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Der Pharma Chemica, 2010, 2(2): 327-335
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X

Removal of copper ions from electroplating waste water by weakly basic chelating anion exchange resins: Dowex 50 X 4, Dowex 50 X 2 and Dowex M-4195

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Abstract

The removal of copper from plating waste water by weakly basic chelating anion exchange resins, such as Dowex 50 x 4, Dowex 50 x 2 and Dowex M-4195, is investigated. Effect of initial metal ion concentration, resin dose and pH on exchange capacities of ion exchange resins was studied in a batch method. The adsorption process, which is pH dependent, shows maximum removal of copper in the pH range 4-6 for an initial copper concentration of 5-30 mg L^{-1} and with resin dose 25-700 mg L^{-1}. The experimental data have been analyzed by using the Freundlich and langmuire isotherm equation. The isotherm constants for all these isotherm models have been calculated. The uptake of copper by the ion exchange resins was reversible and thus has good potential for the removal / recovery of copper from plating waste effluent contains copper in the form of chelating anion. Ion exchange resins, such as Dowex 50 x 4 , Dowex 50 x 2 and Dowex M-4195 can be used for the efficient removal of copper from Plating wastewater.

Key words: weakly basic chelating anion exchange resins.

INTRODUCTION

Currently the electroplating solution often contain one or more anionic ligands because of their three fold functions of keeping metals in solution, dissolving metal compounds, and affecting chemical reactivity of metal and of these anionic ligands, polycarboxylic acids (citrate, oxalate, tartrate, etc.) and phosphoric acids are widely applied. Although amino polycarboxylic acids such as nitro triaceticacid and ethylene diamine tetra acetic acid offer higher complex stabilities and / or buffer capacities than polycarboxylic and phosphoric acids the post treatment of the west solution containing polycarboxylic and phosphoric acids is consequently simpler. The presence of anionic ligands in metal bearing solution likely makes traditional chemical precipitation methods such hydroxides and sulfides less effective because of the formation of negatively charged metal spices. Alternative methods are highly desired. For the treatment of dilute solutions, reverse osmosis / nano filtration, electrolysis dialysis, solvent extraction adsorption and ion exchange have been proposed. Of these methods, ion exchange is the well established technology, particularly in drinking water purification as well as the concentration and removal of hazardous substances as very low concentration in chemical process industries and therefore, ion exchange appears to be promising for this purpose [1-3].

Electroplating waste water continues to be an important water pollution problem in metal finishing industry around the world. When in the last stage or in finishing stage of metal plating industry, the waste water dumped in to water sources like river, lake and pond, which is drunken by human being and cause of disease. Metals of varying composition depend upon the originating mineral deposit types. The metal load is of greater concern than the acidity in the terms of environmental damage [4-8]. An hazardous feature of PWE is that its sources may remain active for decades or even centuries with Metal finishing industries [9]. Metal finishing industries and metal plating industries are active sources of PWE. It can be neutralized using chemicals like lime, calcium carbonate, hydrated lime, caustic soda, soda ash etc. which results in the production of large sludge and this sludge disposal represents a further environmental problem and additional cost [10]. Thus high cost of conventional clean up technologies has produced economic pressure and has caused engineers to search for cost effective and environmental friendly technologies to treat PWE. In the past decades, therefore, research efforts has been directed towards advanced techniques of removing heavy metals from PWE besides domestic, commercial and industrial waste water.

Different techniques such as chemical precipitation, oxidation, reduction, coagulation, solvent extraction, and adsorption have been commonly employed for the removal of metal ions. Among these, ion exchange has been thought to be efficient and economically feasible as a wastewater treatment operation. Several resins can be used to remove metal ions, including activated carbons, alumina, silica, bentonite and peat. The Yi et. al. [11-13] have studied the removal of inorganic metal ions namely cadmium, cobalt, zinc, silver, copper, mercury, chromium and lead from aqueous solution by using different adsorbents. Ion exchange resins with improved sorption capacity as well as adsorbents may have advantages over such non-specific adsorbents [14]. In this regard, S. Rengaraj et. al. reported that ion exchange resins hold great potential for the removal of heavy metals from water and industrial wastewater [15, 16]. In the present study, Dowex 50 x 4, Dowex 50 x 2 and Dowex M-4195 anion exchange resins were used for the removal of copper from aqueous solution. Copper compounds are present in electroplating wastewater. The main objective of this study was to investigate the equilibrium parameters of these ion exchange resins. In addition, parameters that influence ion exchange, such as initial copper concentration, resin dose and pH on ion exchange adsorption, isotherm and kinetic studies were investigated.

RESULTS AND DISCUSSION

Effect of pH

The effects of initial pH on the removal of Cu (II) by Dowex 50 x 4, Dowex 50 x 2 and Dowex - 4195 ion exchange resins were investigated intensively. The percentage of adsorption decreases rapidly when the pH is increased above 6 due to the formation of a copper precipitate at higher pH values. Clearly, Cu(II) removal by adsorption by both the resins is much more efficient. Both the resins are effective for the maximum removal of Cu(II) over the pH range 4 to 7, for a solution containing 5 mg L^{-1} of copper. It is, therefore, in the subsequent studies the solution pH of 6 was used.

Table : 1 Effect of pH

pH	% Cu removed
1	30
2	49
3	53
4	60
5	65
6	69
7	70
8	68
9	60

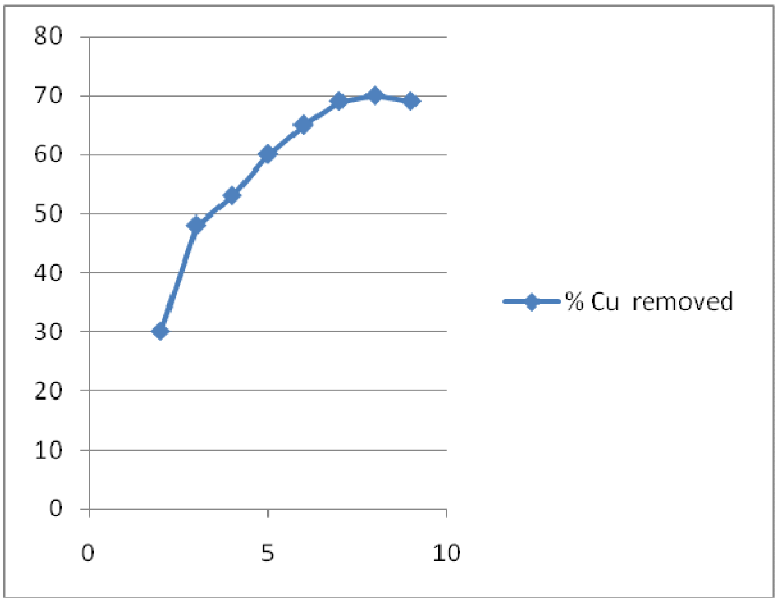


Fig.1

Effect of contact time

Experiments were carried at different contact time using Copper chloride and Oxalic acid solutions passes through Dowex M-4195 chelating resin in a chromatography coloum for several times. The results are tabulated in Table: 2. The result shows that the increase in removal efficiency with contact time is due to the increase more active sites are available for the ion exchange.

Table: 2 Effect of contact time

Time (in hr)	% Cu (removed)
½	10
1	33
2	43
3	58
4	64
5	66

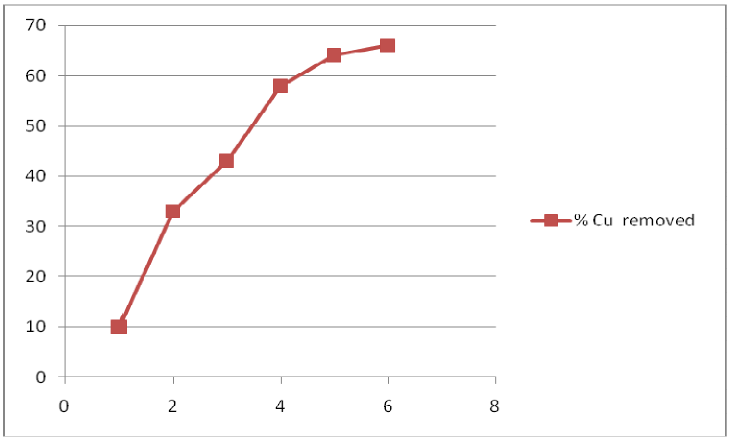
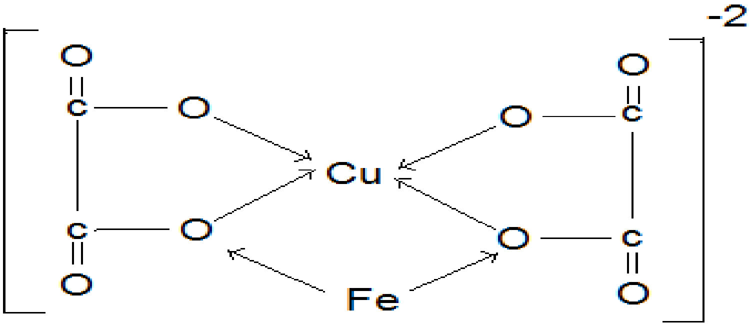


Fig. 2 Time v/s % Cu removed

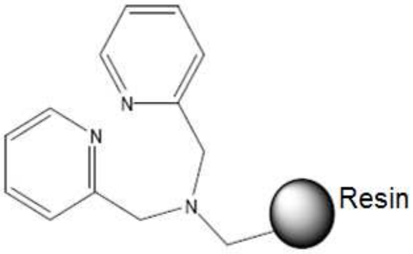
Effect of Resin Dosage

The removal of Cu (II) was investigated intensively as a function of resin dosage by Dowex 50 x 4, Dowex 50 x 2 and Dowex – 4195. Resin dosage was varied from 25 to 700 mg at the solution pH 5 and equilibrated for 24 hrs. Increasing resin dosage increased the percent removal of Cu (II). For the quantitative removal of Cu(II) from 5 mL solution containing 30 mg L^{-1} of Cu(II), a minimum resin dosage of 500 mg L^{-1} each of Dowex 50 x 4, Dowex 50 x 2 and Dowex - 4195 is required for the maximum removal of Cu(II). The results also clearly indicate the removal efficiency increases up to the optimum dosage beyond which the removal efficiency has no change with the resin dosage [15,16]. It may be concluded that by increasing the adsorbent dose the removal efficiency increases but adsorption density decreases. This decrease in adsorption density is because of the adsorption sites remain unsaturated, whereas the number of available adsorption sites increases by an increase in adsorbent and this results in an increase in removal efficiency. As expected, the equilibrium concentration decreases with increasing adsorbent doses for a given initial copper concentration, because for a fixed initial solute concentration, increasing the adsorbent doses provides a greater surface area or adsorption sites.

Copper oxalate anion chemical formula is as under,



Dowex M4195 is weakly basic chelating anion exchange resin it has bispicolyamine functional group. The figure is as under,



Bispicolylamine functional group present on Dowex 4195

Table: 2 Effect of Resin dosage time

Weight of resin in g. (Dowex M4195)	**% Cu removed**
1	30
2	51
3	69
4	90
5	92

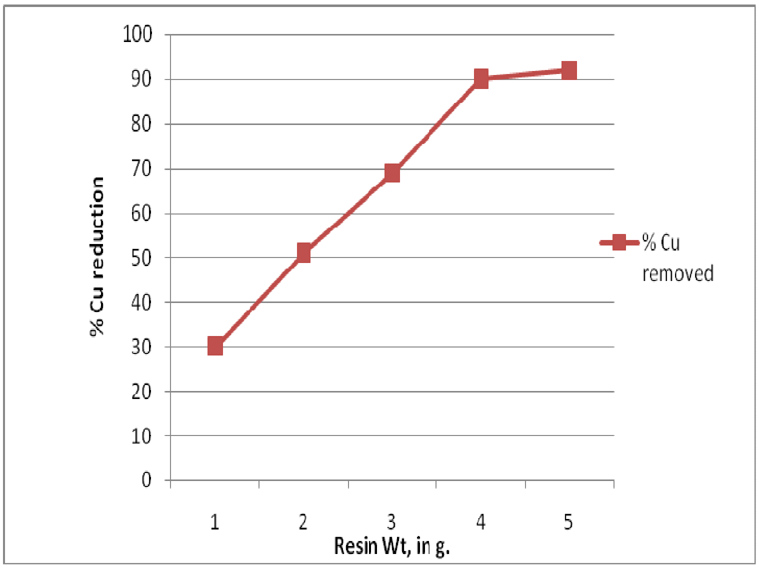


Fig. 3 Resin dosage v/s % Cu reduction

Effect of initial Concentration

Copper (II) concentrations was selected in the range of 5 to 30 mg L^{-1} for three different resin (studied pH: 5). Experiments were done using 100 mg of resin with different metal concentrations (5 - 30 mg L^{-1}). It was found that the metal amounts retained were almost stable in this concentration range for copper and two types of resin. Adsorption of copper was a bit higher in Dowex 50 x 4 than that of in Dowex - 4195 In the beginning values of concentration, the results show that there was high adsorption of the metal. The maximum adsorption was obtained as 100 % for 5 mg L^{-1} concentration.

Table : 3 Effect of initial concentration

Cu+2 Con. in m mol / L	% Cu reduction
5	70
10	63
15	53
20	40

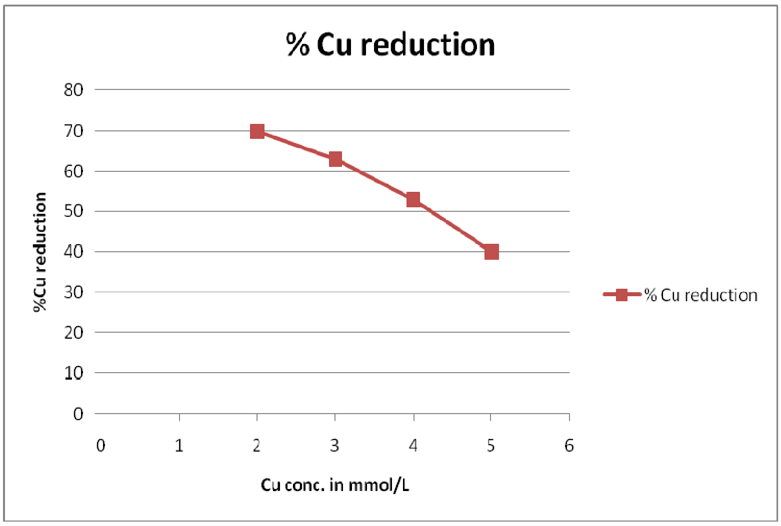


Fig. 3 Initial conc v/s % Cu reduction

Equilibrium Modeling

In order to optimize the design of a sorption system for the removal of metal from wastewater, it is important to establish the most appropriate correlation for the equilibrium curves. Two isotherm equations have been tested in the present study: Freundlich and Langmuir. These plots were used to calculate the isotherm parameters given in Table 2 for copper. Freundlich proposed that if the concentration of solute in the solution at equilibrium, Ce, is raised to the power n, the amount of solute adsorbed being qe, then Ce^{n}/qe is a constant at a given temperature. The Freundlich isotherm is derived by assuming a heterogeneous surface with a non uniform distribution of heat of adsorption over the surface. Hence the empirical equation can be written:

$$qe = K_F C_e^{n} \qquad (1)$$

where, K_F is the Freundlich constant and n the Freundlich exponent. Therefore a plot of log qe vs. log Ce enables the constant K_F and exponent n to be determined.

Langmuir proposed a theory to describe the adsorption of gas molecules onto metal surfaces. The Langmuir adsorption isotherm has been successfully applied to many other real sorption processes and it has been used to explain the sorption of metal onto ion exchange resin. A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the adsorbent. It is then assumed that once a metal ion occupies a site, no further adsorption can takes place at that site. Theoretically, therefore, a saturation value is reached beyond which no further sorption can take place. The saturated monolayer curve can be represented by the expression:

$$qe = \frac{Q^{o}\, b\, Ce}{1 + b\, Ce} \qquad (2)$$

where b and Q^{o} are the Langmuir constants. Therefore, a plot of 1/ qe vs. 1/Ce yields a linear plot of Langmuir isotherm. As shown in Table 2, maximum uptake of Dowex 50 x 4 is greater than that of Dowex M - 4195.This may be due to the intrinsic characteristics such as exchange capacity of resins Table1.

Table 2: The summary of isotherm parameters for copper on Dowex 50 x 4,Dowex 50 x 2 and Dowex - 4195 ion exchange resin system

Isotherm	**Resin**					
	Dowex 50 x 4			**Dowex M- 4195**		
Freundlich isotherm	Kf=0.074	n=0.480	R^2=0.994	Kf=0.117	n=0.497	R^2= 0.98
Langmuire isotherm	Q= -1.73	b= -0.54	R^2= 0.98	Q=-1.63	b=-0.54	R^2= 0.99

A value of both the resins was found to be same.

MATERIALS AND METHODS

The anion exchange resins Dowex 50 x 4, Dowex 50 x 2 and Dowex M-4195 (Sigma Aldrich, Germany) are used in this study for the removal of heavy metals from electroplating waste water. Their physical properties and specifications are presented in Table 1. All the chemicals used were of analytical grade.

A stock solution of Cu^{2+} (1000 mg / lit) was prepared by dissolving 1.705 g. of $Cucl_2$..2 H_2O (Sd. Fine Chemicals Mumbai) in distilled water. The stock solution was diluted as required to obtain standard solutions containing 5 to 30 mg L^{-1} of Cu (II). 5 ml of Cu(II) solution of a desired concentration and 2.5 ml of 0.1 M oxalic acid to prepare copper oxalate anion as a desired pH in chromatography column containing fixed resin bed to pass the solution. The pH of the solution was adjusted by using dilute hydrochloric acid and sodium hydroxide. The resins were separated and the filtrate was analyzed by systronic uv-vis spectrophotometer (119 with pc) for copper content. Adsorption isotherms studies were carried out with different initial concentrations of Cu (II) while maintaining the resin dosage at constant level. For pH effects, 100 mg L^{-1} copper and ion exchange resins each of dose of 100 mg L^{-1} were used.The synthetic solution of copper was used to study with ion exchange resins.For the study of dosage, the sample was used at solution pH and agitated with different dosage of ion exchange resins for 24 hrs.

Table 1: Characteristics properties of the ion exchange resins used

Dowex 50 x 4 (weak base anion exchange resin)

Physical form	moist beads
Ionic form as supplied	Chloride
Moisture holding capacity	50 – 56 %
Particle size	0.3 – 1.2 mm
Uniformity coefficient	1.8 max
Total exchange capacity	1.0 meq m L^{-1}
pH range	0 – 14

Dowex M-4195 (weak basic anion exchange resin)

Physical form	Spherical opaque beads
Ionic form as supplied	free base
Moisture holding capacity	34%
Particle size	0.3 – 1.2 mm
Uniformity coefficient	1.7 max
Total exchange capacity	1.0 meq mL^{-1}
pH range	0 – 7

CONCLUSION

In this study, the effects of parameters such as pH, resin dose, initial concentration on removal of Cu^{+2} metal ions from electroplating waste water have been presented. In this paper, it has been shown that adsorbent materials of ion exchange resins can be used for the removal of copper from electroplating waste water. We conclude that ion exchange resins could be used for applications in the advanced treatment of potable water as well as industrial effluents. Detailed studies will be needed to further evaluate ion exchange resins in terms of their competitive adsorption and their reaction chemistry of the different ion exchange resins studied(Dowex 50 x 4, Dowex 50 x 2 and Dowex - 4195), the resin Dowex 50 x 4 was the most efficient in removing the Cu^{+2}. Two isotherm models have been tested and the equilibrium data fits very well to all sorption isotherms. Uptake capacity of Dowex 50 x 4 is larger than that of Dowex - 4195 due to the intrinsic exchange capacity.

Acknowledgements
The authors gratefully acknowledge the laboratory facilies from Arts, Commerce and Science College, Pilvai (North Gujarat), India.

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