

Removal of Transition Metals from Dilute Aqueous Solution by Carboxylic Acid Group containing Absorbent Polymers

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Abstract

A carboxylic acid group containing resin with cation exchange capacity, 12.67 meq/g, has been used to remove Cu^{2+} , Co^{2+} and Ni^{2+} ions from dilute aqueous solution. The resin had Cu^{2+} , Co^{2+} and Ni^{2+} removal capacity, 216 mg/g, 154 mg/g and 180 mg/g, respectively. The selectivity of the resin for Cu^{2+} over Co^{2+} and Ni^{2+} was investigated in the presence of 1.0 M or 0.5 M sodium chloride. The resin was found to offer high capacity and selectivity for Cu^{2+} . The sorbed metal ions (Cu^{2+} , Co^{2+} and Ni^{2+}) were easily stripped with dilute HCl. The sorbed Co^{2+} and Ni^{2+} could also be stripped with 1.0M NaCl.

Keywords: Ion-exchange; Selectivity; Sodium chloride; Carboxylic acid group-containing absorbents

Introduction

During the past two decades, high water absorbing polymers have received considerable interest from both academic and applied research laboratories. These materials show very high water retention capacities, which make them useful for new industrial and biomedical applications [1-3]. The synthetic polyacrylate derived from acrylic acid has emerged as one important high water absorbing polymer, because acrylic acid is cheap and easy to polymerize to products with high molecular weight. The development of high water absorbing polymers prepared by reacting acrylic acid and acrylamide copolymer with formaldehyde (crosslinker) was reported in our previous publication [4]. This cross linked co-polymerization of acrylic acid and acrylamide, referred to as CCPAA absorbent, was found that its absorption capacity depends on the cross linking density. With high cross linking density, e.g. high acrylamide content, it shows relatively low swelling in water. However, these materials are suitable for use as ion-exchange resins, where some swelling is necessary but high swelling ratio must be avoided. It is well known that resin capacity, selectivity and rate behavior for loading and elution are three important functional properties of ion-exchange resins for influencing their applications. The equilibrium sorption capacity of a resin is often observed in practice to be much less than the theoretical capacity calculated from resin composition. This is attributed to the inaccessibility of the many sorption sites buried inside the resin matrix. It is expected that this swelling property of the CCPAA resin will benefit its sorption capacity for the metal ions.

Maxim and co-workers [5] recently reported the retention process of the Cu^{2+} and Ni^{2+} cations from CuSO_4 and NiSO_4 aqueous solution by eight acrylic ion exchangers. Liu and coworkers recently reported removal of Cu^{2+} , Co^{2+} and Ni^{2+} from aqueous solution using bio-based carboxylate containing resins [6]. Rivas and coworkers studied the metal retention properties of resins containing amino and carboxylic acid groups (cross linked poly[3-(methacryloylamino)propyl]dimethyl(3-sulfopropyl)ammonium hydroxide], P(MAPDSA), and poly[3-(methacryloylamino)propyl]dimethyl(3-sulfopropyl)ammonium hydroxide-co-acrylic acid], P(MAPDSA-co-AA). They investigated under competitive and noncompetitive conditions for Cu^{2+} , Cd^{2+} , Hg^{2+} , Zn^{2+} , Pb^{2+} , and Cr^{2+} ions by batch and column equilibrium procedures. The resin showed that a maximum retention capacity value for Hg^{2+} at pH 2 was 1.89 meq/g. The resin also showed a high selectivity to Hg^{2+} ion

[7]. In this work, the water swellable CCPAA resin with 5% acrylamide has been used for studying sorption characteristics and selectivity for copper over cobalt and nickel. Consequently the distribution behavior of the Cu^{2+} , Co^{2+} and Ni^{2+} in the presence of salt (NaCl) in the solution was calculated presented in this paper. This resin will be explored further for its application in waste water treatment.

Experimental Details

Preparation of the CCPAA resin

Details for the synthesis of the CCPAA resin (5% acrylamide) were given in the literature (4). Typically, a solution of 90 ml distilled water, 0.048 g (18 mmol) of potassium persulfate and 0.02 g (0.09 mmol) of potassium metabisulfite were added into a flask fitted with a mechanical stirrer, condenser, thermometer and dropping funnel. At 65°C, 11.40 g (0.16 mol) of acrylic acid and 0.60 g (0.008 mol) of acrylamide in 15 ml distilled water were added dropwise in 10 minutes, followed by adjusting pH to about 4.5 with sodium hydroxide solution. The mixture was heated to 75°C. The polymerization began in about 10 minutes. The system was maintained for 2 hrs at 70°C. 3.7 ml formaldehyde solution was then added at 45°C and maintained for 1 hr. The system was heated to 70°C and maintained for 3 hrs. The product was dewatered with ethanol and dried to solid product at 80°C overnight. The resin was ground to pass 60 mesh sieves. The cation exchange capacity of the CCPAA resin was measured according to the method described by Kunin [8] and was found to be 12.67 meq/g.

Reagents

Copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and cobalt sulphate, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ were obtained from J. T. Baker, USA. They were Baker analyzed reagents. Nickel sulphate, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ was obtained from Fisher

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Scientific Company, USA. It was a Fisher certified reagent. Copper, cobalt and nickel atomic absorption standard solutions were obtained from Aldrich, USA. They were 1,000 ppm in 1% HNO₃.

Analysis

Metal ions in aqueous solution were measured with ARL (applied Research Laboratories) SpectraSpan-7 DCP emission spectrometer.

Sorption experiments

In all equilibrium studies, measured amounts of sorbent was vigorously shaken with definite volumes of solution of known metal concentration for 20 hrs in tightly stoppered glass bottles at ambient temperature, using a gyratory shaker with 2 cm eccentricity at 300 rpm. The residual metal concentrations in solution were measured. A range of concentrations (1 mM/L to 10 mM/L) was employed for each of the metal species, Cu²⁺, Co²⁺ and Ni²⁺ chosen for the study. The pH values of the solution for CuSO₄, CoSO₄ and NiSO₄ are 5.0-5.4, 5.1-5.3 and 5.7-6.0, respectively. The sorption was also measured as a function of time under vigorous agitation.

The sorption capacity of the CCPAA resin for Cu²⁺, Co²⁺ and Ni²⁺ was measured by agitating the resin (0.50 g) in excess of 0.1 M CuSO₄, 0.1 M CoSO₄ and 0.1 M NiSO₄ solution (50 mL), respectively, for 20 hrs. The results showed that the sorption capacities of CCPAA resin for Cu²⁺, Co²⁺ and Ni²⁺ were 216 mg/g, 154 mg/g and 180 mg/g, respectively. The sorption capacity of the CCPAA resin showed higher than that of ion-exchange resin prepared by conversion of soybean oil, which are 192 mg/g, 78 mg/g and 96 mg/g, respectively [6]. The accessibility of functional groups on the resin may be a key factor because of swell ability of the resin.

Selectivity experiments

The selectivity of the sorption for Cu²⁺ over Co²⁺ and Ni²⁺ was studied. The measured amounts of the sorbent were vigorously shaken with definite volumes of solution of known metal concentration (combinations of 2 metals at a time) in the presence of varying concentrations of sodium chloride for 20 hrs at ambient temperature. The residual metal concentration in solution was determined. A range of concentrations (1 mM/L to 10 mM/L) was employed for each pair of metal species.

pH Runs

Sulphuric acid was used to acidify the solution. The pH range employed for the pH profiles was from 1.85 - 6.84. Once 20 mL of the metal solution (4 mM/L) was added, the bottles were placed evenly on a platform shaker at 300 rpm for 20 hrs at ambient temperature. The residual metal concentration in solution was measured.

Stripping behavior

In the stripping experiments, 0.04 g of the CCPAA resin, on which sorbed 8.64 mg Cu²⁺, or 6.16 mg Co²⁺, or 7.2 mg Ni²⁺, was used. The bottles were placed evenly on a platform shaker at 300 rpm at ambient temperature. The time was started when the acid solution (HCl) first hit the resin particles. The bottles were removed at 15 min, 30 min, 1 hr, 2 hrs, 3 hrs and 4 hrs intervals. The metal concentrations in the solutions were measured. Sorbed Co²⁺ and Ni²⁺ ions were also stripped by using 1.0 M NaCl solution. The bottles were removed at 4 hrs, 12 hrs, 24 hrs and 30 hrs intervals.

Results and Discussion

Sorption isotherm

The sorption isotherm was studied using metal concentrations between 1 mM/L to 10 mM/L at pH 5.0-6.0 and ambient temperature. The equilibrium data for the sorption of Cu²⁺, Co²⁺ and Ni²⁺ from aqueous solutions by the CCPAA resin was plotted against equilibrium solution in Figure 1. The results showed that the CCPAA resin could take up significant quantities of Cu²⁺, Co²⁺ and Ni²⁺. At lower metal concentrations (< 6 mM/L), the sorption capacity of the CCPAA resin for Cu²⁺, Co²⁺ and Ni²⁺ did not change significantly. However, at higher concentrations (> 8 mM/L), the metal ions were adsorbed in roughly the order Cu²⁺ > Ni²⁺ > Co²⁺.

The equilibrium sorption data of copper in Figure 1 fitted well to the Freundlich isotherm, whereas they were fitted poorly by a Langmuir isotherm. The equilibrium sorption data of cobalt and nickel fitted well both to the Freundlich isotherm and to the Langmuir isotherm. Thus, for the sorption of Cu²⁺, Co²⁺ and Ni²⁺, the Freundlich isotherm might be written as:

$$X^* = mC^n \quad (1)$$

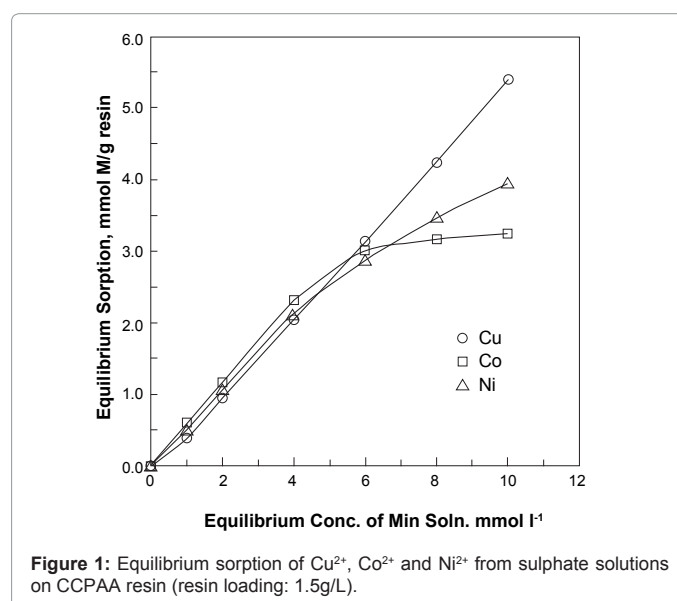
where X^* and C^* are the equilibrium sorption and equilibrium concentration of sorbate, respectively, and m (mmol/g dry resin) and n are adjustable parameters. To solve for the isotherm constants, the function may be linearized by taking the natural logarithm of each side (eq.2).

$$\ln X^* = \ln m + n \ln C^* \quad (2)$$

Values of m and n were determined by least-squares fit of the sorption data in Figure 1 and were presented in Table 1. For the sorption of Co²⁺ and Ni²⁺, the Langmuir isotherm may be written as:

$$C_A^*/X^* = 1/K_b A_s + C_A^*/A_s \quad (3)$$

where X^* and C_A^* are the equilibrium sorption (mmol/g dry resin) and equilibrium concentration (mM/L) of metal ion in solution, respectively. The values of the saturation constant, A_s (mmol/g dry resin), and the binding constant, K_b (l mM⁻¹) were determined by least-squares fit and were presented in Table 1.



Effect of salt

Experiments were conducted to determine the effect of high background concentration of sodium chloride. It was found that neither of NaCl concentrations of 0.5 M and 1.0 M has any significant effect on the Cu^{2+} sorption capacity of the CCPAA resin as seen in Figure 2. However the Co^{2+} and Ni^{2+} sorptions capacity on the CCPAA resin decreased drastically over the whole range of sorbate concentrations employed as seen in Figure 3 and Figure 4. This may lead to a method of separating Cu^{2+} from Co^{2+} and Ni^{2+} , since commercial cation-exchange

Sorbate	Freundlich isotherm eq. (2)			Langmuir isotherm, eq. (3)		
	m (mmol/g dry resin)	n	corr. coeff.	As (mmol/g dry resin)	K_b (l mmol ⁻¹)	corr. coeff.
CuSO_4	0.4041	1.139	0.998			
CoSO_4	0.5455	0.900	0.989	47.62	0.011	0.996
NiSO_4	0.6703	0.764	0.959	10	0.065	0.995

Table 1: Parameters of Freundlich and Langmuir isotherm for sorption on the CCPAA resin.

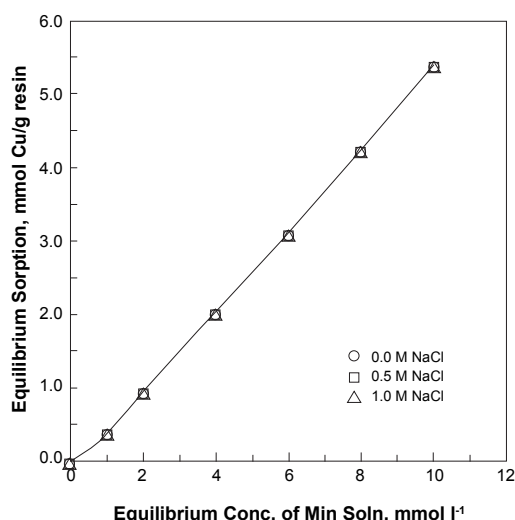


Figure 2: Equilibrium sorption of Cu^{2+} from CuSO_4 solution with 0.5 M NaCl and 1.0 M NaCl on CCPAA resin (resin loading: 1.5g/L).

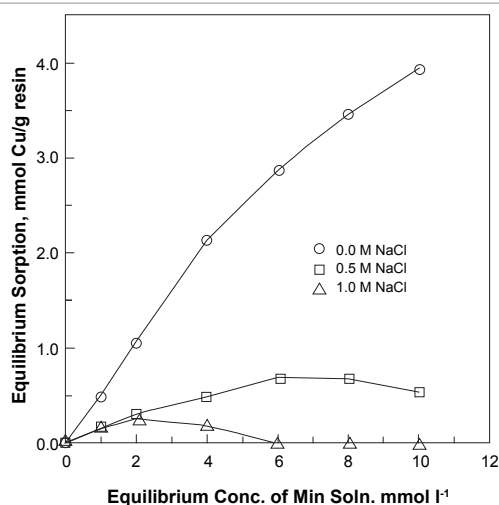


Figure 3: Equilibrium sorption of Co^{2+} from CoSO_4 solution with 0.5 M NaCl and 1.0 M NaCl on CCPAA resin (resin loading: 1.5g/L).

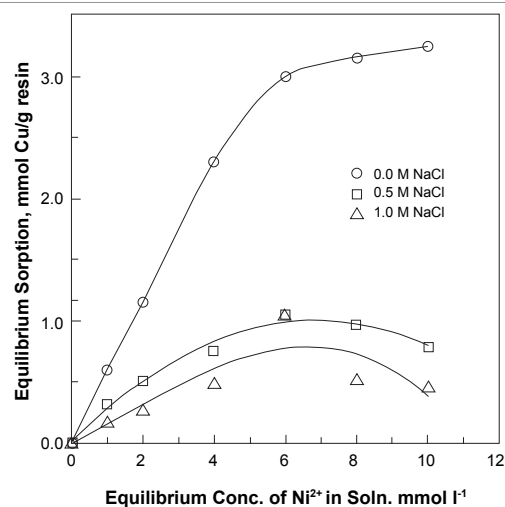


Figure 4: Equilibrium sorption of Ni^{2+} from NiSO_4 solution with 0.5 M NaCl and 1.0 M NaCl on CCPAA resin (resin loading: 1.5g/L).

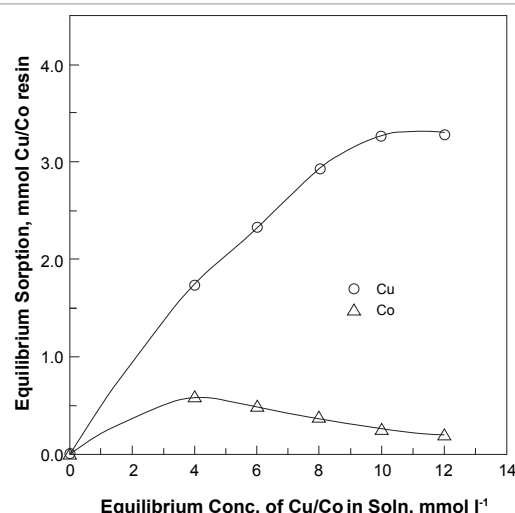


Figure 5: Equilibrium sorption of $\text{Cu}^{2+}/\text{Co}^{2+}$ from sulphate solution with 1.0 M NaCl on CCPAA resin (resin loading: 1.5g/L).

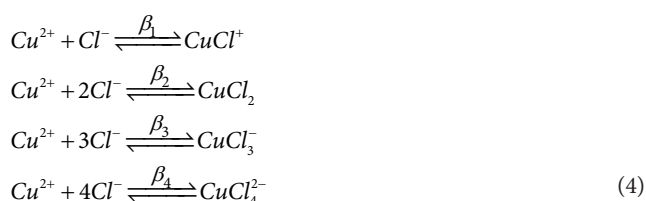
resins containing sulfonic or carboxylic functional groups have limited potential for removal and recovery of heavy metals from process solutions and waste streams because of their low selectivity.

Selectivity for copper (II)

In hydrometallurgy, considerable interest exists in the separation of Cu^{2+} from Co^{2+} and Ni^{2+} , therefore, the selectivity of the CCPAA resin for Cu^{2+} over Co^{2+} or Ni^{2+} with presence of 1.0 M NaCl in the solution was investigated. Figure 5 and Figure 6 showed the results of two mixed solutions, in which each metal ion concentration was varied from 4 mM/L to 12 mM/L. It can be seen from Figure 5 and Figure 6 that the CCPAA resin is able to absorb about 10 times more Cu^{2+} than Co^{2+} and Ni^{2+} at higher metal concentrations (> 8 mM/L). However, the sorption capacity differences between Cu^{2+} , Co^{2+} and Ni^{2+} were also rather large at lower metal concentrations (< 6 mM/L). It may be predicted that the separation of Cu^{2+} from Co^{2+} and Ni^{2+} is possible with the CCPAA resin in the presence of salt in solution.

Fraction of copper, nickel and cobalt among several complex species

It is well known that in the presence of Cl^- in solution, the four coordinate M (II) complexes are formed, which reported in literature [6,9]. Taking copper as an example, the stepwise formation constant K_i , which stands for K_1 to K_4 , associated with each of four equilibria, may be obtained from the book of "Stability Constants," edited by Silfén et al. [10] and literature [11], it was found that the values of stepwise formation constants K_i are 2.80, 1.60, 0.49 and 0.73, respectively. Considering the overall formation, the equation may be written as follows:



From equation (4), the mass balance equation for each species of complex can be obtained as equation 5.

$$\begin{aligned} \beta_1 &= \frac{[\text{CuCl}^+]}{[\text{Cu}^{2+}][\text{Cl}^-]} \\ \beta_2 &= \frac{[\text{CuCl}_2]}{[\text{Cu}^{2+}][\text{Cl}^-]^2} \\ \beta_3 &= \frac{[\text{CuCl}_3^-]}{[\text{Cu}^{2+}][\text{Cl}^-]^3} \\ \beta_4 &= \frac{[\text{CuCl}_4^{2-}]}{[\text{Cu}^{2+}][\text{Cl}^-]^4} \end{aligned} \quad (5)$$

The formation constants, β_1 , β_2 , β_3 , and β_4 , are found to have relationships to K constants as follows:

$$\beta_1 = K_1, \beta_2 = K_1 K_2, \beta_3 = K_1 K_2 K_3, \text{ and } \beta_4 = K_1 K_2 K_3 K_4.$$

By substituting the K values (already known from the literature), the numerical values for β_1 , β_2 , β_3 and β_4 may be calculated. If [C] is the total concentration of copper, then

$$[\text{C}] = [\text{Cu}^{2+}] + [\text{CuCl}^+] + [\text{CuCl}_2] + [\text{CuCl}_3^-] + [\text{CuCl}_4^{2-}]$$

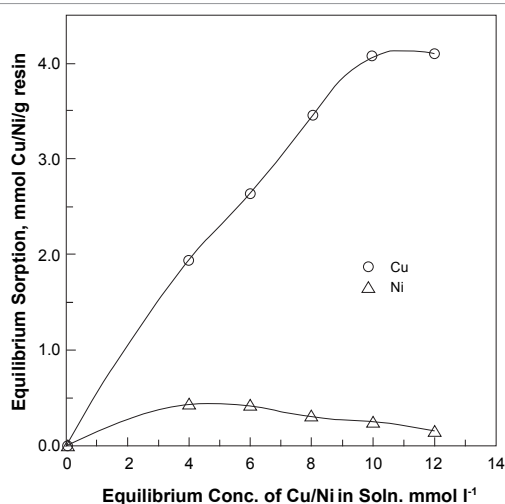


Figure 6: Equilibrium sorption of $\text{Cu}^{2+}/\text{Ni}^{2+}$ from sulphate solution in 1.0 M NaCl solution on CCPAA resin (resin loading: 1.5g/L).

Fraction	Copper		Nickel		Cobalt	
	[Cl ⁻] 1.0M	[Cl ⁻] 0.5 M	[Cl ⁻] 1.0M	[Cl ⁻] 0.5 M	[Cl ⁻] 1.0M	[Cl ⁻] 0.5 M
α_0	1.92×10^{-6}	2.36×10^{-5}	0.206	0.56	0.455	0.68
α_1	1.21×10^{-3}	7.45×10^{-3}	0.153	0.21	0.314	0.23
α_2	4.80×10^{-2}	1.48×10^{-1}	0.161	0.11	0.232	0.087
α_3	0.15	0.23	0.243	0.083		
α_4	0.80	0.61	0.237	0.04		

Table 2: The fraction of metal ions presented as each species.

Fraction	[Cl ⁻]1.0M		[Cl ⁻] 0.5 M		[Cl ⁻]1.0M		[Cl ⁻] 0.5 M	
	copper	nickel	copper	nickel	copper	cobalt	copper	cobalt
α_0	1.92×10^{-6}	1.92×10^{-6}	2.36×10^{-5}	2.36×10^{-5}	1.92×10^{-6}	1.92×10^{-6}	2.36×10^{-5}	2.36×10^{-5}
α_1	1.21×10^{-3}	1.42×10^{-6}	7.45×10^{-3}	8.70×10^{-6}	1.21×10^{-3}	1.32×10^{-6}	7.45×10^{-3}	8.10×10^{-6}
α_2	4.80×10^{-6}	1.50×10^{-6}	1.48×10^{-1}	4.60×10^{-5}	4.80×10^{-6}	9.80×10^{-7}	1.48×10^{-1}	3.00×10^{-6}
α_3	1.49×10^{-1}	2.27×10^{-6}	0.23	3.50×10^{-6}	1.49×10^{-1}	N/A	0.23	N/A
α_4	0.8	2.21×10^{-6}	0.61	1.70×10^{-6}	0.8	N/A	0.61	N/A

Table 3: The fraction of metal ions presented in the mixture of metal ion system.

Substitution in terms of the formation constants, listed in equation 5, it gives

$$[\text{C}] = [\text{Cu}^{2+}] (1 + \beta_1 [\text{Cl}^-] + \beta_2 [\text{Cl}^-]^2 + \beta_3 [\text{Cl}^-]^3 + \beta_4 [\text{Cl}^-]^4)$$

The fraction of Cu (α) presented as each species may be calculated as a function of $[\text{Cl}^-]$ alone:

$$\alpha_0 = [\text{Cu}^{2+}] / \text{C} = (1 + \beta_1 [\text{Cl}^-] + \beta_2 [\text{Cl}^-]^2 + \beta_3 [\text{Cl}^-]^3 + \beta_4 [\text{Cl}^-]^4)^{-1}$$

$$\alpha_1 = [\text{CuCl}^+] / \text{C} = \beta_1 [\text{Cl}^-] \alpha_0$$

$$\alpha_2 = [\text{CuCl}_2] / \text{C} = \beta_2 [\text{Cl}^-]^2 \alpha_0$$

$$\alpha_3 = [\text{CuCl}_3^-] / \text{C} = \beta_3 [\text{Cl}^-]^3 \alpha_0$$

$$\alpha_4 = [\text{CuCl}_4^{2-}] / \text{C} = \beta_4 [\text{Cl}^-]^4 \alpha_0$$

By substituting of β values and concentrations of 1.0 M and 0.5 M $[\text{Cl}^-]$, respectively, the fractions of Cu (α) were calculated and summarized in Table 2.

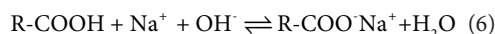
The formation constants for β_1 , β_2 , β_3 , and β_4 of Ni and the formation constants for β_1 and β_2 of cobalt may also be obtained from literature [10,12,13]. For the nickel, they were respectively, 0.74, 0.78, 1.18, and 1.15. For the Co, they were 0.69 and 0.51. The same procedure discussed above was used to calculate the fractions of Ni (α) and Co (α). The results were summarized in Table 2.

In the presence of Cu^{2+} and Ni^{2+} in mixed system, the total metal concentration was defined as follows:

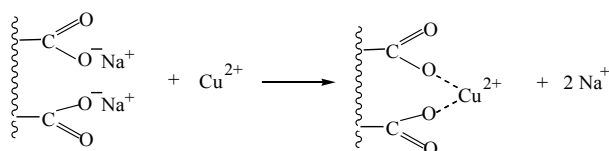
$$[\text{C}] = \{[\text{Cu}^{2+}] (1 + \beta_{1,\text{Cu}} [\text{Cl}^-] + \beta_{2,\text{Cu}} [\text{Cl}^-]^2 + \beta_{3,\text{Cu}} [\text{Cl}^-]^3 + \beta_{4,\text{Cu}} [\text{Cl}^-]^4) + \{[\text{Ni}^{2+}] (1 + \beta_{1,\text{Ni}} [\text{Cl}^-] + \beta_{2,\text{Ni}} [\text{Cl}^-]^2 + \beta_{3,\text{Ni}} [\text{Cl}^-]^3 + \beta_{4,\text{Ni}} [\text{Cl}^-]^4)\}$$

when concentrations of Cl^- , Cu^{2+} and Ni^{2+} are 1.0 M, 0.01 M and 0.01 M, respectively, the fractions of copper and nickel complexes may be calculated using the same procedure discussed above. The results were summarized in Table 3. When Cl^- was changed to 0.5 M, the calculated fractions of copper and nickel complexes in the mixed system were shown in Table 3. The same procedure was used to calculate the fractions of copper and cobalt and results were summarized in Table 3. Because CCPAA resin is a weak acid cation exchange resin, once resin in the protonated form contacted water, a small percentage of

carboxylic groups were ionized, which was reported in the article [6]. When it reacted with base, NaOH, (the CCPAA resin was neutralized during the preparation), some of the carboxylic groups would be converted to a more highly ionized form (eq. 6).



Scheme 1 showed the proposed exchanging process of the CCPAA resin with Cu^{2+} .

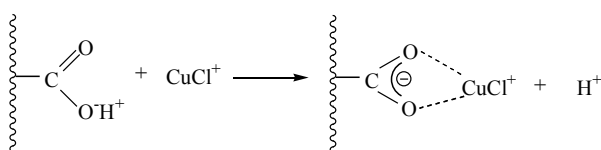


Scheme 1: Ion exchange process of resin with Cu^{2+} ion.

In contrast, the CCPAA resin reacted with a neutral salt (NaCl) to a very minor degree. This is because one of the products is a highly ionized acid. Therefore pH value of the solution will be low, and as a result the ionization of the resin will be depressed and driven to the left, as seen from equation 7.



Consequently, it only exchanges with CuCl^+ . Scheme 2 showed the proposed exchange process of the resin with CuCl^+ .



Scheme 2: Ion exchange process of resin with CuCl^+ .

By comparison of α_i values (corresponding to CuCl^+ , CoCl^+ , and NiCl^+ species, respectively) from Table 3, it was clear that α_i values for CuCl^+ are much larger than those for CoCl^+ and NiCl^+ at 0.5 M and 1.0 M NaCl solution. This is one of the possible explanations of separation of Cu^{2+} from Co^{2+} and Ni^{2+} . It is well known that other factors such as ionic radius and hydration energies of metal ions also affect selectivity and stability of metal complexes, which were reported by other authors [14,15].

Effect of pH

The effect of pH on Cu^{2+} , Co^{2+} and Ni^{2+} sorption by the CCPAA resin was shown in Figure 7. The sorption of these metal ions was relatively unaffected by pH value above 3. However, the sorption of metal ions was found to fall drastically at pH levels below 3. This is attributed to acidic pH, $-\text{COO}^-$ groups are protonated preferably and metal uptake is decreased consequently. The results indicated that the sorbed Cu^{2+} , Co^{2+} and Ni^{2+} could be easily stripped by dilute acid.

Sorption rate behavior

The sorption of Cu^{2+} , Co^{2+} and Ni^{2+} on the CCPAA resin was measured as a function of time at ambient temperature. Taking copper as an example plotted in Figure 8, it can be seen that the rate of sorption on the CCPAA resin was very high for CuSO_4 . 80% of the equilibrium sorption was being attained within 15 minutes from 10 mM solution. However, the rate of sorption on the CCPAA resin was relatively lower for CoSO_4 and NiSO_4 , with only 41.7% and 58.9% of the equilibrium sorption being attained within 15 minutes from 10 mM CoSO_4 and 8 mM NiSO_4 solution, respectively. The rate of attainment of equilibrium

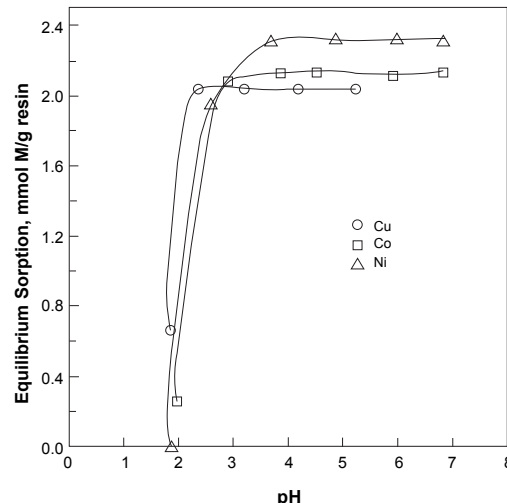


Figure 7: Effect of pH on equilibrium sorption of Cu^{2+} , Co^{2+} and Ni^{2+} from sulphate solution (4.0 mM/L) on CCPAA resin (resin loading: 1.5g/L).

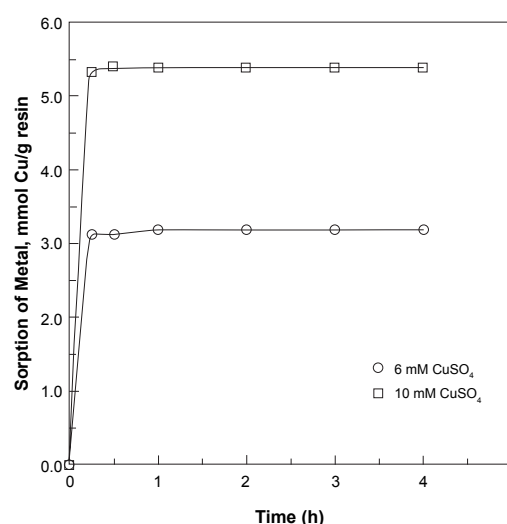


Figure 8: Rate of sorption of Cu^{2+} from sulphate solution (○) 6.0 mM/L, (□) 10.0 mM/L) by CCPAA resin (resin loading: 1.5g/L).

sorption appeared to be dependent on the solution concentrations of Cu^{2+} , Co^{2+} and Ni^{2+} .

Stripping behavior

Since the metal sorption capacity of the CCPAA resin is very low at lower pH values, for example, Ni^{2+} sorption nearly zero at pH level below 2, therefore, 1.0 N HCl was used as a stripping agent. The resin was mixed with the stripping agent at ambient temperature and the solutions were analyzed for Cu^{2+} , Co^{2+} and Ni^{2+} , respectively. The stripping characteristics of metal loaded resin were shown in Figure 9. Very rapid stripping of sorbed Cu^{2+} , Co^{2+} and Ni^{2+} on the CCPAA resin was obtained. The sorbed Co^{2+} and Ni^{2+} sorbed could be stripped completely within 1 hour. However sorbed Cu^{2+} was stripped to 89% in 4 hours. This is in accord with the resin showing relatively higher sorption capacity of Cu^{2+} than Co^{2+} and Ni^{2+} .

Based on the study results of salt effect, it is assumed that sorbed Co^{2+} and Ni^{2+} could be stripped by NaCl solution. The results showed

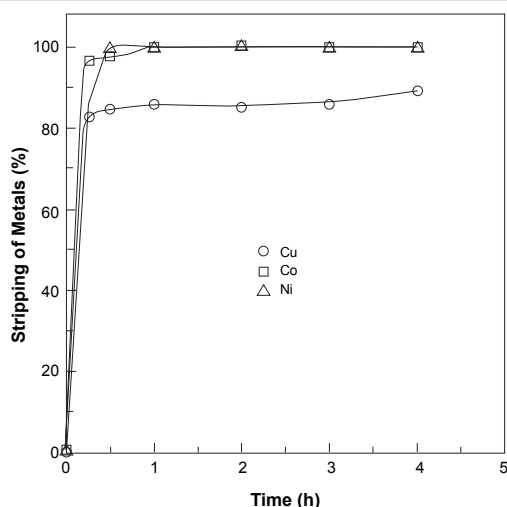


Figure 9: Rates of stripping of CCPAA resin containing metal ions with 1.0 N HCl (resin loading: 2g/L).

that the sorbed Co^{2+} and Ni^{2+} could be successfully stripped using 1.0 M NaCl. However, the stripping rate was relatively low. 85% of sorbed Ni^{2+} and 97% of sorbed Co^{2+} was stripped in 30 hours.

The CCPAA resin showed high sorption capacity for Cu^{2+} , Co^{2+} and Ni^{2+} ions, but in order to be useful on a commercial scale, the resin would have to be reusable. As mentioned above, sorbed metals on the CCPAA resin could be easily stripped. The recycled CCPAA resin was treated with 0.1 N sodium hydroxide solutions and used to adsorb Cu^{2+} . The profiles of fresh and reused resin have shown that the first recycling of the resin decayed around 5%. That means the resin could be reusable, but might have a finite number of regeneration cycles.

Conclusions

The carboxylic acid group containing CCPAA resin could be used for efficiently removing Cu^{2+} , Co^{2+} and Ni^{2+} from dilute aqueous solutions. This resin with cation exchange capacity, 12.67 meq/g, has Cu^{2+} sorption capacity, 216 mg/g, Co^{2+} sorption capacity, 154 mg/g and Ni^{2+} capacity, 180 mg/g, respectively. It was found that pH affected the equilibrium sorption of the metals on the resin at lower pH values. The sorption of Cu^{2+} , Co^{2+} and Ni^{2+} ions on the resin fell drastically at pH levels below 2.3, 2.8 and 3.6, respectively, which indicated the sorbed metals could be stripped by dilute acid. The stripping behaviour of the sorbed metals on the CCPAA resin was studied. It was found that the sorbed Co^{2+} and Ni^{2+} could be completely removed by stripping with 1 N HCl in 1 hour. The sorbed Cu^{2+} was stripped to 89% in 4 hours. This was in accord with the relatively higher absorption strength of Cu^{2+} than Co^{2+} and Ni^{2+} . The sorbed Co^{2+} and Ni^{2+} were also removed by 1.0 M NaCl after a longer time.

After studying the effect of NaCl on the sorption capacity of the resin, it was found that NaCl hardly affects Cu^{2+} sorption on the resin over the whole range of sorbate concentrations employed, whereas the Co^{2+} and Ni^{2+} sorption on the resin decreased drastically over the whole range of sorbate concentrations employed. Based on this information, the possibility of separation of Cu^{2+} from mixture of $\text{Cu}^{2+}/\text{Co}^{2+}$, or from mixture of $\text{Cu}^{2+}/\text{Ni}^{2+}$ in the presence of NaCl were studied. The results showed that the resin could take 10 times more Cu^{2+} than Co^{2+} and Ni^{2+} at higher metal concentrations ($> 8 \text{ mM/L}$). However the sorption

capacity difference between Cu^{2+} , Co^{2+} and Ni^{2+} were also rather large at lower metal concentrations ($< 6 \text{ mM/L}$). The CCPAA resin could be reusable, but it was noted that the resin had a finite number of regeneration cycles, because of the decrease in sorption capacity of the resin.

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