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Research Paper

Synthesis and Characterization of the Amide Resin (R3A2-20.7 n.H) Dowex 50×4, Dowex 50×2, Dowex M-4195 and its Performance for the Removal of Ni (II) and Cu (II) from Electroplating Waste Effluent

G. B. Dave*[1]

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ABSTRACT

The removal of nickel from plating waste water by weakly basic chelating anion exchange resins, such as Dowex 50×4, 50×2 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 nickel in the pH range 4-6 for an initial nickel concentration of 05-30 mg L^{-1} and with resin dose 25-700 mg L^{-1}. The experimental data have been analyzed by using the Freundlich and Langmuir isotherm equation. The isotherm constants for all these isotherm models have been calculated. The uptake of Nickel by the ion exchange resins was reversible and thus has good potential for the removal/recovery of nickel from plating waste effluent contain nickel in the form of anion exchange. The investigated ion exchange resins can be used for the efficient removal of nickel from plating wastewater.

***Key words*:** Plating waste effluent, Ion exchange, Isotherms, Nickel (II), Resins

Plating waste water continues to be an important water pollution problem in metal finishing industry around the world [1]. 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 drunked by human being and cause of disease [2]. Metals of varying compositions are dependent upon the originating mineral deposit types [3]. The metalload is of greater concern than the acidity in the terms of environmental damage [4], [5]. A hazardous feature of plating waste effluent (PWE) is that its sources may remain active for decades or even centuries with metal finishing industries [6]. Therefore, metal finishing industries and metal plating industries are active sources of PWE.

Plating waste effluent (PWE) 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 [7]. Thus, high cost of conventional clean up technologies has produced economic pressure and has pushed engineers to search for cost effective and environmentally friendly technologies to treat PWE. In the past decades, therefore, research efforts have been directed towards advanced techniques of removing heavy metals from PWE besides domestic, commercial and industrial waste water.

Several techniques such as chemical precipitation, oxidation, reduction, coagulation, solvent extraction, and adsorption have been commonly employed for the removal of metal ions [8]. Among these, ion exchange has been thought to be efficient and economically feasible as a wastewater treatment operation [9]. Several resins can be used to remove metal ions, including activated carbons, alumina, silica, bentonite and peat. The Yi group [10] has also 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 [11]. In this regard, ion exchange resins hold great potential for the removal of heavy metals from water and industrial wastewater [12].

In the present study, Dowex 50×4, Dowex 50×2 and Dowex M-4195 anion exchange resins were used for the removal of Nickel from aqueous solution. Nickel compounds are present in electro plating 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 Nickel concentration, resin dose and pH on ion exchange adsorption, isotherm and kinetic studies were investigated.

MATERIALS AND METHODS

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

*G. B. Dave
gunjandave84@yahoo.com

[1]Shri Kokilaben Karsanbhai Patel Girls Science College, Nani Kadi, District Mahesana - 382 715, Gujarat, India

A stock solution of Ni^{+2} (1000 mg L^{-1}) was prepared by dissolving 1.705 g of $Nicl_2.6H_2O$ (Std. Fine Chemicals Mumbai) in distilled water. The stock solution was diluted as required to obtain standard solutions containing 05 to 30 mg L^{-1} of Cu (II). Five mL of Ni (II) solution of a desired concentration, then make a desired pH, solution was fed in column having 25mm diameter and 50 mm hight, and passed through 5 BV/hrs resin contain subsequently Dowex 50×4, Dowex 50×2 and Dowex M-4195. The solution pH was adjusted by using dilute hydrochloric acid or sodium hydroxide. Then after regeneration stage, the filtrate was analyzed by UV-VIS Spectro photometer (sistronic-119).

Adsorption isotherm studies were carried out with different initial concentrations of Ni (II) while maintaining the resin dosage at constant level. For pH effect, 05 mg L^{-1} Nickel and ion exchange resins Dowex 50×4, Dowex 50×2 and Dowex M-4195 each of dose of 100 mg L^{-1} were used.

In addition, all mixing vessels were kept sealed throughout the duration of each isotherm test to minimize dissolution of gaseous species in the atmosphere. The Nickel containing simulated Electro plating waste water was prepared on the basis of the analysis of chemical composition from the Electro plating waste water. This simulated solution was used for the 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 50×4	Dowex M-4195
Physical form	moist beads	Spherical opaque beads
Ionic form as supplied	Chloride	free base
Moisture holding capacity	49 – 56%	30%
Particle size	0.3 – 1.2 mm	0.3 – 1.2 mm
Uniformity coefficient	1.7 max	1.7 max
Total exchange capacity	1.0 meq mL^{-1}	1.0 meq mL^{-1}
pH range	0 – 14	0 – 7

RESULTS AND DISCUSSION

Effect of pH

The effects of initial pH on the removal of Ni (II) by Dowex 50×4, Dowex 50×2 and Dowex M-4195 ion exchange resins were investigated. The percentage of adsorption decreases rapidly when the pH is increased above 6 due to the formation of a Nickel precipitate at higher pH values. Clearly, Ni (II) removal by adsorption by both the resins is much more efficient both the resins are effective for the maximum removal of Ni (II) over the pH range 4 to 6, for a solution containing 05 mg L^{-1} of Nickel Therefore in the subsequent studies the solution pH of 5 was used.

Effect of resin dosage

The removal of Ni (II) was investigated as a function of resin dosage by Dowex 50×4, Dowex 50×2 and Dowex M-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 Ni (II). For the quantitative removal of Ni (II) from 5 mL solution containing 30 mg L^{-1} of Ni (II), a minimum resin dosage of 500 mg L^{-1} each of Dowex 50×4, Dowex 50×2 and Dowex M-4195 is required for the maximum removal of Ni (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 [13]. 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 [14]. As expected, the equilibrium concentration decreases with increasing adsorbent doses for a given initial Nickel concentration, because for a fixed initial solute concentration, increasing the adsorbent doses provides a greater surface area or adsorption sites.

Effect of initial concentration

Ni (II) concentrations was selected in the range of 0.5 to 30 mg L^{-1} for three different resin (studied pH: 5). Experiments were done using 100 mg of resin with different metal concentrations (0.5-30 mg L^{-1}). It was found that the metal amounts retained were almost stable in this concentration range for Nickel and two types of resin. Adsorption of Nickel was a bit higher in Dowex 50×4 that then the Dowex M-4195. The maximum adsorption was obtained as 100% for 05 mg L^{-1} concentration [15].

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 Nickel. 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 is a constant at a given temperature [16]. 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:

$$q_e = K_F\, C_e^n \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

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 [17]. 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:

$$qe = \frac{Qo\ b\ ce}{1+b\ ce} \quad \text{……………………… (2)}$$

Where,
b and Qo 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 50×4 is greater than that of Dowex M-4195. This may be due to the intrinsic characteristics such as exchange capacity of resins (Table 1).

Redlich and Peterson [14] incorporated the features of the Langmuir and Freundlich isotherms into a single equation and presented a general isotherm equation as follows:

$$qe = \frac{K\ R\ ce}{1+aR\ ce} \quad \text{……………………… (3)}$$

Where the exponent,
β, lies between 0 and 1.

There are two limiting behaviors: Langmuir form for β=1, and Henry's law form for β=0. Plotting the Ce/qe of the above equation against Ceβ to obtain the isotherm constants is not applicable because of the three unknowns, aR, KR and β. Therefore, a minimization procedure is adopted to solve the above equation by maximizing the correlation coefficient between the theoretical data for qe predicted from the above equation and experimental data. The fitted values of β for Dowex 50×4, Dowex 50×2 and Dowex M-4195 are 1.0.

Temkin and Pyzhev considered the effects of indirect adsorbate/ adsorbate interactions on adsorption isotherms. The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbate/adsorbate interactions [18]. The Temkin isotherm has been used in the form as follows:

$$qe = \frac{RT\ \ln(AC\ e)}{b} \quad \text{………………… (4)}$$

Where,
RT/b=B.

Therefore, a plot of qe vs. ln Ce enables one to determine the constants A and b.

Table 2 The summary of isotherm parameters for Nickel on Dowex 50×4, Dowex 50×2 and Dowex M-4195 ion exchange resin system

Isotherm	Resin					
	Dowex-50 × 4			Dowex M 4195		
Frundlich	Kf=0.075	n=0.485	R^2 0.994	Kf=0.117	n=0.497	R^2 0.98
Langmuir	Q=-1.75	b=-0.54	R^2 0.99	Q=-1.63	b=-0.54	R^2 0.99

CONCLUSIONS

In this study, the effects of parameters such as pH, resin dose, initial concentration on removal of Ni^{+2} metal ions from acid mine drainage waste have been presented. It has been shown that adsorbent materials of ion exchange resins can be used for the removal of Nickel from acid mine drainage wastewater. 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 exchange resins studied the resin Dowex 50×4 was the most efficient in removing the Ni^{+2}. Two isotherm models have been tested and the equilibrium data fits very well to all sorption isotherms. Uptake capacity of Dowex 50×4 is larger than that of Dowex M-4195 due to the intrinsic exchange capacity.

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