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Adsorptive Removal of Copper from Aqueous Solution By Amberlite Cation-exchange Resin-Equilibrium And Kinetic Studies

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Abstract. In this study, Amberlite weak acid cation-exchange resin has been used as an adsorbent for Cu(II) removal from aqueous solutions. Adsorption studies were performed by varying metal ion concentration, pH, agitation time and weight of resin. Langmuir, Freundlich and Redlich-Peterson isotherm parameters were calculated using the equilibrium adsorption data. The ion-exchange process, which is pH dependant, indicated that maximum removal of Cu(II) was obtained at pH 5±0.1. Kinetic studies were carried out and the data obtained were applied to pseudo-first order and pseudo-second order kinetic models. Finally, the metal-laden resin can be regenerated effectively by HCl solution. Thus the results obtained from batch mode studies and various isotherm models indicate that Amberlite IRC86 is a promising adsorbent for removal of Cu(II) from contaminated waters.

Key words: Adsorption, Cu(II) removal, Kinetic models, Isotherms, Desorption

1. INTRODUCTION

The pollution of water resources due to the indiscriminate disposal of heavy metals has been causing worldwide concern for the last few decades. Heavy metals in water remain a serious threat to environmental and public health. Among various techniques, ion exchange technique on polymeric ion-exchangers is widely used for treatment of metal-contaminated wastewater [1], due to high efficiency; easy handling; cost effectiveness; reusability and ease of separation. Environmental pollution due to copper arises from industrial and agricultural operations. Copper has broad industrial applications, such as alloy industries, paper and pulp, basic steel works foundries and petroleum refining industries [2]. Copper has been reported to cause neurotoxicity commonly known as “Wilson’s disease” due to the deposition of copper in the ventricular nucleus of the brain and liver. The other effect of copper to human includes congestion of nasal mucous membranes and pharynx, ulceration of nasal septum and metal fume fever**.** Eye irritation has been reported by factory workers exposed to copper dust. In some individuals, exposure to copper metal produces dermatitis [3]. Therefore, it is very important to reduce the residual copper concentration below the safety limit from industrial wastewater before discharging. In the present work, the removal of Cu(II) ions from aqueous solutions using a weak acid cation exchange resin containing acrylic matrix (Amberlite IRC-86) was investigated.

2. MATERIALS AND METHODS

Commercial synthetic Amberlite IRC-86, weak acid cation exchange resin in H^+ form was obtained from Sigma Aldrich Co. The properties of the resin are given in Table 1.A stock solution of 1000 mg /L of Cu(II) was prepared by dissolving 3.931g of $CuSO_4.5H_2O$ in double distilled water, acidified with 5ml of conc.H_2SO_4 to prevent hydrolysis and diluting to 1000ml.To 50 ml of Cu(II) solution in 100ml conical flask, added desired amount of resin, shaken at 250 rpm in a mechanical shaker at room temperature. After

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agitation, resin was filtered and the filtrate was analyzed using UV spectrophotometer at 445nm with potassium ferrocyanide. Amount of Cu(II) adsorbed ,q_e was calculated using the equation $q_e = V/W (C_o - C_e)$ where,V= volume of Cu(II) solution; C_o and C_e are initial and equilibrium concentration of Cu(II); W= weight of resin taken.

Table 1. Physico-chemical properties of weakly acidic Amberlite IRC-86 cation exchange resin

Characteristics	Value
Physical Characteristics	
Appearance	Transparent yellow beads
Particle size range	16-50 mesh
Temperature limitations	120 ˚C
Chemical Characteristics	
Structure	Gel
Matrix	Acrylic Polymer
Functional Group	Carboxylic Acid
Ionic form	H^+
Total Exchange capacity	10.7 meq /g by dry weight

3. RESULTS AND DISCUSSION

3.1. Effect of agitation time, initial concentration, resin dose and initial pH on the adsorption of Cu(II) ions from aqueous solution

As the concentration of Cu(II) increased, adsorption decreased. The removal amount of Cu(II) increased as the contact time elapsed. The equilibrium time was reached within 100 min The kinetic curves are single, smooth and continuous, indicating the possible monolayer coverage of metal ions on the surface of the resin [4].Adsorption increased with increase in resin dose and agitation time. Optimum resin dosage was fixed as 0.1g.The effect of pH on the sorption of Cu(II) ions was tested at different pH values (2.0-8.0). The results indicated that the maximum uptake of Cu(II) ions occurred at initial pH of 5.0. The adsorption capacity of the resin increased with increase in pH of the aqueous solution. This can be explained on the basis of decrease in competition between protons (H^+ ions) and metal cations (Cu^{2+} ions) for the same functional groups ($-COO^-$) and by decrease in the positive surface charge on the resin resulting in a lower electrostatic repulsion between the surface of resin and Cu(II) ions [5].

3.2. Adsorption Kinetics

3.2.1. Lagergren Pseudo - first order kinetic model

The rate constant of adsorption was determined from Lagergren Pseudo - first order equation which is generally expressed as [6],

$$\log (q_e - q_t) = \log q_e - K_1 t / 2.303$$

where, q_e and qt are the adsorption capacity (mg/g) at equilibrium and at time t, respectively and K_1 is the rate constant for pseudo - first order adsorption.

3.2.2. Ho Pseudo - second order kinetic model

The linear form of Ho pseudo - second order kinetic model is expressed as [7]

$$t/q_t = 1/K_2 q_e^2 + t/q_e$$

where, K_2 is the rate constant of second order adsorption (g/mg/min).

Kinetic parameters for the removal of Cu(II) by the resin are given in Table 2.

The q_e values (experimental and calculated) show that pseudo-first-order model fits well into the data.

Table 2. Kinetic parameters for the removal of Cu(II) by Amberlite IRC86 resin

Conc of Cu(II) (mg/L)	Pseudo-first-order model				Pseudo-second-order model		
	q_e(mg/g) (Exp)	**q_e(mg/g) (Cal)**	**K_1 x10^{-2} (1/min)**	**R^2**	**q_e(mg/g) (Cal)**	**K_2 x10^{-2} (g/ mg min)**	**R^2**
10	4.487	3.381	2.57	0.9683	5.238	0.8354	0.9861
20	8.75	8	2.832	0.9511	10.37	0.3872	0.9808
30	13	12.568	2.594	0.9513	15.87	0.2198	0.9760
40	17.059	17.474	2.538	0.9570	22.724	0.1094	0.9633
50	20.886	20.281	2.518	0.9724	26.267	0.0917	0.9749

3.3. Adsorption Isotherms

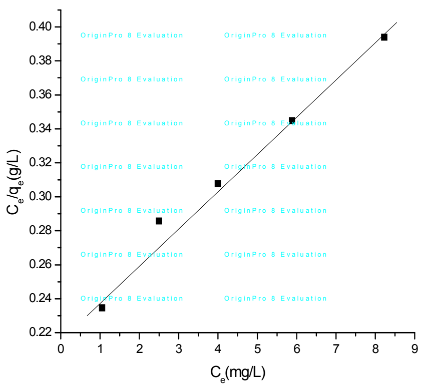
Various isotherm models (Fig.1, Fig.2 and Fig.3) and their parameters are presented in Table 3.

Table 3. Isotherm parameters for removal of Cu(II) by Amberlite IRC86 resin

Isotherm models	**Constants**	**Value**	
Langmuir [8]	Q_0 (mg/g)	47.21	
$C_e/q_e = l/Q_o b + C_e/ Q_o$	b (L/mg)	0.0956	
	R^2	0.9924	
Freundlich [9]		Cu(II) concentration	
$\log q_e = \log K_f + 1/n \log C_e$		20 (mg/L)	50 (mg/L)
	K_F (mg/g)	7.279	15.093
	N	5.4	4.99
	R^2	0.9752	0.9844
Redlich-Peterson [10]	K_R (L/g)	5.867	
$q_e = K_R C_e/1+a_R Ce^{\beta}$	a_R (L/mg)	0.3700	
	R^2	0.9955	

The Langmuir equation assumes that the solid surface presents a finite number of identical sites which are energetically uniform and a monolayer is formed when the solid surface reaches saturation. The Freundlich expression is an empirical equation based on sorption on a heterogeneous surface suggesting that binding sites are not equivalent. Redlich-Peterson isotherm is a combination of Langmuir and Freundlich models.

Equilibrium adsorption data fitted well into Langmuir and Redlich-Peterson isotherm models.



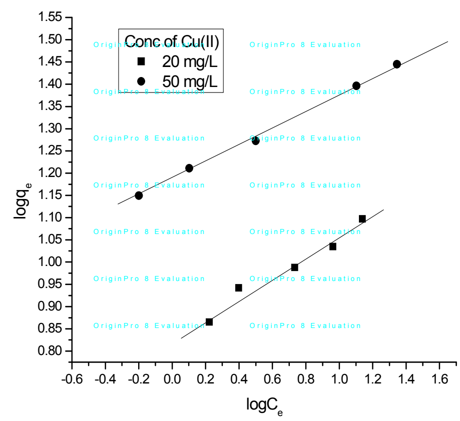


Fig.1. Langmuir isotherm.

Fig.2. Freundlich isotherm.

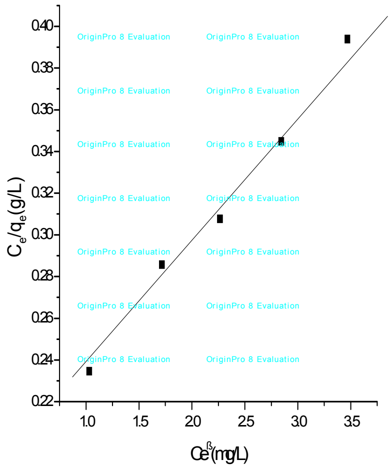


Fig.3. Redlich-Peterson isotherm.

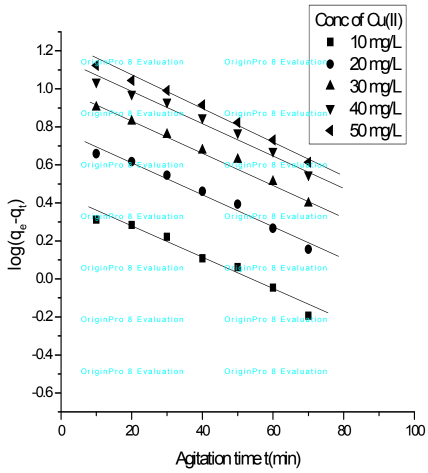


Fig.4. Lagergren Pseudo-first-order model.

3.4. Desorption studies

Desorption studies were carried out by treating the spent resin with varying concentrations of HCl (0.01 to 0.25N). It was found that regeneration of resin was possible using 0.25N HCl for 20 and 50 mg/L of Cu(II) solution. The results indicate that adsorption is through ion-exchange mechanism.

4. Conclusion

Feasibility of using Amberlite IRC-86 resin for Cu(II) removal was studied. Optimum resin dose was found to be 0.1g at pH 5±0.1 and the equilibrium time was obtained within 100 min. Redlich-Peterson isotherm was found to be the best fit model. The Langmuir adsorption capacity was 47.21 mg/g at 303K. Kinetic studies revealed that pseudo-first order model was obeyed. Desorption studies showed that the resin can be regenerated and reused. Overall results predict that Amberlite-IRC-86, weak acid cation-exchange resin with acrylic matrix is a highly efficient adsorbent for Cu(II) removal from aqueous solutions

5. References

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