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Adsorption of Ni (II) From Aqueous Solution by Chelating Anion Exchange Resin : Dowex - M 4195

R. S. Dave

Department of Chemistry, Arts, Science & Commerce College, Pilvai, North Gujarat, India

ABSTRACT

The removal of Ni (II) from electroplating waste water have been studied by using chelating anion exchange resin Dowex M-4195. Adsorption was carried out in a batch process with different concentrations of Ni (II) ions by varying pH and agitation time. The uptake of the metal ion was very fast in initially, but gradually slowed down indicating penetration into the interior of the adsorbent particles. The adsorbent had a considerably high. Langmuir monolayer capacity of 300 mg/g. A small amount of the adsorbent (1 g/L) could remove as much as 87 % of Ni (II) in 300 min from a solution of concentration 5 mg/L at 300K. The adsorption continuously increased in the pH range of 2.0-4.0, beyond which the adsorption could not be carried out due to the precipitation of the metal ion. The experimental data closely followed both Langmuir and Frundlich isotherms.

Keywords : Copper, Adsorption, Anion Exchange Resin, Dowex-M 4195.

I. INTRODUCTION

Effect of pH on the adsorption of selected heavy metal ions from concentrated chloride solution by the chelating resin Dowex M 4195 have been studied (Claudia V. Diniz , 2002). The reisa growing need for an environmentally sustainable method to separate heavy metals, sometimes present in only trace concentrations, from manganes ean dironin acidic leach solutions. This growth in demand reflects both an increasing amount of manganese ores undergoing hydro metallurgical treatment, along with growing problems associated with managing the waste materials generated in the more traditional hydro metallurgical processes. As for the production of battery-grade manganese dioxide, it would be highly desirable to separate heavy metals values such as Cu(II), Ni(II), and Co(II) from manganese and iron (III), present at relatively high concentrations. We have screened several commercial resins for their suitability for this separation, in a very acidic manganese chloride solution; the chelating resin Dowex M-4195 appears to be very promising (Dinizetal.,2000). Dowex M-4195, formerly marketed as Dow XFS 4195, is a macro porous resin, with a polystyrene divinyl benzene matrix, and a weakly basic chelating bis picolylamine (bis (2-pyridylmethyl) amine) functional group (Grinstead and Nasutavicus, 1977, 1978).Bispicolylamine is a heterocyclic polyamine with three nitrogen donor atoms, as shown in Fig.1. Dowex M-4195 was developed in the early 1970s and has found some commercial applications, notably for adsorption of heavy metals. The resin is used at INCO's Port Colborne refinery in Canada (Melling and West, 1984), and at the Zambia Chambishi Cobalt Plant (Raoetal.,1993), for purifying cobalt electrolytes. Batch equilibration tests have shown that even at high total chloride and very low pH, Dowex M-4195 can adsorb many heavy metal ions from single-metal chloride solutions, but has a low affinity for manganese (Dinizetal.,2002). However, single metal tests cannot fully predict the behavior that would be expected when using the resin on a real process solution, where the individual metal-bearing species would be competing for functional groups on the resin. Nor can equilibrium batch tests easily predict the behaviour that might be expected in a packed NNNCH2CH2 Resin Fig.1 .Bis (2-pyridylmethyl)aminefunctionalgroup on Dowex M-4195. C.V. Dinizetal./Hydrometallurgy 78 (2005) 147–155148 column, wherea solution element does not necessarily equilíbrate with a given element of resinas it flows through the resin bed. Finally, the strong affinity of Dowex M-4195 form any heavy metals, even in acidic solution swith high chloride concentrations, suggests that elution may not be straightforward. Y et effective elution would be crucial in a commercial application of this resin. To address these issues, the adsorption behaviour of Dowex M-4195 was studied using a packed column of resin, and a concentrated, multi-component solution obtained by leaching a manganese ore with hydro chloric acid. These studies confirmed that M-4195 is capable of removing a range of heavy metal impurities from an acidic copper chloride solution. Elution studies were also done, and confirmed that elution would be the mos tchallenging step in developing a commercial process for separating heavy metals from acidic copper chloridesolutions.

II. Materials and methods

All the chemicals used were of A.R. grade. A stock solution of Ni^{+2}(1000 mg L^{-1}) was prepared by dissolving 1.705 g. of $NiCl_2.2H_2O$ (s.d. fine Chemicals, Mumbai) in distilled water and it was diluted further as required for test samples containing 5 to 30 mg $L^{-1}$of Ni^{+2}. Then 5 ml of Ni^{+2} 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. DowexM-4195 resin was purchased from Supelco–Sigma Aldrich Division. The as received resin was rinsed with water several times to remove any leached materials. It then under went a wetting procedure (Supelco–Sigma-Aldrich, 1997) to ensure that it was wet, with out introducing extra neous water in to 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 sulfuricacid (certified, Fisher Chemicals) and 4 mol/L ammonium hydroxide (certified, Fisher Chemicals).

Loading and elution

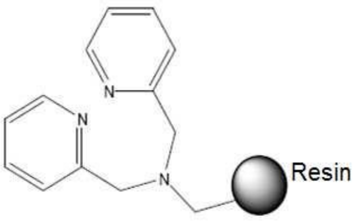
Resin was placed in a Plexi glas column, 750 mmlong, 25 mm in diameter, with a bed height of 500 mm. The sedimensions comply with the minimum recommended by Slater (1991) for a fixed bed. Distilled water was then introduced from the base of the column to eliminate air bubbles in the resin bed and associated channeling (Slater, 1991) .A peristaltic pump was used to add feed solutions and eluant (ambient temperature) to the top of the column at a rate of 2 mL/minor1. 78 BV (bed volumes) per hour. 46 BV were run for the loading tests. The elution tests were run in two different sequences, each using both eluants. In the first sequence, 10 BV of sulfuric acid was initially passed through the column, followed by 10 BV of the ammonium hydroxide solution. These cond sequence reversed the order in which these eluants were applied. To avoid contamination of each solution, 10 BV of distilled water were passed through the column before starting the elution tests, then another 10 BV were passed after using the first eluant. During both loading and elution tests, samples of the column effluent or eluate were taken from the base of the column every hour, for 26 h.

III. Analysis

Metal concentrations were analyzed using a systronic uv-vis spectrophotometer (119 with pc). All analyses were run at 25 C in duplicate, except the samples from elution, where the low sample volume dictated a single analysis. The pH of solutions and samples was measured using an Orion pH/ISE meter with an Orion Ross combination pH electrode, calibrated 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^{-1}
pH range	0 – 7



Bispicolylamine functional group present on Dowex 4195

Figure 1. Chemical formula of copper oxalate anion

The adsorption was carried out in 100 mL borosil conical flasks by agitating a pre-weighed amount of the powder with 50 mL of the aqueous Ni (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 (Remi Research Centrifuge, R24) when the adsorbent settled quickly and Ni (II) remaining unabsorbed in solution was determined with uv-Vis spectrophotometer (uv-vis Spectrophotometer 118).

The amount of Ni (II) adsorbed per unit mass of the adsorbent (q in mg/g) was computed by using the following expression:

$$q = \frac{Co - Ct}{m}$$

where C0and Ct are Ni (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 Ni (II) solution. The extent of adsorption in percentage is found from the relation

$$\%Adsorption = \frac{Co - Ct}{Co} X\ 100$$

Effect of pHThe effects of initial pH on the removal of Ni (II) by ion exchange resin

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

Table. 2 Effect of pH on adsorption of Ni (II) on Dowex-M 4195.

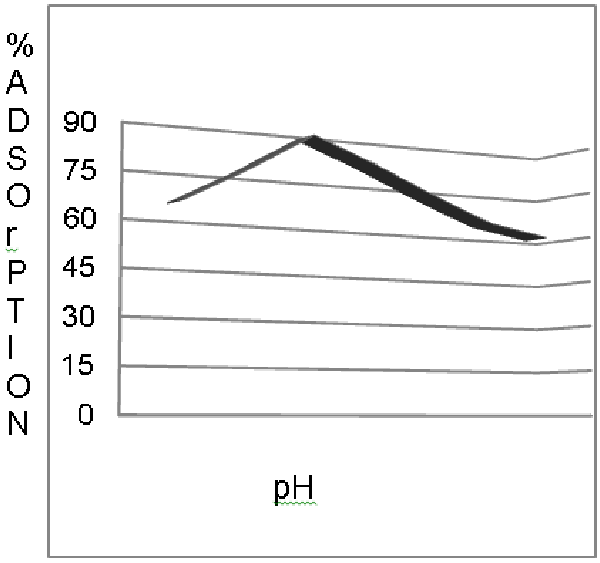


Figure. 2 Effect of pH on adsorption of Cu (II) on Dowex-M 4195. Ni (II) Concentration : 1 mg/L, Adsorbent Dose:mg/L,Temp. 303 K

Dowex - 4195 was investigated intensively. The percentage of adsorption 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 Ni (II) in the pH range 4.0 to 7.0 for a solutioncontaining 5 mg $L^{-1}$of nickel.

Desorption and regeneration

For carrying out desorption and regeneration studies, Dowex M- 4195 resin as first saturated with Ni (II) by taking 4 g of resin in apyrex glass column (1.5 cm internal diameter) and continuously passing a solution of Ni(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. 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 Ni(II) could not be detected in the outlet in each case.

Equilibrium Modeling

In order to optimize the design of a sorption system for the removal of metal from waste water, 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 Nockel. 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 KF 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:

$$qe = Q^{O}bCe\ (2)\ 1+ b\ Ce \qquad (2)$$

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 Table

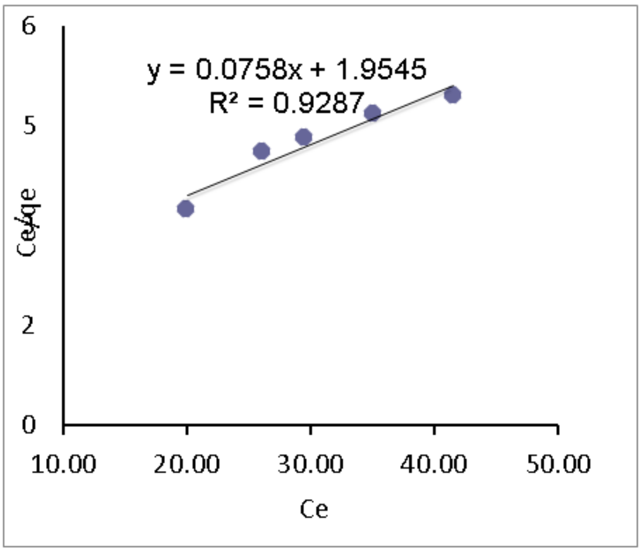


Figure 3. Langmure Adsorption isotherm for Adsorption of Ni (II) from aqueous solutionon to Dowex- M 4195 Con; 1 mg/L, Temp: 303 K Amount of adsorbent:

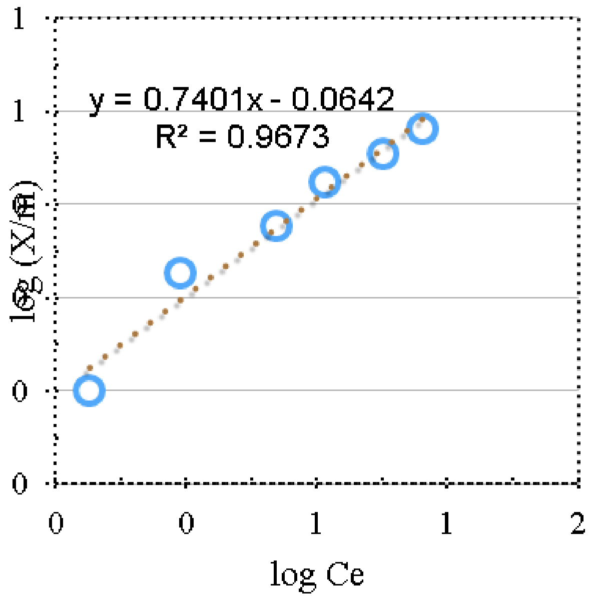


Figure 4. Fruindlich Adsorption isotherm for Adsorption of Ni (II) from aqueous solutionon to Dowex- M 4195 Con; 1 mg/L, Temp: 303 K Amount of adsorbent:

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

Isotherm	Resin Dowex - 4195		
Freundlich isotherm	K_f = 0.117	n = 0.497	R^2 = 0.9673
Langmuire isotherm	Q = 1.63	b = 0.54	R^2 = 0.9287

IV.CONCLUSION

In this study, various parameters like effects of pH, resin dose and initial concentration on removal of Ni(II) ions from electroplating waste water have been reported. Two isotherm models have been tested and it is proved that equilibrium data fits very well to Frundlich and Langmuir adsorption isotherms. This paper shows 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 than other ion exchange resins.

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