using 4M NH_4OH of which 94% of the copper was recovered. In the study conducted by [11], a known amount of TulsionA-23 was contacted with the solution containing copper ions. The pH of the solution was varied between 2 and 12 and maximum copper sorption onto the resin was observed in thepH range of 5-7. A related study by [12] evaluated Dowex 50X4, Dowex 50X2 and Dowex M4195 ion exchange resins for their capability to adsorb copper from electroplating waste water.

DOW^{TM} XUS 43578.00 is a relatively new ion exchange resin in terms of the recovery of copper hydrometallurgically. It is commercially available and has been used in pilot plant studies of cobalt and nickel recovery.This resin has good characteristics, for example, it works very low at low pH which makes it attractive for copper recovery from strong acid leach liquors. Consequently, the aim of the study was to examine the suitability of DOW^{TM} XUS 43578.00IX resin for the recovery of copper from a pregnant leach solution (PLS) containing zinc as the major impurity metal.

The specific objectives of the study were to determine the:

i) Separation factor of copper over the zinc in the acid leach solution,
ii) Effects of pH, resin dosage and agitation time on the adsorption of copper onto the resin, and
iii) Effects of eluant concentration and pH on the recovery of copper from DOWTM XUS 43578.00.

2. Materials and methods

2.1. Materials and instruments

Materials used wereDOW^{TM} XUS 43578.00ion exchange resin (see Fig. 1), sulphuric acid (1M, and 2M solutions), ammonium hydroxide (1M, 2M, and 4Msolutions), 0.1M sodiumhydroxide and 0.1M hydrochloric acid. The DOW^{TM} XUS 43578.00resin was supplied by the Dow Chemical Company, whoare the manufacturers. The resin is present in spherical bead form as shown in Fig. 1, and the resin specifications are described inTable1.Instruments used included aJones Riffle splitter, Particle Size Analyser(BT-9300H),pH meter (Thermo Scientific Orion Star A111),Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES),metabolic shaker (EcoBath Labotech), X-ray Fluorescence (XRF) spectrometer, and a hotplate with a magnetic stirrer.

Fig. 1: DOW^{TM} XUS 43578.00resin.

Table 1: Properties and Specifications of DOW^{TM} XUS 43578.00 [5]

Item	Specification Limit	Typical property range
Copper loading (pH2, 6g/L feed)	Min, 35 g/L	35-42 g/L
Functionality	-	Multidentate amine ligand
Particle Size	-	410 µm, uniform particle size
Form	-	Weak base/partial H_2SO_4 salt
Physical appearance	-	Opaque bead
Colour	-	Tan to dark brown to dark green
Bulk density	-	672.8kg/m^3
Moisture	-	40-60%
Shelf life	-	8-10 years
Physical appearance	-	Opaque bead
Colour	-	Tan to dark brown to dark green

2.2. Methods

2.2.1. Sampling

Bulk samples from the tailings dump were obtained from which a sub-sample of 4 kg averaging 0.18% Cu and 0.19% Zn was weighed out. A Jones Riffle Splitter was used to split the sample into two samples of roughly equal sizes. One half of the sample that was collected onto the tray weighed 1.98 kg and was discarded while the other sample collected on the collector pan was further reduced in size.The chosen sample weighed 2.02 kg and was further reduced to half the mass into two collecting pans. Mass of each sample weighed 1.01 kg. A sample of 100 g from the discarded sample pan was taken for particle size analysis to determine the particle size distribution of the tailings sample. Particle size analysis was done with a Particle Size Analyser (BT 9300H).

2.2.2. Leaching

Leaching tests were done on the chosen size collected on the Riffle Splitter pans.The leaching was done using sulphuric acid as the main leaching reagent and hydrogen peroxide as an oxidant. A 20 g sample was placed in a conical flask together with 100 mL of 2M sulphuric acid and 1M hydrogen peroxide. The reagent and the sample was allowed to react for 4 hours, at a temperature of 70°C, feed particle size of 75 µm, agitation speed of 500 rpm and pH of 1. The pregnant leach solution was filtered from the residue and solution samples were taken for chemicalanalysis.

2.2.3. Ion exchange tests

a) Resin pre-conditioning

The DOW^{TM} XUS 43578.00 chelating resin was rinsed with distilled water in order to remove impurities. The resin was then soaked in 1M $H_2SO_4$for 2 hours in order to ensure that it was in the correct ionic form (see photograph in Fig. 2). The resin was then rinsed further with a few bed volumes (BV) of distilled water in order to remove excess acid.

When a resin is received from the manufacturer it is usually in another form or in a form partly different from the one specified, therefore there is a need to subject the resin to several rinsing methods in order to stabilize its characteristics such as capacity, density and size distribution as well as to convert it into an ionic form as pointed out by [13] before it can be utilised for the subsequent adsorption studies.

Fig. 2: DOW^{TM} XUS 43578.00resinpre-Treatment in Acid and Distilled Water.

b) Resin screening

The pre-conditioned resin was now placed ina beaker and then contacted with the feed solution while in the beaker, with the solution maintained at pH 3 (constant monitoring using a pH meter) for a period of 24 hours to ensure that equilibrium had been attained. After 24 hours, samples were taken from the beakers for analysis. Solution samples were analysed using an ICP-OES to obtain the concentrations of copper and zinc in the solution after the screening tests.

c) Adsorption

The pre-treated DOW^{TM} XUS 43578.00resin was contacted with the leach solution in 500mL beakers and the mixture was stirred using a magnetic stirrer. The temperature of the solution was kept constant at 25°C. The batch kinetic tests were carried out at pH 3. Small aliquots of the solution were removed at time intervals of 2 hours over a 24-hour period [9].

According to [14], ion exchange batch processing operations are of limited use in industry and therefore mainly used in laboratories for fundamental sorption and kinetic studies. Batch kinetic tests were carried out on the loaded DOW^{TM} XUS 43578.00resin to evaluate the adsorption kinetics of copper onto the resin. Liebenberg et al., [9] conducted batch kinetic tests on developmental resin Dow XUS43605 in order to ensure that equilibrium was reached; similar tests were also done on Dowex M4195 which has the same chemistry as DOW^{TM} XUS 43578.00 over the same period of time of 24 hours. The amount of copper loaded onto the resin was calculated from mass balances.

d) Tests for effects of pH, resin dosage and agitation time on copper adsorption

Solution pH is considered to be one of the most important parameters in the adsorption process [9]. The pH values that were used to evaluate pH influence on adsorption were 1, 3 and 5. A small amount of resin weighing 0.4 g was contacted with 50 mL of the pregnant leach solution and the mixture was agitated at140 rpm at 25ºC in a metabolic shaker (see Fig. 3).

The effects of resin dosage on adsorption of copper onto DOW^{TM} XUS 43578.00IXresin were studied by contacting a mass of 0.2, 0.4 and 0.6g of the resin with 50 mL of pregnant leach solution. The temperature of the solution was kept constant and the reaction was allowed to react in a metabolic shaker at 140 rpm.

The effects of agitation time on adsorption of copper onto the resin was studied by contacting a known amount of the resin with 50 mL of the pregnant leach solution for various time intervals of 1 hour, 2 hours, and 3 hours. The mixture was allowed to react in a metabolic shaker at 140 rpm, temperature of 25ºC, and pH 3.

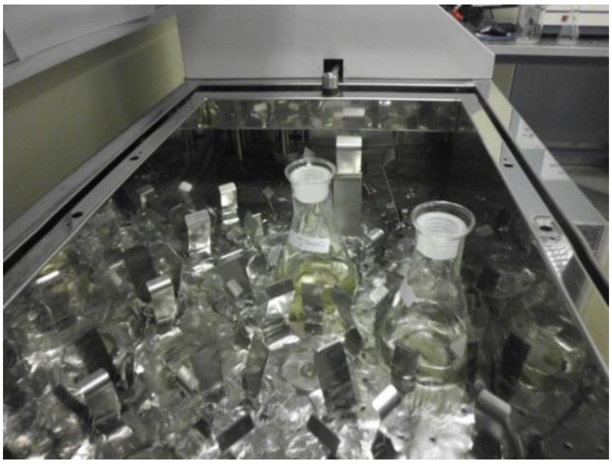

Fig. 3: Adsorption Tests Being Conducted in a Metabolic Shaker.

2.2.4. Batch elution tests

Batch elution tests were carried out on the loaded resin by contacting the loaded copper resin with various concentrations of ammonium hydroxide (1M, 2M and 4M) while varying pH of the solution at 8, 10 and 12. Adsorption of the copper onto DOW^{TM} XUS 43578.00 was done according to the optimum parameters obtained from the previous experiments in Section 2.2.3.5 above. The loaded resin was then rinsed with distilled water before eluting. The eluant and loaded resin were contacted for 2 hours. The elution tests were carried out in a metabolic shaker at a constant agitation speed of 140 rpm.

2.2.5. Chemical analysis

50 mL volumes of the leach and ion exchange solutions were analysed for copper and zinc were done using an ICP-OES.

3. Results and analysis

The tailings were leached at a P_{80} of 75 microns. Fig.4shows the particle size distribution of the flotation plant tailings of with more than80% of the material passing 75 microns.

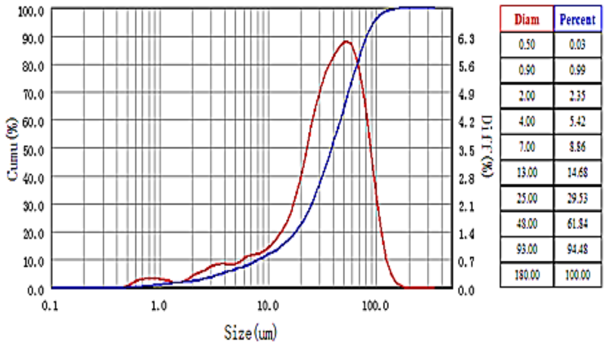

Fig. 4: Particle Size Distribution of the Flotation Plant Tailings.

Chemical analyses were only carried out for copper and zinc, while ignoring other elements present in the solution in order to reduce the costs since this was being done at a certified private laboratory. Thestock leach solution assayed 26 mg Cu/L and 225 mg Zn/Land was used for all ion exchange tests. Table 2shows the amount of copper and zinc left in solution after the reaction time period was complete as well as the amount loaded onto the resin. The separation factor ($\boldsymbol{\alpha_{A/B}}$) for copper over zinc in solution is defined as the ratio of the distribution of copper between the resin and the solution phases to the distribution of zinc between the resin and solution phases. The separation factor for copper over zinc present in the solution was calculated using Equation 3 [7, 9]:

$$\alpha_{A/B} = \alpha_{Cu^{2+}/Zn^{2+}} = \frac{D_{Cu^{2+}}}{D_{Zn^{2+}}} = \frac{C_{Cu,r}\,C_{Zn,s}}{C_{Cu,s}C_{Zn,r}} \qquad (3)$$

According to [5], if ion A is preferred then the factor $\boldsymbol{\alpha_{A/B}}$ is larger than unity and if B is preferred, the factor is smaller than unity.
The distribution coefficient was calculated using Equation 4 [15]:

$$D_{Cu} = \frac{C_{Cu^{2+},r}}{C_{Cu^{2+},s}} \times \frac{V_s}{M_r} \qquad (4)$$

Where D_{Cu} is the distribution coefficient of copper; $C_{Cu^{2+},r}$is the amount of copper on the resin; $C_{Cu^{2+},s}$ is the amount of copper in solution; $V_s$is the volume of solution (mL); and M_r is the mass of resin (g).
The separation factor for copper over zinc and the respective distribution coefficients for copper and zinc at a pH of [3] are presented in Table 3.

Table 2: Concentration of Copper and Zinc in Solution and Resin Phase Respectively

	Copper	Zinc
Metal concentration (mg/L)	0.04	8.09
Metal loaded onto resin (mg/g)	20.80	139.0

Table 3: Separation Factor and Distribution Coefficients at Ph 3

Separation Factor (mg/g)	Distribution Coefficient of CopperD_{Cu}(L/g)^2	Distribution Coefficient of ZincD_{Zn}(L/g)^2
30.26	65	2.148

The separation factor and distribution coefficients were calculatedbased on the results of the resin screening tests. Liebenberg et Al [8] reported separation factors of copper of 153, 26.6, and 0.767 for Dowex M4195, Dow XUS 43605, and Amberlite IRC 748 respectively.The 30.26obtained in the present study for DOW^{TM} XUS 43578.00 compares favourably with these figures. The resin loaded139 mg/g of Zn^{2+} and 20.8 mg/L of Cu^{2+}. Despite the selectivity of the resin for Cu^{2+} over, a lot of zinc is also extracted, warranting co-recovery of the zinc with copper or a zinc removal step prior to recovery of copper from solution using the IX process.
Copper adsorption onto the resin was examined at pH values of [1], [3] and [5]. Optimum amount of copper extracted was observed at a pH of [3]. The results are shown in Fig.5.

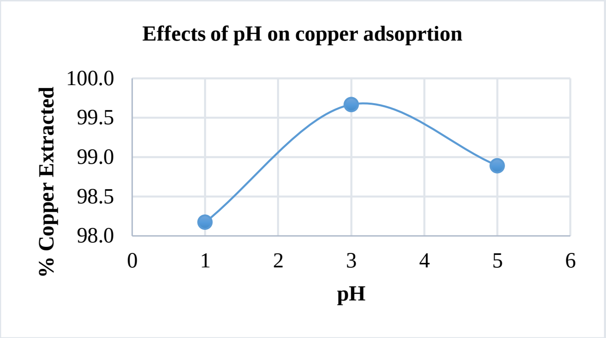

Fig. 5: Effect of Ph on Adsorption of Copper onto DOW^{TM} XUS 43578.00IX Resin.

An increase for copper removed from the solution was observed as the solution pH was increased from [1] to [3]. At a pH of [5], the amount of copper removed decreased, therefore optimum pH for copper removal from solution was at apHof 3.
The effect of resin dose on copper adsorption from the pregnant leach solution was studied. The pH was fixed at3 and temperature kept constant at 25°C. Copper adsorption on the resin was examined at resin dose of 0.2, 0.4 and 0.6 g. The results are shown in Fig.6.

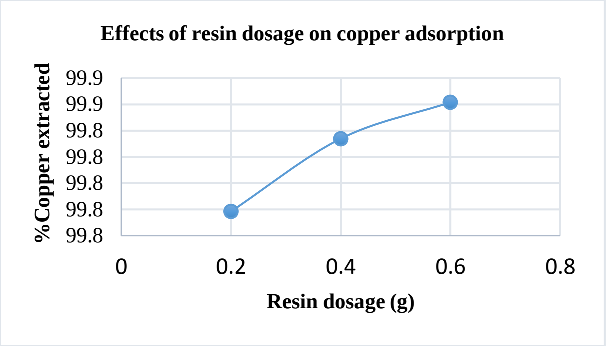

Fig. 6: Effects of Resin Dose on Copper Adsorption.

Fig. 6shows that the percentage of copper extracted from solution increases as the resin dosage is increased from 0.2 g to 0.6 g. This is to be expected as the number of active sites on the ion exchange resin increases which subsequently provides an increase in the number of active surfaces available for adsorption. Although the percent removal of copper from the leach solution increased as resin dosage was increased, the equilibrium loading of copper onto the resin decreased as the resin dosage was increased as shown in Fig.7.

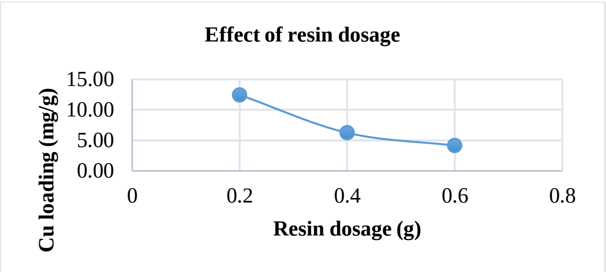

Fig. 7: Equilibrium Loading of Copper as Resin Dose Was Increased

The effect of contact time on the adsorption of copper onto DOW^{TM} XUS 43578.00IXresin was studied at constant solution pH and temperature. The flasks were shaken for different time intervals of 1 hour, 2 hours, and 3 hours. The results are shown in Fig.7.

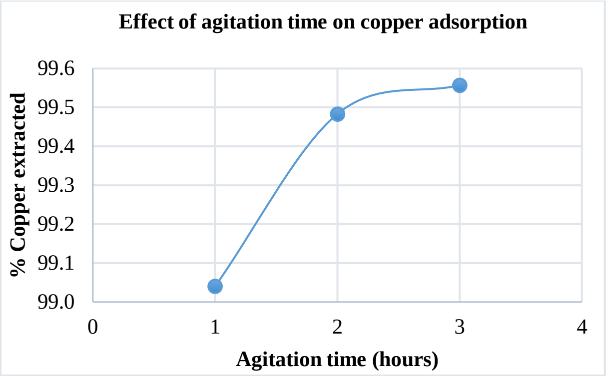

Fig. 8: Effects of Agitation Time on Copper Adsorption.

The effect of agitation time for adsorption was studied at three levels (1, 2 and 3 hours). Fig. 8 shows that the percentage of copper removal from the solution increased as the time was increased from [1] to [3] hours. The maximum amount of copper removed from the solution was observed at 3 hours.

The elution of copper from the loaded resin was conducted using ammonium hydroxide at different concentrations while varying pH of the eluant. Prior to elution, copper loading onto the resin was accomplished at the optimum copper adsorption parameters for the DOW^{TM} XUS 43578.00IX resin of pH 3, 0.2 g of resin and 3 hours contacting time as determined from the first set of tests. Fig.9illustrates variation of copper eluted from the resin with eluant pH. It is evident that the amount of copper in the eluate (copper recovered from the resin) increased gradually as eluant concentration was increased from 1M to 4M.

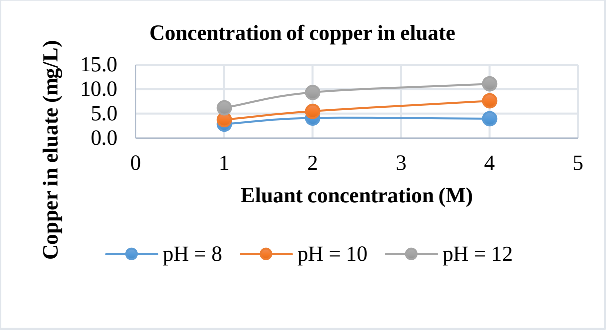

Fig. 9: Copper Eluted From the Resin Using Different Ammonium Hydroxide Concentrations

Chemical analysis of the aqueous solution after loading showed that the amount of copper remaining in solution was 0.98 mg/L from an initial amount of copper of 26 mg/L. The amount of copper loaded onto the resin was calculated by the mass balance relation;

$$q_e = \frac{(C_0 - C_e)V}{m\,(1-x)} \qquad (5)$$

Where $q_e$is the amount of copper loaded onto the resin (mg/g), $C_0$is the initial metal concentration (mg/L), $C_e$is the final metal concentration (mg/L), V is the volume of the solution (L), m is the mass of resin (grams), an xis moisture content of resin. Fig. 10 shows the percent copper recovered in the eluate. Percent copper extracted from the resin was calculated using the equation:

$$\text{Recovery} = \{(C_{eluate} \text{x } V_{eluate}) / (C_{loaded} \text{x } V_{loaded})\} \text{ x}100\% \qquad (6)$$

Where C_{eluate} is the concentration of copper in the eluate (mg/L), $C_{loaded}$is the copper concentration of the loaded resin (mg/L), $V_{eluate}$is the volume of the eluate (L), and $V_{loaded}$is the mass of resin (grams).

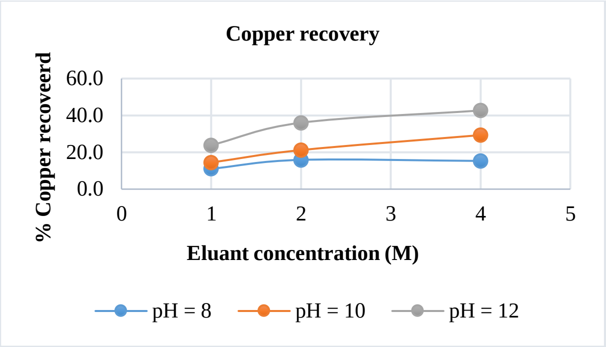

Fig. 10: Percentage of Copper Recovered From the Loaded Resin following Elution.

Copper recovered from the solution increased as the concentration of the eluant was increased from 1M to 4M while the pH of the solution was being controlled at 8, 10 and 12. The maximum percent recovery of copper by elution was calculated as 42.7% at a pH of 12 and eluant concentration of 4M. According to [9] a split elution is possible by using different concentrations of the eluant to first elute co-loaded counter ions from the resin, followed by the elution of copper. This could have been done with the zinc in this case and improve copper recoveries.

The highest concentration of ammonium hydroxideof 4M that was used generated an eluate with the highest concentration of $Cu^{+2}$of about 11 mg/L. The input [Cu^{+2}] was 26 mg/L. The final solution was of lower concentration than the leach solution. The objective in elution is to obtain a concentrated, lower volume eluate amenable to processing to recover metals. These results imply that purification and concentration of the acid leach solution did not satisfactorily occur. Nonetheless, this can be ascribed to the very low grade (0.18 % Cu) of the tailings to begin with, which also yielded an extremely low grade leach liquor of 26 mg/L Cu. Reference to the DOW^{TM} XUS 43578.00 IX resin properties and specifications in Table 1 show that copper loading onto the resin is best in leach solutions containing at least 6 g/L Cu.The apparent failure of this IXresin to concentrate the leach liquor can also be attributed to the very low copper concentration in both the tailings and the liquor. Another possible explanation for this failure is the much higher concentration of the Zn^{2+}counter ions compared to the Cu^{2+}ions in the leach liquor (225 mg Zn/L to 26 mg Cu/L).

4. Conclusions

Despite the copper concentration in the eluate being much lower than in the leach solution, the DOW^{TM} XUS 43578.00IXresin exhibited a high preference for copper over zinc.The distribution coefficient was quite high therefore copper recovery from solution using this resin is quite feasible. A 4M solution of ammonium hydroxide eluant proved the most effective in the recovery of copper from the loaded resin. Effects of factors such as temperature and agitation speed on the adsorption and recovery of copper from the ion exchange resin can be investigated in order to further assess the resin's capabilities of copper extraction from the leach solution. In industrial practice the IX process is a multi-stage process for all the unit operations e.g. sorption and desorption which was not the case in this bench scale study. Thus, the IX experiments can be modified tosimulate industrial practice by having a three-stage elution process for example.It is recommended that column tests be conducted on the resin in order to assess the effects of flowrate, temperature, and pH on the metal breakthrough. The elution process only recovered less than 50 % of the copper loaded on the resin, and thus also contributed to the poor overall result of the solution concentration process.Again, the Zn^{2+}counter ions might have consumed some of the eluant. This necessitates a zinc removal step before the IX process or split elution with a different concentration of the eluant to extract the zinc first. The tailings are a waste product of a highly efficient chalcopyrite flotation process. If the price of the copper metal on the market rises to warrant commercial exploitation of the tailings dam, perhaps focus should be on a flotation process utilizing suitable oxide collectors and scavengers to concentrate most of the residual copper.

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