



## Effect of PH on the adsorption of copper (ii) ions from concentrated chloride solutions by the chelating resin Dowex M-4195

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### Abstract

In the present study chelating anion exchange resin Dowex M-4195 was used for removing Cu (II) from electroplating waste water. Adsorption was carried out in a batch process with different concentrations of Cu (II) ions by varying pH and agitation time. The uptake of the metal ion was very fast initially, but gradually slowed down in indicating penetration in to the interior of the adsorbent particles. The experimental data closely followed both Langmuir and Freundlich isotherms. A small amount of the adsorbent (1.2 g/L) could remove maximum 87 % of Cu (II) in 300 min from a solution of concentration 100 mg/L at 300 K. The highest adsorption was shown at pH 4.0 and then decreased.

**Keywords:** copper, adsorption, anion exchange resin, Dowex-M 4195

### Introduction

Heavy metals like copper and nickel are widely used in electroplating industry. The typical form of copper and nickel which are used in plating is the toxic divalent copper and nickel. If wastewater contaminated with divalent copper and nickel is discharged to water ways without adequate treatment, soil and water resources become polluted. Electroplating operations form part of large scale manufacturing plants (e.g. automobile, cycle, engineering and numerous other industries) or performed as job-work by small and tiny units They are spread across the entire country with significant concentration in several states like Punjab, Haryana, part of U.P., Maharashtra, Karnataka, Andhra Pradesh, Tamil Nadu and West Bengal. Electroplating is considered a major polluting industry because it discharges toxic materials and heavy metals through wastewater (effluents), air emissions and solid wastes into the recipient environment. It is harmful to humans and other living organisms. Inhalation of divalent copper and nickel causes an increase in the incidence of lung cancer. Moreover, soluble nickel compounds are carcinogenic, giving rise to cancers of the nasal cavities, lungs and other organs such as stomach and kidney<sup>[1, 3]</sup>.

Copper is also toxic to aquatic organisms even at very small concentrations<sup>[6]</sup>. It is found in sizeable amounts in the liquid effluent streams of printed circuit board plants<sup>[7]</sup> and other effluents. It is desirable, therefore, to undertake investigations on the removal of these metal ions from water. Among the various cleanup methods available for metal ions removal adsorption appears to have the least adverse effects. It includes a broad range of carbon aqueous materials at a high degree of porosity and large surface area<sup>[8]</sup> and finds use for the removal of toxic, biodegradable and non-biodegradable substances from waste water. It is attractive as it can treat waste water to acceptable quality suitable for reuse<sup>[4, 7]</sup>. The removal efficiency of synthetically prepared resin towards copper (II) was carried out in the present study. Various

parameters like effect of adsorbate dose, effect of pH, effect of contact time and effect of concentration have been studied intensively<sup>[9]</sup>. In view of the uncertainty over the behavior of DowexM-4195 at high-chloride concentrations, the present study was undertaken to examine the uptake of copper, at different pH values from chloride solutions more concentrated than those studied hitherto. The study was made under conditions that provide an excess resin capacity for copper. The behavior of the resin is discussed in terms of the chemistry of the bis (2-pyridylmethyl) amine functional group. DowexM-4195 was developed in the early 1970 s and has found some commercial applications, notably for adsorption of heavy metals. Deniz *et al.* reported that the use of the chelating resin Dowex M-4195 in the adsorption of selected heavy metal ions from manganese solutions<sup>10</sup>. Finally, the strong affinity of DowexM-4195 for many heavy metals, even in acidic solutions with high chloride concentrations, suggests that elution may not be straightforward. The studies confirmed that M-4195 is capable of removing an array of heavy metal impurities from an acidic copper chloride solution. Elution studies were also done, and confirmed that elution would be the most challenging step in developing a commercial process for separating heavy metals from acidic copper chloride solutions<sup>[11, 14]</sup>.

### Material and Methods

All the chemicals used were of A.R. grade. A stock solution of copper chloride (1000 mg L<sup>-1</sup>) was prepared by dissolving 1.705 g. of copper chloride (s.d. fine Chemicals, Mumbai) in distilled water and it was diluted further as required for test samples containing 5 to 30 mg L<sup>-1</sup> 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 test solutions containing fixed amount of resin. Dowex M-4195 resin was purchased from Supelco Sigma Aldrich Division. The resin was rinsed with water several times to remove any

leached materials. It was then underwent a wetting procedure to ensure that it was wet, without introducing extraneous water into the test solutions. The pH was then adjusted using NaOH (certified, Fisher Chemicals) to a typical free acid concentration of about 1.0 mol/L. The total chloride concentration was 3.6 mol/L. Elution was done at 25 C using 1mol/L sulfuric acid (certified, Fisher Chemicals) and 4 mol/L ammonium hydroxide (certified, Fisher Chemicals).

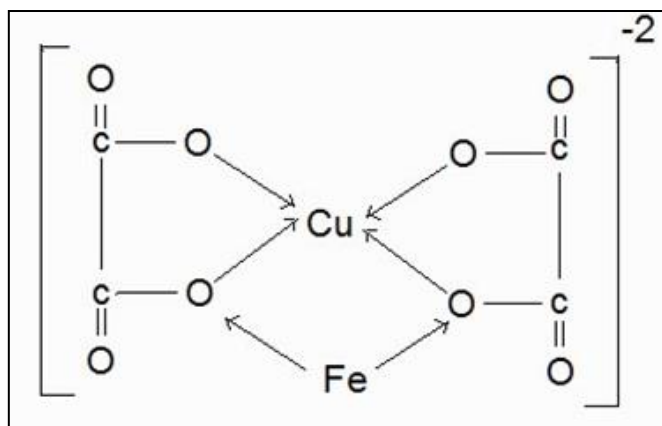
### Analysis

Metal concentrations were analyzed using a systronic uv-vis spectrophotometer 119 with pc. All analysis were run at 25 C in duplicate, except the samples from elution, where the low sample volume dictated a single analysis. The pH of solution and sample was measured using an Orion pH/ISE meter with an Orion Ross combination pH electrode, calibrated by using pH 1.0, 3.0 and 7.0 buffers (certified, Fisher Chemicals).

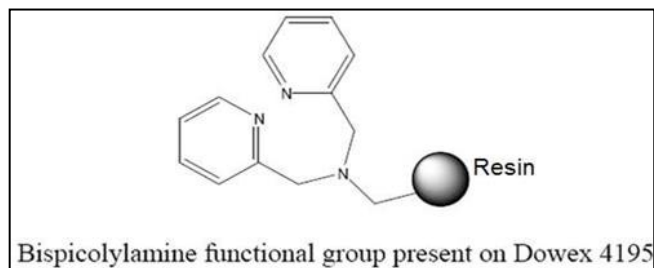
**Table 1:** Characteristics properties of the ion exchange resins used

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 m L <sup>-1</sup>
pH range	0 – 7

Chemical formula of copper oxalate anion is as under,



**Fig 1**



**Fig 2**

### Results and Discussion

The adsorption was carried out in 100 mL borosil glass bottle by agitating a preweighed amount of the resin powder with 50 mL of the aqueous Cu (II) solution in a constant temperature, water bath shaker (NSW, Mumbai) for a predetermined time interval at a constant speed. After adsorption, the mixture was centrifuged. Filtrate was separated out and unadsorbed Cu (II) was determined with uv-Vis spectrophotometer 119. The amount of Cu (II) adsorbed per unit mass of the adsorbent ( $q$  in mg/g) was computed by using the following expression:

$$q = \frac{C_0 - C_t}{m}$$

Where  $C_0$  and  $C_t$  are Cu (II) concentrations in mg/L before and after adsorption for time  $t$ , and  $m$  (g) is the amount of adsorbent taken for 1 L of Cu (II) solution. The extent of adsorption in percentage is found from.

$$\% \text{ Adsorption} = \frac{C_0 - C_t}{C_0} \times 100$$

### Effect of pH

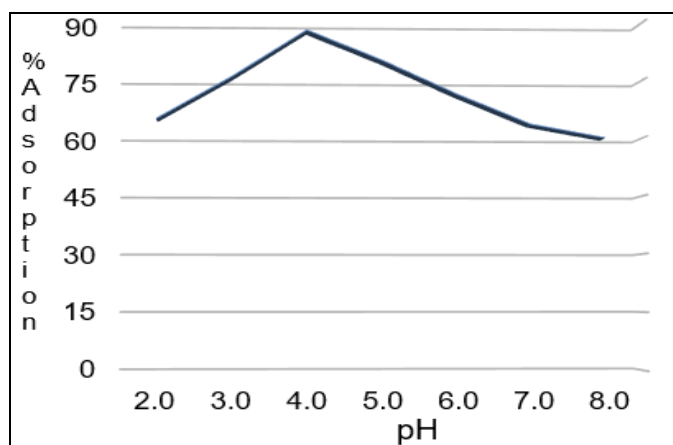
The effects of initial pH on the removal of Cu (II) by ion exchange resin Dowex - 4195 was investigated intensively. The percentage of adsorption was gradually increased up to pH 4.0 and then it decreases rapidly with the increase in pH which may be due to the formation of a copper hydroxide at higher pH values. The results are graphically represented in the figure 3. The pH value 6.0 was used for present investigation. Result shows that the ion exchange resin Dowex - 4195 is effective for the removal of Cu (II) in the pH range 4.0 to 7.0 for a solution containing 5 mg L<sup>-1</sup> of copper.

### Desorption and Regeneration

For carrying out desorption and regeneration studies, Dowex M- 4195 resin as first saturated with Cu (II) by taking 4 g of resin in apyrex glass column (1.5 cm internal diameter) and continuously passing a solution of Cu (II) (60 mg/L) through it For carrying out desorption and regeneration studies, while keeping a constant head of 2 cm till the concentration at the outlet equaled the initial concentration.

**Table 2:** Effect of pH on adsorption of Cu (II) on Dowex-M 4195

pH	% Adsorption
2.0	64.59
3.0	75.50
4.0	87.67
5.0	80.00
6.0	71.31
7.0	63.50
8.0	60.05



**Fig 3:** Effect of pH on adsorption of Cu (II) on Dowex-M 4195. Cu (II) Concentration: mg/L, Adsorbent Dose: mg/L, Temp. 303 K

Desorption was carried out by passing successively (i) deionised water (pH 7.0) and (ii) dilute nitric acid (pH 4.0) through the column till Cu (II) could not be detected in the outlet in each case.

**Equilibrium Modeling**

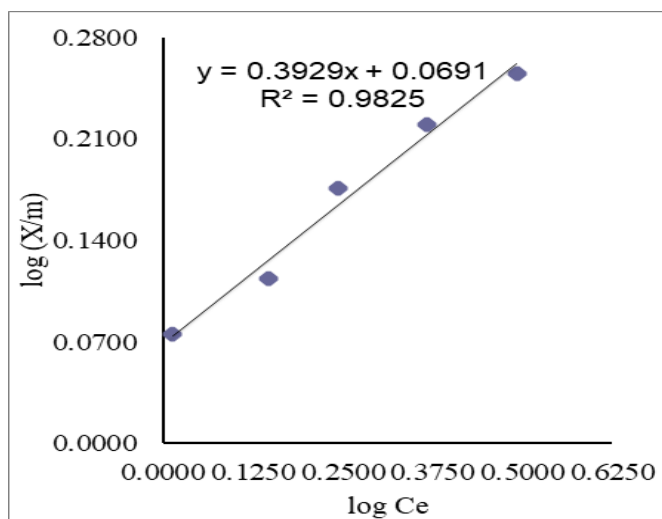
It is important to establish the most appropriate correlation for the equilibrium curves for the removal of metal from industrial wastewater. Two isotherm equations have been tested in the present study: Freundlich and Langmuir. These plots were used to calculate the isotherm parameters given in Table 3 for copper. Freundlich proposed that if the concentration of solute in the solution at equilibrium,  $C_e$ , is raised to the power  $n$ , the amount of solute adsorbed being  $q_e$ , then  $C_e^n / q_e$  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:  $q_e = K F C_e^n$  (1)

Where,  $KF$  is the Freundlich constant and  $n$  is the Freundlich exponent. Therefore a plot of  $\log q_e$  vs.  $\log C_e$  enables the constant  $KF$  and exponent  $n$  to be determined [15, 18].

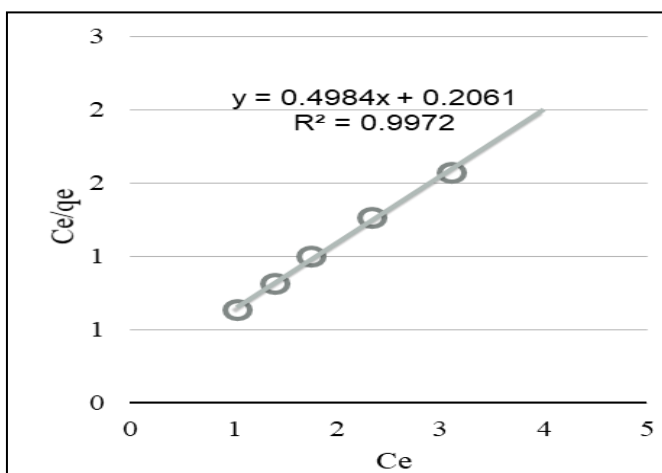
Langmuir proposed a theory to describe the adsorption of gas molecules onto metal surfaces. The Langmuir adsorption isotherm has been successfully applied to many other real sorption processes and it has been used to explain the sorption of metal onto ion exchange resin. A basic assumption of the Langmuir 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 take 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 [19, 21]:

$$q_e = \frac{Q_0 b C_e}{1 + b C_e}$$

where  $b$  and  $Q_0$  are the Langmuir constants. Therefore, a plot of  $1/q_e$  vs.  $1/C_e$  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.



**Fig 4:** Freundlich adsorption isotherm for adsorption of Cu (II) on Dowex-M 4195



**Fig 5:** Langmuir adsorption isotherm for adsorption of Cu (II) on Dowex-M

**Table 3:** The summary of isotherm parameters for Cu (II) on Dowex - 4195 by ion exchange resin system.

Isotherm	Resin Dowex - 4195		
	Freundlich isotherm	$K_f = 0.110$	$n = 0.490$
Langmuire isotherm	$Q = 1.60$	$b = 0.55$	$R^2 = 0.9972$

**Conclusion**

In this study, various parameters like effects of pH, resin dose and initial concentration on removal of Cu (II) ions from electroplating waste water have been reported. Two isotherm models have been tested and the equilibrium data fits very well to Frundlich and Langmuir adsorption isotherms. In this paper, it can be seen that ion exchange resins Dowex M- 4195 can be used for the removal of Cu (II) ions from electroplating waste water and it is most efficient. Uptake capacity of Dowex M- 4195 is higher than other ion exchange resins.

**Acknowledgements**

The author is thankful UGC New Delhi for providing financial support to complete this project in form of Minor Research

Project. The author gratefully acknowledge the Arts, Commerce and Science College, Pilvai (North Gujarat), India. For providing laboratory facilities during this project.

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