



Adsorption of copper from the sulphate solution of low copper contents using the cationic resin Amberlite IR 120

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ABSTRACT

In view of the increasing importance of the waste processing and recycling to meet the strict environmental regulations, the present investigation reports an adsorption process using the cationic exchanger Amberlite IR 120 for the recovery/removal of copper from the synthetic sulphate solution containing copper ≤ 0.7 mg/mL similar to the CMP waste effluent of electronic industry. Various process parameters, viz. contact time, solution pH, resin dose, and acid concentration of eluant were investigated for the adsorption of copper from the effluents. The 99.99% copper was found to be adsorbed from the sulphate solution containing copper 0.3–0.7 mg/mL of solution (feed pH 5) at A/R ratio 100 and eq. pH 2.5 in contact time 14 min. The mechanism for the adsorption of copper was found to follow Langmuir isotherm and second order rate. From the loaded organic, copper was eluted effectively by 1.8 M sulphuric acid at A/R ratio 25. The raffinate obtained after the recovery copper could be disposed safely without affecting the environment.

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1. Introduction

The electronic industry includes the manufacture of resistors, capacitors, inductors, semiconductor components, printed circuit boards and printed wiring assemblies. In electronic industry, copper metal is widely used as interconnecting material for the manufacturing of electronic components due to its higher conductivity and greater residence to electro-migration. Such industries generate a large amount of copper bearing waste streams during different processing steps, viz. electroplating, etching, rinsing, and chemical and mechanical polishing (CMP), etc. Electronic process waste is one of the major contributors to heavy metal pollution in surface water [1]. CMP is a process used by semiconductor industry to produce very smooth surfaces on each layer of a microchip by “sanding” the microchip with water slurry of silica or alumina. In making microchips for computers, pagers, phones and other electronic equipment, a large volume of purified water is used for the dilution and rinsing steps of CMP process [2]. Therefore, a large amount of copper bearing sulphate waste effluent is generated. The waste water from the process contains relatively large amount of dissolved copper. The discharge of these waste wash water not only pollutes the environment but also affects health. The copper content in the solution varies and generally contained less than 1000 ppm [2].

The recovery and removal of copper from the waste effluents has received considerable attention because of their association with various health problems. The excessive intake of copper by human leads to severe mucosal irritation, widespread capillary damage, hepatic and renal damage, central nervous problems followed by depression, gastrointestinal irritation, and possible necrotic changes in the liver and kidney [3]. The World Health Organisation (WHO) recommended a maximum acceptable concentration 1.5 mg/L of Cu(II) in drinking water [4]. Due to stringent pollution control regulations, the treatment of these effluents is essential before discharge in the environment. Generally, the metallic ions from effluents are removed by precipitation with lime/caustic soda and sulphide, etc. It consumes large quantity of chemicals to effectively decrease the metal contents to acceptable pollution norms and generates sludge, which needs costly disposal procedure as landfill [5,6]. Other treatment procedures for the removal and recovery of metals from solutions are evaporation, solvent extraction, ion exchange, reverse osmosis, membrane separation [7,8]. The recycling of metallic value by evaporation of rinse water is highly energy intensive. The use of solvent extraction process is also not effective for the separation of metals from dilute solutions as the loss of organic extractant in aqueous solution due to solubility and entrainment makes the process unattractive [8].

Ion exchange process has been developed as a major option for separation of metals from different aqueous solutions/purification of wastewaters. The hydrogen ions released from the cationic ion exchange resin neutralize the hydroxide ions, so that the equilibrium shifts until all the metal ions are leached into solution and

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adsorbed onto the ion exchange resin [8]. The influence of complex formation on ion exchange adsorption equilibrium and on the distribution of metal ions between the liquid and resin phase has been extensively studied [9–12]. Many studies on the adsorption of metal ions on ion exchange resins such as Amberlite IR-120, Dowex A-1, Duolite GT-73 [13], IRN77 [14], and NKA-9 [15] were reported. An experimental study of heavy metal extraction from sludge was conducted by the researchers [16], using both Amberlite IRC-718 and Amberlite IR-120. Ion exchange technique also finds major application in the purification of aqueous, extraction of acid from pickle solution, extraction and separation of metals [17]. The process is effective particularly for the removal of metallic ions from the dilute solutions (<0.5 g/L) [18], where the precipitation is not efficient. Ion exchange resins are made up variety of exchange materials, which are distinguished into natural or synthetic resin. Furthermore, it can be as well categorized on the basis of functional groups such as cationic exchange resins, anion exchange resins, and chelating exchange resins [19]. Depending on the functional groups, ion exchange resin can deal properly with several heavy metals such as copper, nickel, cobalt, cadmium, zinc, and aluminum. Selective resins reduce the concentration of heavy metals in the solution below the permissible limit.

In view of the above, ion exchange (IX) studies have been carried out for the adsorption of copper from the low copper containing synthetic sulphate solution (copper 0.3–0.7 mg/mL) similar to the CMP waste effluent of electronic industry. Various parameters, viz. contact time, pH of the solution, resin dose, acid concentration for elution, etc. have been studied to understand the adsorption phenomena, loading capacity of the resin and kinetics of adsorption of copper from the aqueous feed. Based on the studies, a process is developed for the recovery of copper. The process could be simulated for the operation in continuous mode to enrich the copper concentration in the solution. The studies will be applicable for the adsorption of copper and recycling of waste electronic effluents containing copper.

2. Experimental

2.1. Materials

The cationic resin, Amberlite IR-120 Na (Styrene di-vinylbenzene copolymer with an active group $-\text{SO}_3\text{Na}$) supplied by M/s Rohm & Haas Co., USA was employed without any further purification. As per the standard process, the resin was activated by immersing it in 1 M HCl for 24 h. The resin was then washed several times by de-ionised water to remove all chloride content. Then the resin was dried at temperature 45°C . The synthetic solution similar to CMP waste effluent containing copper 0.3–0.7 mg/mL in required proportion was prepared from their sulphate salt using distilled water. The chemical reagents such as copper sulphate, sulphuric acid, hydrochloric acid, sodium hydroxide, etc. were laboratory reagent (L.R.) grade.

2.2. Procedure

The batch experiments for the adsorption of copper were carried out in a conical flask using wrist action shaking machine at atmospheric condition. The adsorption studies in vertical Pyrex column (internal diameter 0.9 cm and filled area height 1.75 cm for 0.5 g resin) were carried out by taking weighed amount of resin of standard mesh size (0.32–1 mm). The resin was thoroughly washed with distilled water and then studies were conducted under different concentration of copper maintaining a constant flow rate at room temperature. After the copper adsorption, the

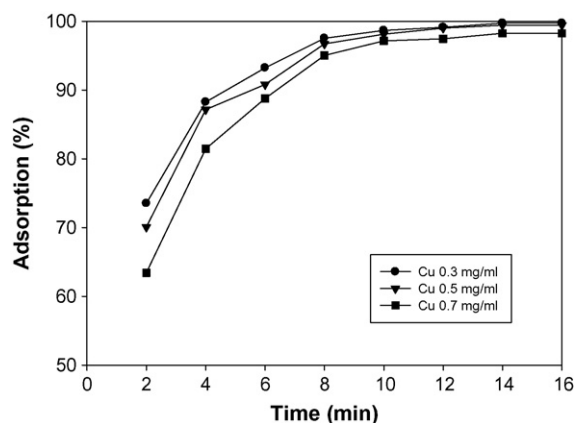


Fig. 1. Effect of contact time on the adsorption of copper by Amberlite IR-120 resin (aq. feed, 'A' = copper sulphate solution, feed pH 5.25, resin 'R' = Amberlite IR-120, A/R = 100).

resin bed was washed with distilled water and loaded metal ions were eluted by passing dilute sulphuric acid. The pH of the solution was adjusted by adding dil. sulphuric acid or sodium hydroxide. The aqueous raffinate and eluted solution were analysed for copper content using Atomic Absorption Spectrophotometer (A Analyst 400, PerkinElmer, USA). Fourier transform infrared spectroscopy (FTIR-NICOLET 380, USA) was used to characterize the activated and copper loaded resin.

3. Results and discussion

In order to develop a process for the recovery of copper from the CMP waste effluent of electronic industry, the studies for the adsorption of copper from synthetically prepared solutions containing copper 0.3, 0.5 and 0.7 mg/mL (similar to the waste stream generated in electronic industry) by Amberlite IR 120 resin were carried out [2]. The effects of various process parameters, viz. contact time, pH of the solution, resin dose, acid concentration for elution, etc. were studied for the adsorption/recovery of copper from the aqueous solutions.

3.1. Effect of contact time

The effect of time on adsorption of copper from the sulphate solution containing copper 0.3, 0.5 and 0.7 mg/mL was studied using Amberlite IR-120 resin. The A/R ratio was maintained to 100. The percentage adsorption vs. time curve is shown in Fig. 1. The smooth leading to equilibrium adsorption of copper on the surface of the resin was obtained. With increase in contact time from 2 to 14 min the percentage adsorption of copper was increased from 73.52, 70.09 and 63.43 to equilibrium 99.73, 99.42 and 98.25 for the aqueous feed containing copper 0.3, 0.5 and 0.7 mg/mL, respectively. Subsequent increase in time had no effect on the adsorption of copper. Therefore, the maximum contact time 14 min is suitable to reach the reaction in equilibrium.

3.2. Effect of pH

The studies were made to see the effect of pH on the adsorption of copper from the aqueous feed solutions containing copper 0.3, 0.5 and 0.7 mg/mL with a fixed quantity of Amberlite IR 120 resin. The pH of the solution was adjusted by the addition of sodium hydroxide. The results presented in Fig. 2 shows that the adsorption of copper increases with the increase in equilibrium pH of the solution. At lower pH, the hydrogen ions compete with metal cations for

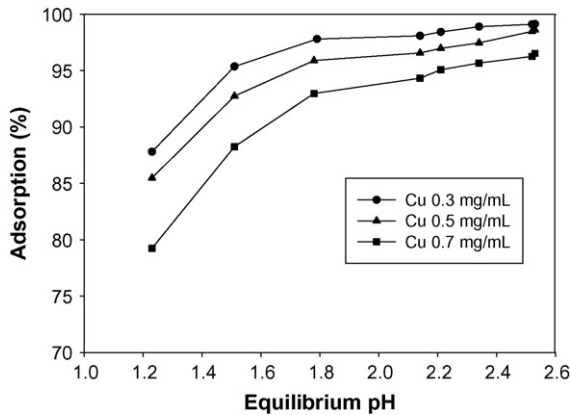


Fig. 2. Effect of pH on the adsorption of copper by Amberlite IR-120 resin (aq. feed, 'A' = copper sulphate solution, resin 'R' = Amberlite IR-120, A/R = 100, contact time = 14 min).

the exchange site in the system. The metal cations are completely released under extreme acidic condition. At equilibrium pH 2.5, the maximum adsorption of copper 99.13, 98.62 and 96.92% was found from the solution containing copper 0.3, 0.5 and 0.7 mg/mL, respectively. At lower pH, the adsorption of copper was found low due to the high concentration and mobility of hydrogen ions. The hydrogen ions are preferentially adsorbed by the resin in comparison to copper (II) ions. At pH 2.53 the amount of Cu(II) adsorbed was found 29.741, 44.874 and 65.422 mg/g for the aqueous feed containing copper 0.3, 0.5 and 0.7 mg/mL. Equilibrium distribution coefficient values (K_d) for the copper ions at various initial solution concentrations were calculated using obtained experimental data. $K_d = q_e/C_e$, where q_e is the amount of metal ion adsorbed at equilibrium and C_e is the equilibrium concentration of metal ions in solution. The plot of $\log K_d$ is presented in Fig. 3. Good regression coefficient values 0.974, 0.981 and 0.978 were obtained for the aqueous feed solution containing copper 0.3, 0.5 and 0.7 mg/mL, respectively.

3.3. Effect of resin dose

The effect of resin dose on adsorption of copper from the aqueous feed containing copper 0.3, 0.5 and 0.7 mg/mL at aq. feed pH 5 was studied keeping retention time for mixing 14 min. Resin dose was varied from 0.1 to 0.5 g (3.3–16.66 g resin/L of aqueous solution) in 30 mL solution. The results presented in Fig. 4 indicate the increase in adsorption of copper with increase in resin dose as avail-

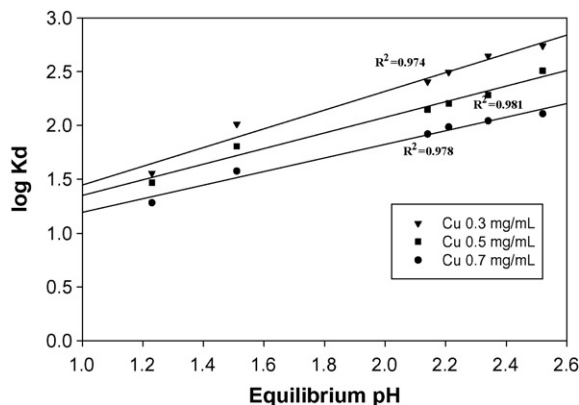


Fig. 3. The distribution coefficients of copper ions on Amberlite IR-120 resin as a function of pH.

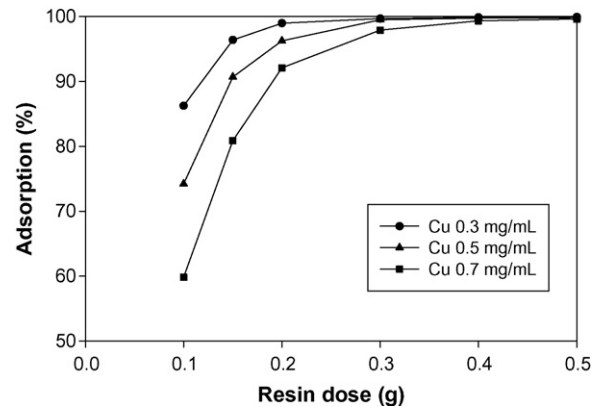


Fig. 4. Effect of resin dose on the adsorption of copper by Amberlite IR-120 resin (aq. feed = copper sulphate solution, feed pH 5.25, resin = Amberlite IR-120, contact time = 14 min).

able sites or surface area increases with higher quantity of resin. An increase in surface area of resin automatically enhances the rate of adsorption reaction. The total adsorption of copper was found with resin dose of 16.66 g resin/L. Further increase in resin dose has shown negligible effect towards increase in percentage adsorption of copper from the solution.

3.4. Kinetics of adsorption

The data for copper adsorption obtained from the solution containing copper 0.3–0.7 mg/mL in various contact time with Amberlite IR 120 resin were calculated to determine the order of reaction rate. Well known kinetic expressions, namely pseudo-first and second order were used to fit the experimental data [8]. The pseudo-first-order rate expression of Lagergren [20,21] is generally described by the following equation:

$$\frac{dq}{dt} = k_1(q_e - q) \quad (1)$$

where q_e and q are the amounts of copper(II) ion (mg/g) adsorbed on the resin at equilibrium and at time t , respectively and k_1 is the rate constant (min^{-1}). Integrating and applying the boundary conditions, $t = 0$ and $q = 0$ to $t = t$ and $q = q_e$ at maximum equilibrium adsorption, equation takes the form:

$$\log(q_e - q) = \log(q_e) - \left(\frac{k_1}{2.303}\right) t \quad (2)$$

The rate constant k_1 was obtained from the slope of linear plots $\log(q_e - q)$ against t for aqueous feed containing copper 0.3, 0.5 and 0.7 mg/mL. The value of correlation coefficient R^2 and rate constant k_1 is listed in Table 1.

The pseudo-second-order rate reaction was also analysed by fitting the same data for copper adsorption and described by

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (3)$$

where k_2 is the rate constant of pseudo-second-order sorption (g/mg min). Integrating and applying boundary conditions $t = 0$ and $q = 0$ to $t = t$ and $q = q_e$, Eq. (3) can be presented in a linear form as

$$\frac{t}{q} = \left(\frac{1}{h}\right) + \left(\frac{1}{q_e}\right) t \quad (4)$$

where $h = k_2 q_e^2$ is the initial sorption rate.

If second order kinetics is applicable, the plot of (t/q) against t of the above equation should give a linear relationship from which the constants k_2 could be determined for aqueous feed containing copper 0.3, 0.5 and 0.7 mg/mL (Fig. 5). The value of correlation

Table 1
Rate constants for first and second order for adsorption of copper on Amberlite IR-120 resin

Concentration of aq. feed, Co (mg/mL)	Constants of kinetics expression: first order rate expression	
	k_1 (min ⁻¹)	R^2
0.3	0.522	0.9125
0.5	0.410	0.9769
0.7	0.398	0.9867
Concentration of aq. feed, Co (mg/mL)	Constants of kinetics expression: second order rate expression	
	k_2 (g/mg min)	R^2
0.3	0.024	0.9970
0.5	0.021	0.9997
0.7	0.020	0.9980

coefficient R^2 and rate constant k_2 is listed in Table 1. The second order rate expression fits the data most satisfactorily similar to one reported by several authors [22–25]. The correlation coefficient R^2 for the second order rate was found greater than first order. Another thing is that the value of k_2 (Table 1) was found more constant up to two digits with changing concentration of copper 0.3–0.7 mg/mL in aqueous feed. Thus, second order rate expression fits the data most satisfactorily.

3.5. Adsorption in multi-stage contacts

Column studies were carried out to determine the loading capacity of resin. 0.5 g of resin was taken in column and 50 mL of aqueous feed containing copper was contacted. The repeated contact of the same resin was made with fresh aqueous feed containing copper 0.295 and 0.475 mg/mL to achieve equilibrium adsorption. The results presented in Figs. 6 and 7 indicate the extraction of copper in different stages. In the first stage of contact, the adsorption of copper was found 29.40 mg/g resin from the aqueous feed containing copper 0.295 mg/mL at 2.5 pH and A/R of 100 mL/g. In subsequent stages of contacts, the adsorption of copper from the aqueous feed decreased as the available site for the adsorption decreased in each contact. A cumulative adsorption at aqueous to resin ratio of 100 in 7 and 6 stages (Figs. 6 and 7) was found to be 115.05 and 114.794 mg copper per gram of resin from the aqueous feed containing copper 0.295 and 0.475 mg/mL, respectively. Satisfactory material balance was obtained on comparing the results of copper adsorbed and eluted with sulphuric acid.

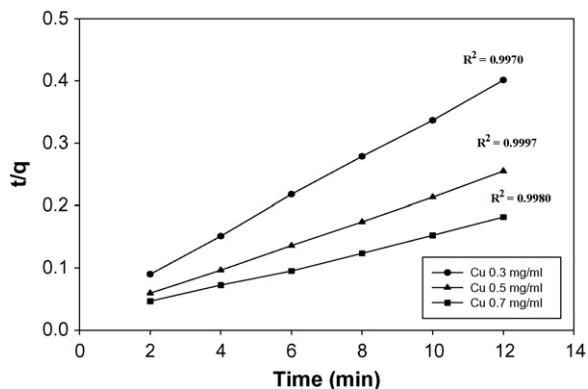


Fig. 5. Fitting of second order rate for copper adsorption onto Amberlite IR-120 resin.

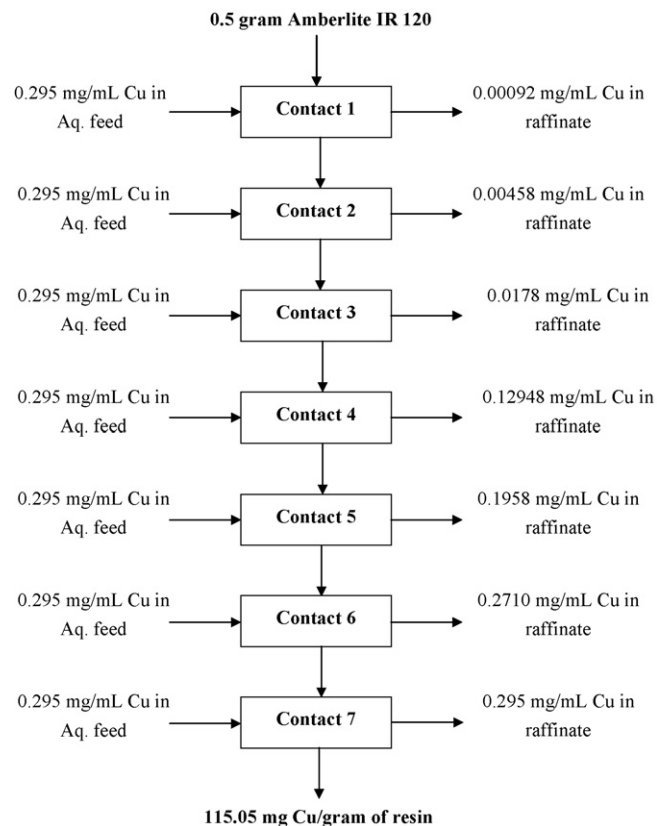


Fig. 6. Dynamic loading of copper on Amberlite IR-120 from aq. feed of 0.295 mg/mL copper (A/R = 100, flow rate = 51 mL/h, initial pH 5, equilibrium pH 2.52).

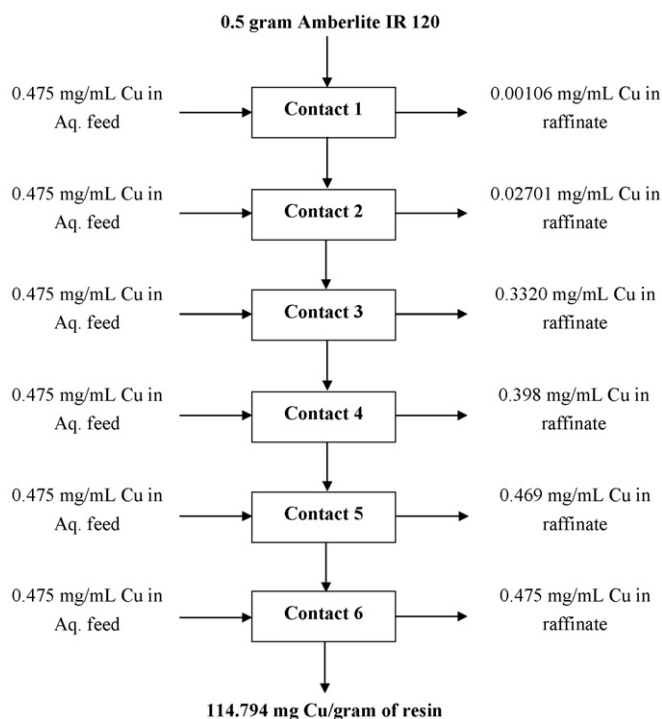


Fig. 7. Dynamic loading of copper on Amberlite IR-120 from aq. feed of 0.475 mg/mL copper (A/R = 100, flow rate = 51 mL/h, initial pH 5, equilibrium pH 2.52).

Table 2
Constants and correlation coefficients of Langmuir and Freundlich isotherm for adsorption of copper

Resin	Solution, concentration (mg/mL)	Freundlich isotherm			Langmuir isotherm		
		n	k_f	R^2	q_m (mg/g)	k_1	R^2
Amberlite IR-120	0.295	5.319	163.07	0.925	107.526	465	0.971
	0.475	5.988	135.26	0.916	106.38	470	0.988

3.6. Adsorption isotherm

The equilibrium data obtained from the experiment for copper adsorption on Amberlite IR 120 were analysed using the Langmuir and Freundlich equations [26–29]. The Langmuir model assumes that the uptake of metal ions occurs on a homogeneous surface by monolayer adsorption without any interaction between adsorbed ions. The model can be represented in the linearised form as

$$\frac{1}{q} = \left[\left(\frac{1}{k_1 q_m} \right) \left(\frac{1}{C_e} \right) \right] + \left[\frac{1}{q_m} \right] \quad (5)$$

where C_e = equilibrium concentration of metal in solution (mg/mL), q = amount of metal adsorbed on the resin at equilibrium, k_1 = equilibrium constant related to the affinity of the binding sites for the metals or the Langmuir constant. q_m = the resin capacity (maximum possible amount of metallic ion adsorbed per unit mass of adsorbent).

Freundlich model assumes that the uptake or adsorption of metal ions occurs on a heterogeneous surface by monolayer adsorption. The model is described by the following equation:

$$q = k_f (C_e)^{1/n} \quad (6)$$

$$\log(q) = \left(\frac{1}{n} \right) \log(C_e) + \log k_f \quad (7)$$

The common terms in above equation are described in Langmuir expression, and k_f and n are Freundlich constants that can be related to the adsorption capacity and adsorption intensity, respectively. The plots ' $1/C_e$ vs. $(1/q)$ ' and ' $\log(C_e)$ vs. $\log(q)$ ' to validate the Langmuir and Freundlich isotherms respectively for the aqueous feed containing copper 0.295 and 0.475 mg/mL were evaluated and data presented in Table 2. The plot for Langmuir isotherm is presented in Fig. 8. The least square values of correlation coefficient (R^2) were obtained to compare the suitability of the adsorption process. The constants for each isotherm were also calculated. Data presented in Table 2 showed that the Langmuir equilibrium isotherm was found to fit the experimental data better than the Freundlich isotherm equation.

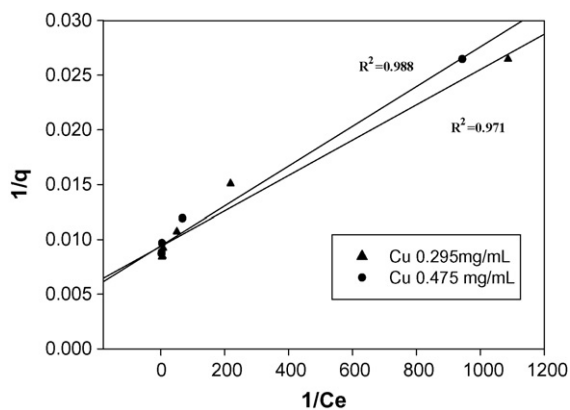


Fig. 8. Plot for Langmuir isotherm for the adsorption of copper by Amberlite IR-120 resin.

3.7. FT-IR spectroscopic studies of resin on the copper extraction

The FT-IR spectrum of activated Amberlite IR 120 resin and copper loaded resin were recorded and plotted in Fig. 9. IR absorption frequencies assignments for the matrix were examined. The comparison study was made to analyse the change of FT-IR spectrum of the resin after adsorption of copper. The spectrum associated with the polymeric matrix of styrene exhibits strong band at 2980 cm^{-1} , ascribed to the stretching mode of C–H group [30,31]. The band at 1691 cm^{-1} , assigned to ring vibration of benzene ring [30,31]. The bands observed at 1413 cm^{-1} , assigned the stretching of O–S–O group [30], at 832.9 cm^{-1} presented aromatic out of plane C–H bend, at 669.177 cm^{-1} showed the S–O bend [30]. When the spectra of copper loaded resin was compared with activated resin, the relative peak intensities of peak series at 1214 , 1153 and 1122.2 cm^{-1} region were changed because of metal complex formation between copper ions and sulfonate groups of resin [32]. The sulfonate ($-\text{SO}_3^-$) groups participating in ion exchange are located under 1122.2 – 1214 cm^{-1} region for resin.

3.8. Elution of copper from loaded resin

The solution pH plays very important role during the elution of metal from the loaded resin. The control of solution pH/acid concentration in solution is necessary to elute all the copper from the resin. Sulphuric acid was used to elute all the copper from the copper loaded resin. From the sulphate solution containing copper 0.4 mg/mL , the sufficient amount of copper loaded resin was generated. The elution studies were carried out by varying the sulphuric acid concentration from 0.09 to 1.80 M keeping A/R ratio 100 and contact time 20 min . The elution of copper increased with increasing concentration of the acid in eluant (see Fig. 10). The 99.99% copper was found to be eluted by 1.8 M sulphuric acid at A/R ratio 100 in 20 min . To enrich the copper content in the eluted solution, effect of A/R ratio was also studied with 1.80 M sulphuric acid. Result presented in Fig. 11 shows that the 99.99% copper could

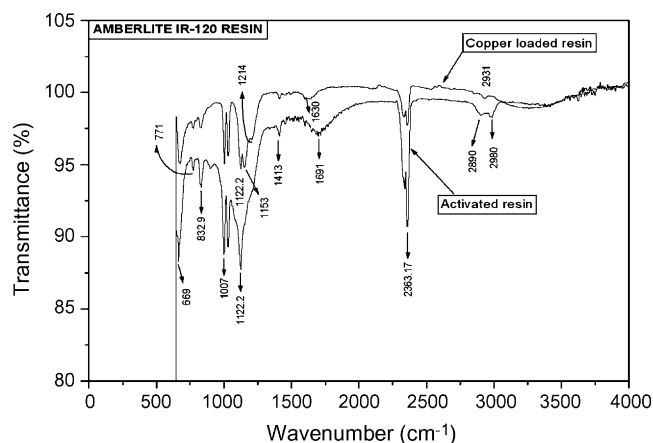


Fig. 9. FT-IR spectra of activated and copper loaded Amberlite IR-120 resin.

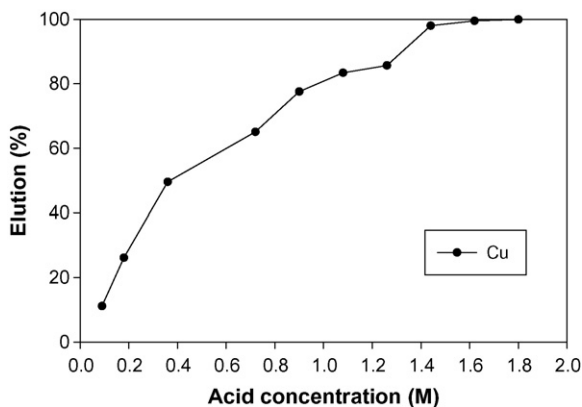


Fig. 10. Effect of acid concentration in elution process (loaded resin = Cu 40 mg/g of Amberlite IR 120 resin, elution solution = sulphuric acid, A/R = 100, contact time = 20 min).

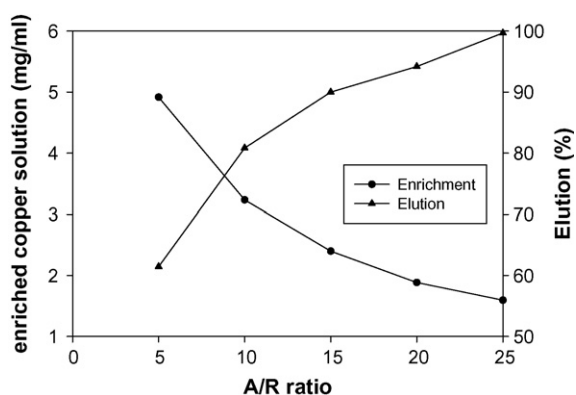


Fig. 11. Elution of copper from loaded resin (loaded resin = Cu 40 mg/g of Amberlite IR 120 resin, elution solution = sulphuric acid, A/R = 100, contact time = 20 min).

be eluted even at A/R ratio 25 to get the copper enriched solution of concentration 1.60 g/L.

4. Conclusions

Bench scale studies carried out in shake out flask showed increase in adsorption of copper with increase in time and reaches equilibrium in 14 min. The 99.99% copper was found to be adsorbed from the sulphate solution containing copper 0.3–0.7 mg/mL of solution (feed pH 5) at A/R ratio 100 and eq. pH 2.5 in contact time 14 min. Adsorption of copper studied in different contacts in column showed the copper loading capacity 115.05 and 114.794 mg/g of resin from the aqueous feed containing copper 0.295 and 0.475 mg/mL, respectively. The data for adsorption of copper was found to be fitted well for Langmuir isotherm. The kinetic studies showed that the copper adsorption was found to follow the second order rate equation better. The copper could be eluted from loaded resin by 1.8 M H_2SO_4 at A/R ratio 25 to get the copper enriched solution of concentration 1.60 g/L. The raffinate obtained after the adsorption of copper could be disposed safely without affecting the environment.

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