

Removal of Cu(II) from Aqueous Solutions Using Modified Amberlite XAD-7HP Polymeric Resin as an Adsorbent

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The removal of Cu(II) from aqueous solutions by using modified Amberlite XAD-7HP resin was investigated. The modified resin was prepared by complete mixing of Amberlite XAD-7HP resin with sodium dioctyl sulphosuccinate (SDOSS-anionic surfactant) and EDTA in an aqueous solution. The effect of contact time, pH, modified resin dosage and initial metal ion concentration on the removal of Cu(II) were studied in a batch process mode. The optimum pH required for maximum removal of Cu(II) was found to be 5. The data were fitted with the Langmuir and Freundlich equations to describe the equilibrium isotherms. The maximum adsorption capacity of Cu(II) on modified resin was found to be 34.87 mg/g. Adsorption kinetics data were modelled using the pseudo-first and pseudo-second-order models. The results indicate that the pseudo-second-order model best describes adsorption kinetic data. The modified resin was regenerated by using 5 % NaCl and used again to remove Cu(II) ions. The efficiency of modified resin was also tested with synthetic industrial wastewater and has considerable adsorption capacity.

Key Words: Cu(II) removal, Amberlite XAD-7HP resin, SDOSS, EDTA, Isotherms, Kinetics.

INTRODUCTION

Heavy metal contamination in the aquatic environment has been of great concern because of their increased discharge, toxic nature and other adverse effects on receiving waters. Unlike most organic pollutants, heavy metals are non-biodegradable nature. It is well established that heavy metals obstruct with functional groups of enzymes even at very less concentration¹.

Copper is one of the most common toxic metals that finds its way to water sources from various industries, i.e., electroplating, mining, electrical and electronics, iron and steel production, non-ferrous metal industry, printing and photographic industries. Alongwith other heavy metals, small amounts of copper are necessary for life functions. However, copper concentrations in humans have increased to toxic levels causing various diseases and disorders, such as liver damage², etc. According to US Environmental Protection Agency (EPA) standards, the permissible limit of copper discharge in industrial effluents into water bodies is limited² to 0.25 mg/L. Hence, the elimination of heavy metals from water and wastewater is very important in terms of public health and also environment. The most widely used methods for removing heavy metals from wastewater include ion exchange, chemical precipitation, reverse osmosis, electro dialysis, evaporation and membrane filtration³. Most of these methods suffer from some drawbacks such as high capital, operation cost and the disposal of the residual metal sludge which are not suitable for small-scale industries.

The development of chelating resins as adsorbents for heavy metal ions removal has been increased significantly. Their advantages include good selectivity, preconcentration factor, binding energy and mechanical stability, easy regeneration for multiples sorption-desorption cycles and good reproducibility in sorption characteristics⁴⁻⁶. Polymeric XAD resins as the backbone for the immobilization of chelating ligands have physical superiorities such as porosity, uniform pore size distribution, high surface area, durability, chemically homogeneous non-ionic structure and chemical stability towards acids, bases and oxidizing agents^{7,8}.

Surface modification method using impregnation of surfactants can significantly enhance the capacities of adsorbents to adsorb heavy metals from aqueous medium⁹⁻¹¹. Surfactant modified adsorbents are not only superior in terms of removal efficiency than the conventional adsorbents, but also encourage the selective separation and recovery of precious and noble metals as well^{12,13}. The aim of this article is to assess the potential of modified Amberlite XAD-7HP resin for the removal of Cu(II) ion from aqueous solutions. The adsorption capacity of modified Amberlite XAD-7HP resin was investigated using batch experiments. The influence of contact time, pH, modified resin dose and initial Cu(II) concentration were investigated and the experimental data obtained were evaluated and fitted using adsorption equilibrium isotherms and kinetic models.

EXPERIMENTAL

The copper(II) concentrations in the sample were determined using atomic absorption spectrophotometer (Elico SL 163). The pH measurements were made using a pH meter (Elico LI 120). All experimental treatments in this study were conducted in acid washed (2 % HNO₃) polyethylene bottles.

Reagents and solutions: The synthetic solutions were all prepared by diluting Cu(II) standard stock solutions (concentration 1000 ± 2 mg/L) obtained by dissolving CuCl₂·2H₂O (SD fine chem, India) in distilled water. Fresh dilutions were used in each experiment. The Amberlite XAD-7HP resin (acrylic ester) was supplied by Rohm Hass (Philadelphia, PA, USA). The SDOSS (LOBA chemi, India) and EDTA-disodium salt (SD fine chem, India) were used as such for the preparation modified resin. The pH of the solution was adjusted with 0.1 M HCl or 0.1 M NaOH.

Preparation of modified Amberlite XAD-7HP resin: The Amberlite XAD-7HP resin was purified with a 50 % ethanolwater solution containing 4 M HCl to remove inorganic impurities and monomeric materials. After that, the resins were rinsed thoroughly with distilled water to eliminate chloride ions. 1 g of fresh Amberlite XAD-7HP resin was well mixed with an equal ratio (1:1) mixture of 20 mL of 66.6 % (v/v) water-ethanol mixture containing 2 g of SDOSS and 20 mL of water containing 2 g of EDTA-disodium salt⁶ for 24 h. The polymeric beads were separated from the impregnated solutions by filtration using Whatman filter paper (No. 1) and then beads were thoroughly washed with water and dried at 50 °C. The dried resins were used for further experiments. The amount of ligand (micellar solubilized chelating agent complex) loaded on Amberlite XAD-7HP resin was calculated from the material balance. The amount of ligand impregnated onto dry resin was found to be 0.26 g/g.

Batch experiments: Batch adsorption tests were conducted by mixing known weight of modified resin and 100 mL of Cu(II) ion solution of known concentration adjusted to a known pH. The mixture was taken in a polythene bottle of 300 mL capacity and shaken in a mechanical shaker (200 rpm) for a predetermined period at 30 ± 1 °C. Then the equilibrated solutions were centrifuged and the concentration of Cu(II) ions in the supernatant solution was measured by atomic absorption spectrophotometer. Adsorption isotherm and kinetic studies were carried out with different initial concentrations of Cu(II) ions by maintaining the modified resin dosage at constant level. Metal ion removal (%) was calculated using the following equation:

$$\operatorname{Removal}(\%) = \frac{C_i - C_f}{C_i} \times 100$$
(1)

where C_i and C_f are the initial and final Cu(II) concentrations, respectively.

RESULTS AND DISCUSSION

Effects of modification on the removal of Cu(II): Both surfactant and EDTA-disodium salt were individually loaded on Amberlite XAD-7HP resin and then tested for the removal of Cu(II) ions. However, individually loaded resins could not remove the Cu(II) ions from the solution effectively. The primary studies indicated that percentage removals were found to be 78 % for surfactant modified resin and 37 % for EDTA modified resin for an initial Cu(II) concentration of 10 mg/L and for a modified resin dosage of 0.2 g/100 mL, respectively. When the surfactant-EDTA complex loaded on Amberlite XAD-7HP resin, the results showed that both surfactant-EDTA complex could stimulate the adsorption Cu(II) ions from the solution. Hence the complex effect of surfactant and EDTA on the polymeric resin has been considered for the present study.

Effect of contact time: Contact time is an important parameter for successful use of adsorbents for practical applications¹³. Fig. 1 shows the effect of contact time on the removal of Cu(II) by modified resin. It could be seen that the removal of Cu(II) increases with increase in time and attains equilibrium at 2 h. The removal efficiency was found to be 99 % for an initial concentration of 10 mg/L of Cu(II). Therefore, optimum contact time was selected as 2 h for further experiments.



Fig. 1. Effect of contact time on removal of Cu(II) by modified resin: (Cu(II) concentration: 10 mg/L; pH: 5; modified resin dosage: 150 mg/ 100 mL)

Effect of pH: The pH of the aqueous solution is an important controlling parameter in the heavy metal ions adsorption process¹⁴. Moreover, due to the different functional groups on the adsorbent surface, this became active sites for the metal binding at a specific pH. The effect of pH on percentage removal of Cu(II) for pH ranging between 1-10 is shown in Fig. 2. It could be seen that 99 % removal of Cu(II) was achieved by the modified resin over the pH range of 5-8. It is evident from Fig. 2, the adsorption of efficiency of Cu(II) increased with increasing the pH of the medium until reaching to the optimum pH range.

At lower pH values, H_3O^+ ions compete with Cu^{2+} ions for exchange sites in the adsorbent. The Cu^{2+} uptake decreased because the surface area of the adsorbent was more protonated. Competitive adsorption occurred between H⁺ protons and free Cu^{2+} ions and their hydroxide fixation sites¹⁵. Moreover, the stability of the SDOSS-EDTA complex which was loaded on the polymer matrix surface might be reduced with the result the adsorption of Cu(II) decreases at lower pH. When the pH



Fig. 2. Effect of pH on removal of Cu(II) by modified resin: (Cu(II) concentration:10 mg/L; time: 2 h; modified resin dosage: 150 mg/ 100 mL)

value increased, adsorbent surfaces were more negatively charged and functional groups of the modified resins more deprotonated which results higher attraction of Cu(II) ions. The reduction in Cu(II) removal beyond pH 8 and more basic pH conditions, may suggest the possibility of Cu(OH)₂ precipitates occupying the adsorption sites and preventing further removal of Cu(II)¹⁴. Hence, all experiments were carried out at pH 5.

Effect of modified resin dosage: Adsorbent dosage is an important parameter because it determines the capacity of an adsorbent for a given concentration of the adsorbate. The influence of modified resin dosage on the removal of Cu(II) ion is shown in Fig. 3. The removal of Cu(II) increases with increasing the modified resin dosage. The removal efficiency was found to be 99 % at a modified resin dose of 0.15 g for an initial concentration of 10 mg/L. The results showed that the adsorption increases with the increase in the dose of modified resin. This is because of the availability of more binding sites on the surface at higher concentration of the adsorbent for complexation of metal ions.



Fig. 3. Effect of modified resin dosage on removal of Cu(II): (Cu(II) concentration: 10 mg/L; time: 2 h; pH: 5)

Effect of initial Cu²⁺ concentration: The removal of Cu²⁺ ions was carried out at different initial Cu²⁺ ion concentrations ranging from 10-60 mg/L at pH 5.0. The results are presented in Fig. 4. The removal percentage of Cu(II) increases when the initial Cu(II) ion concentration decreases. At low Cu(II) concentration the surface active sites to the total metal ions in the solution is high and hence all the Cu(II) ions may interact with the binding sites of the modified resin and may be removed from the solution. However, the amount of Cu(II) adsorbed per unit weight of modified resin (x/m) is higher at high concentration.



Fig. 4. Effect of initial Cu(II) concentration on removal of Cu(II): (time: 2 h; pH: 5, modified resin dosage: 150 mg/100 mL)

Adsorption isotherm models: An adsorption isotherm is characterized by certain constant values, which express the surface properties and affinity of the adsorbent. It can also be used to compare the adsorptive capacities of the adsorbent for different pollutants¹⁶. In this work, both Langmuir and Freundlich models were used to describe the relationship between the amount of Cu(II) ions adsorbed and its equilibrium concentration in solution at room temperature for 24 h.

Langmuir isotherm: The main assumption of the Langmuir method is that adsorption occurs uniformly on the active part of the surface and when a molecule is adsorbed on an active site, the other molecules could not be interacted with this active site¹⁷.

The linear form of Langmuir equation may be written as

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0} \tag{2}$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g) and C_e is the equilibrium concentration of solute in the bulk solution (mg/L) while q_0 is the monolayer adsorption capacity (mg/g) and b is the constant related to the free energy of adsorption (L/mg). A linear plot of C_e/q_e versus C_e exhibits that the adsorption obeys the Langmuir isotherm and values of Langmuir constants (q_0 and b) calculated from the slope and the intercept (Fig. 5) are presented in Table-1.



Fig. 5. Langmuir adsorption isotherm plot for adsorption of Cu(II): (modified resin dosage: 150 mg/100 mL; time: 24 h; pH: 5.0; temperature: 30 ± 1 °C)

The essential characteristics of the Langmuir isotherm can also be expressed in terms of a dimensionless constant of separation factor or equilibrium parameter, R_L , which is defined as¹⁸

TABLE -1							
LANGMUIR AND FREUNDLICH CONSTANTS FOR Cu(II) ADSORPTION							
Metal ion		Langmuir model		Freundlich model			
	$q_0 (mg/g)$	b (L/mg)	\mathbb{R}^2	$K_{\rm F} ({\rm mg/g})$	l/n	\mathbb{R}^2	
Cu(II) in DW	34.84	0.190	0.92	5.88	0.527	0.98	
Cu(II) in TW	9.57	0.081	0.61	1.53	0.467	0.63	

$$R_{L} = \frac{1}{1 + bC_0} \tag{3}$$

where b is the Langmuir constant and C_0 is the initial concentration of Cu(II) ion. Separation factor shows the nature of adsorption process and its value indicates the sorption process could be favourable, linear and unfavourable when $0 < R_L < 1$, $R_L = 1$, $R_L > 1$, respectively. The R_L values at different concentrations were found be in the range of 0 to 1 indicated a highly favourable adsorption of Cu(II) ions onto modified resin.

Freundlich isotherm: It is an empirical expression that takes into account the heterogeneity of the surface and multi-layer adsorption to the binding sites located on the surface of the sorbent¹⁹. The logarithmic form of Freundlich model is expressed as follows

$$\log \frac{x}{m} = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

where C_e is the equilibrium concentration (mg/L) and x/m is the amount of metal ion adsorbed per unit weight of adsorbent (mg/g). The K_F is Freundlich constant related to the adsorption capacity (mg/g) and n shows the adsorption intensity (L/mg). The linear plot of log (x/m) *versus* log C_e (Fig. 6) exhibits that the adsorption obeys the Freundlich isotherm and value of Freundlich constants (K_F and 1/n) calculated from the intercept and slope of the plot are presented in Table-1. The adsorption intensity 1/n value was found to be between zero and one which indicate the favourable adsorption of Cu(II) ions onto surface of modified resin.



Fig. 6. Freundlich adsorption isotherm plot for adsorption of Cu(II): (modified resin dosage: 150 mg/100 mL; time: 24 h; pH: 5; temperature: 30 ± 1 °C)

It could be seen from the Table-1 that the decrease in the adsorption capacity was noticed in case of modified Amberlite XAD-7HP resins in tap water. This could be due to the presence of common cations available in tap water competing for the adsorption sites on the modified Amberlite XAD-7HP resin.

The correlation coefficient (\mathbb{R}^2) values of Freundlich model are found to be higher than Langmuir model and more closer to unity. These results indicated that the Langmuir model is not able to describe adequately the relationship between the amounts of copper(II) ions adsorbed and their equilibrium concentration in the solution. Therefore, it could be concluded that the Freundlich isotherm model was found to be a best fit with the equilibrium data since \mathbb{R}^2 values were closer to unity.

Kinetic studies: The study of adsorption kinetics is significant as it provides valuable insights into the reaction pathways and the mechanism of the reactions. Several kinetic models are used to explain the mechanism of the adsorption processes. A simple pseudo-first order equation was given by Lagergren equation²⁰

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$$
(5)

where q_e and q_t are the amounts of Cu(II) adsorbed (mg/g) at equilibrium time and any time t, respectively, while k_1 is the rate constant of adsorption (min⁻¹). Plot of log ($q_e - q_t$) *versus* t gives a straight line for first order adsorption kinetics (Fig. 7) which allows computation of the rate constant k_1 and its values are given in Table-2.



Fig. 7. Pseudo first order kinetic plot for adsorption of Cu(II): (modified resin dosage: 150 mg/100 mL; pH: 5.0; temperature: 30 ± 1 °C)

On the other hand, the pseudo-second order equation based on equilibrium adsorption is expressed as²¹

$$\frac{\mathbf{t}}{\mathbf{q}_{t}} = \frac{1}{\mathbf{k}_{2}\mathbf{q}_{e}^{2}} + \frac{\mathbf{t}}{\mathbf{q}_{e}} \tag{6}$$

where k_2 is the pseudo-second order rate constant (mg g⁻¹ min⁻¹), q_e and q_t represent the amount of Cu(II) adsorbed (mg/g) at equilibrium and at any time. The plot of (t/q_t) versus t produces straight line with slope of $1/q_e$ and intercept of $1/k_2q^2_e$. It indicated the applicability of pseudo-second-order model (Fig. 8). The overall rate constants k_2 and other constants of pseudofirst-order kinetics are given in Table-2. The correlation coefficients value (R²) was also calculated and presented in Table-2.

In order to compare the applicability of kinetic models in fitting to data, the per cent relative deviation (P) was calculated using the experimental data as given by the following equation²².

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TABLE-2									
KINETIC PARAMETERS OBTAINED FROM PSEUDO-FIRST-ORDER REACTION									
AND PSEUDO-SECOND-ORDER REACTION FOR Cu(II) ADSORPTION									
Conc. Exp q _e		Pseudo first order kinetics				Pseudo second order kinetics			
(mg/L)	(mg/g)	k ₁ (1/min)	$q_{e(theo)} (mg/g)$	\mathbb{R}^2	Р	k ₂ (g/mg min)	$q_{e(theo)} (mg/g)$	\mathbb{R}^2	Р
3	2.98	0.0259	0.88	0.95	70.28	0.0857	3.00	0.99	0.67
5	4.90	0.0227	1.42	0.91	70.91	0.0565	5.00	0.99	0.04
7	6.90	0.0180	2.13	0.97	69.13	0.0324	6.94	0.99	0.57
10	9.90	0.0168	3.98	0.91	59.79	0.0231	10.00	0.99	1.01



Fig. 8. Pseudo second order kinetic plot for adsorption of Cu(II): (modified resin dosage: 150 mg/ 100 mL; pH: 5.0; temperature: 30 ± 1 °C)

$$P = \frac{100}{N} \left\{ \sum \frac{q_e(exp) - q_e(theo)}{q_e(exp)} \right\}$$
(7)

where $q_e(exp)$ is the experimental value of q_e at any value of C_e, q_e(theo) the corresponding theoretical value of q_e and N is the number of observations. It is found that lower the value of percentage deviation (P), better is the fit. It is generally accepted that when P value is less than 5, the fit is considered to be excellent²². The results were analyzed using equations eqns. 5 and 6. The experimental data fitted well in both equations. The values of q_e(theo) calculated from these models are compared with experimental values q_e(exp) and shown in Table-2. It is found that values of q_e(theo) calculated from the pseudofirst-order kinetic model differed appreciably from the experimental values $q_e(exp)$. The percent deviation (P) is also very high. On the other hand, values of q_e (theo) are found to be very close to q_e(exp) when pseudo-second-order rate equation was applied. The percent deviation (P) is well with in the range and values of correlation coefficients (R^2) are very high for pseudo-second-order when compared with pseudo-first-order kinetics. These results indicated that the adsorption of Cu(II) ions onto modified Amberlite XAD-7HP resin was governed mainly by pseudo-second-order kinetics. Thus, it could be inferred that the loading of Cu(II) onto modified Amberlite XAD-7HP resin appeared to occur by chemical interactions involving valence forces due to sharing or exchange of electrons between copper and modified Amberlite XAD-7HP resin⁹.

Thermodynamic studies: The free energy of adsorption (ΔG°) can be related with the equilibrium constant K (L/mol), corresponding to the reciprocal of the Langmuir constant, b, by the following equation²³⁻²⁵,

$$\Delta G^{o} = -RT \ln b \tag{8}$$

where R is the universal gas constant (8.314 J/mol K) and T is the absolute temperature (K). Gibbs free energy change (ΔG°)

was calculated to be -23.67 kJ/mol for Cu(II). Negative value of ΔG° indicated the feasibility and spontaneous nature of the adsorption.

Desorption studies: Desorption studies were conducted to recover the Cu(II) ion from the modified Amberlite XAD-7HP resin. Attempts were made to desorb Cu(II) ions from the spent resins using NaCl (1-10 %). The final Cu(II) concentration was determined by AAS. Results showed that 99 % of Cu(II) ions could be desorbed from the resin under optimum concentration of 5 % NaCl. After the extraction of Cu(II) from modified resin, it was completely washed with distilled water. The adsorption of capacity of modified Amberlite XAD-7HP resin was again tested for about five cycles of operation. Results showed that the adsorption capacity of NaCl regenerated modified Amberlite XAD-7HP resin was maintained over the range of 99-87 % for Cu(II) even upto five cycles of operation.

Application to wastewater treatment: Experiments were conducted to determine the efficiency of modified Amberlite XAD-7HP resin with respect to treatment of electroplating wastewater (synthetic)²⁶. Characteristics of electroplating wastewater before and after treatment are presented in Table-3. Experiments were carried out with 100 mL of copper(II) wastewater solution at pH 5.0 in the presence of varying amounts of modified Amberlite XAD-7HP resins ranging from 100-1700 mg and the results are presented in Fig. 9. Optimum dosage was found to be 1400 mg/100 mL for the maximum removal (97.2 %) of Cu(II) from the wastewater. In addition to the removal of Cu(II) ions, the material was able to effectively decrease the concentration of other metal ions in the wastewater. Therefore, it could clearly be established that the modified Amberlite XAD-7HP resin can be considered as an effective and alternative adsorbent for the treatment of wastewater containing Cu(II) ions.



Fig. 9. Effect of modified resin dosage on the removal of Cu(II) by modified resin from electroplating wastewater (time: 2 h; pH: 5.0; temperature: 30 ± 1 °C)

TABLE-3						
CHARACTERISTICS OF COPPER						
ELECTROPLATING WASTEWATER						
Composition	Before treatment	After treatment	Removal			
Composition	(mg/L)	(mg/L)	(%)			
Cu(II)	15	0.42	97.2			
Cd(II)	5	0.23	95.4			
Ni(II)	30	0.48	98.4			
Zn(II)	20	1.26	93.7			

Conclusion

In the present study, a simple and modified Amberlite XAD-7HP resin prepared and found to be useful for separating Cu(II) ions from aqueous solution. Separation media was prepared by mixing the resins in an aqueous solution of anionic surfactant and EDTA, without any chemical synthesis, thereby chelating functionality was easily introduced on the solid support surface. The operating parameters such as, contact time, pH, modified resin dosage and initial metal ion concentration were effective on the adsorption efficiency of Cu(II) ions. Experimental results are good agreement with Freundlich isotherm model and have shown a better fitting to the experimental data. The kinetics of Cu(II) adsorption onto modified resin was found to follow more reliably pseudo second order kinetics. Negative Gibbs free energy value (ΔG°) indicated the feasibility and spontaneous nature of the process. Desorption of Cu(II) was effectively be achieved with 5 % NaCl from the modified resin. Moreover, the regenerated modified resins could be used again and again for at least five cycles of operation without major loss in removal capacity and loss of materials. Experiments with wastewater clearly indicated that the modified Amberlite XAD-7HP resin is an effective adsorbent for the removal of higher concentrations of Cu(II) and other metal ions from wastewater. Based on results, it could be concluded that it can be used as an effective and alternative adsorbent to treatment of wastewater containing Cu(II) ions.

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