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Comparison studies of Adsorption Properties on Ni(II) Removal by Strong and Weak acid Cation-exchange Resins

Karthika C. and Sekar M.*
PG and Research Department of Chemistry, Sri Ramakrishna Mission Vidyalaya College of Arts and Science, Coimbatore, INDIA

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Abstract

The use of Amberlite-IRC86, a weak acid cation-exchange resin and Amberlite200C, a strong acid cation exchange resin for the removal of Ni(II) from aqueous solutions and effluent was compared in detail. The adsorption capacity, equilibrium time, resin dose and regeneration capacity of both the resins were compared. The experimental activities include studying the factors affecting the adsorption process, like agitation time, pH of the adsorbate solution, dosage of the adsorbent and finally desorption. The equilibrium data were analyzed by Langmuir, Freundlich, and Redlich-Peterson isotherm models and pseudo first order and second order kinetic models. The experimental results demonstrated that Ni(II) can be effectively removed from aqueous solution and effluent by both the resins and the adsorption capacity of the strong acid resin, Amberlite200C was found to be slightly greater than the weak acid resin.

Keywords: Strong acid cation exchange resin, weak acid cation-exchange resin, Ni(II) adsorption, adsorption isotherms, kinetic models.

Introduction

Contamination of aquatic media by heavy metals is a serious environmental problem, mainly due to the discharge of industrial waste. Heavy metals are highly toxic at low concentrations and can accumulate in living organisms, causing several disorders and diseases[1]. Ions of heavy metals like copper, nickel, zinc, cadmium, lead, chromium and mercury have a significant impact on the environment. They are highly toxic as ions or in compound forms; they are soluble in water and may be readily absorbed into living organisms. Out of these ions, Nickel (Ni^{2+}) is the most abundant element in the Earth's crust, comprising about 3% of the composition of the earth. It is the 5th most abundant element by weight after iron, oxygen, magnesium and silicon[2]. Significant quantities of nickel containing waste water is introduced into water bodies in the form of effluents from nickel plating plants, silver refineries, zinc based casting industries and storage batteries. Other sources of nickel are alkaline cell, alloys and hydrogenation of oil industry. In recent years nickel is used in nuclear power plants, gas turbine engines and cryogenic containers[3]. Nickel is a potent carcinogen and causes cancer in lungs, nose, stomach and bone. Skin when contact with nickel, results in a very painful disease known as nickel itch and is followed by sudden death[4]. The major routes of exposure to toxic levels of nickel compounds in the work place are inhalation and dermal exposure. Hence it is essential to remove Ni(II) before discharged into water bodies. Several methods such as evaporation, electro-deposition, solvent extraction, reverse osmosis, membrane separation process and activated carbon adsorption are employed for the removal of heavy metal ions from waste water[5]. However, these techniques have certain disadvantages such as higher operational cost, requiring additional chemical, high energy consumption and residual metal sludge disposable. Due to forbidding cost of these processes, the uses of resins have been received with considerable attention. In recent years a number of commercial resins such as Amberlite IR-120, Amberlite IRC-748, Amberlite IRC-718, Lewatit TP-207 and a wide range of anion exchange resins with styrenic structures have been used to remove heavy metals from wastewater[6-9]. However, the applicability of cation exchange resin containing acrylic matrix for the removal of heavy metal ions from wastewater is not well documented.

The present study is undertaken to compare the efficiency of a weak acid cation exchange resin containing acrylic matrix (Amberlite IRC-86) and a strong acid cation-exchange resin containing styrenic matrix (Amberlite200C) for the removal of Ni(II) from aqueous solution and effluent. The adsorption behavior of Ni (II) by both the resins was explored in aspects of kinetics, isotherms, pH and dosage. Desorption experiments were also conducted to examine the recycling use capacity.

Material and Methods

Ion-exchange resins: Commercial synthetic Amberlite200C, strong acid cation-exchange resin in sodium form and Amberlite IRC-86, weak acid cation-exchange in hydrogen form were obtained from Sigma Aldrich Co. The properties of the resins are given in table-1 and table-2. The resins were washed with double distilled water to remove impurities and dried in an oven at 60°C for 24h. Dried resins were used for further experimental studies.

Table- 1
Physico-chemical properties of weakly acidic Amberlite IRC-86 cation exchange resin

Characteristics	Value
Physical Characteristics	
Appearance	Transparent yellow beads
Particle size range	16-50 mesh
Temperature limitations	120˚C
Chemical Characteristics	
Structure	Gel
Matrix	Acrylic Polymer
Functional Group	Carboxylic Acid
Ionic form	H^+
pH limitations	4 -14
Total Exchange capacity	10.7 meq /g by dry weight
Matter Soluble in H_2O (%)	4.2 meq/ml wetted bed volume
Moisture retention	Ω 50%

Table-2
Physico-chemical properties of strongly acidic Amberlite 200C cation exchange resin

Characteristics	Value
Physical Characteristics	
Appearance	Grey spherical beads
Particle size range	16-45 mesh
Temperature limitations	120 ˚C
Chemical Characteristics	
Structure	Gel
Matrix	Styrene-divinylbenzene (Macroreticular Copolymer)
Functional Group	Sulphonic Acid
Ionic form	Na^+
Total Exchange capacity	1.7 eq /L by wetted bed volume
Moisture retention	Ω 46-52% (Na^+ form)

Preparation of the adsorbate: A stock solution of 1000mg/L of Ni(II) was prepared by dissolving 4.479g of nickel sulphate in double distilled water and 1ml of concentrated nitric acid was added to prevent hydrolysis and made up to 1000 ml. Fresh dilutions were used in each experiment.

Electroplating Industrial Effluent: The waste water was collected from electroplating industries, Coimbatore, India and the characterization of the effluent was carried out using standard procedures[10]. For different pH of the waste water, 100 mg of the resin was agitated with 50 ml of 50mg/L of waste water for 180 min. The effect of resin dosage on percent removal of Ni(II) from industrial effluent was carried out with 50 ml of 50mg/L of waste water at natural pH, with an agitation time of 180 min. Some of the characteristics of waste water were given in table-3.

Batch mode, adsorption isotherms and kinetic studies: The working solution of 10, 20, 30, 40 and 50 mg/L of Ni(II) was prepared from stock solution. Batch mode adsorption studies were carried out with 100 mg of the adsorbent and 50 ml of Ni(II) solution of desired concentration at a pH of 5 ±0.2, agitated at 150 rpm in a mechanical shaker (TECHNO-model) at room temperature (30 ± 2 ^oC). The adsorbate solution was separated from the resin by filtration and the metal adsorbed was estimated spectrophotometrically by using a UV-visible spectrophotometer (ELICO SL 164) at 470 nm using dimethylglyoxime reagent[9]. The amount of metal ion adsorbed was computed by the following equation:

$$q_e = V/W\ (C_o - C_e) \quad (1)$$

Table-3
Characteristics of electroplating effluent

pH	6.5
Total dissolved solids (mg/L)	8030
Total suspended solids (mg/L)	750
Sodium (mg/L)	360
Potassium (mg/L)	20
Calcium (mg/L)	130
Chloride (mg/L)	410
Nickel (mg/L)	250
Sulphate (mg/L)	300

Where C_e and C_o (mg/L) are the liquid -phase concentrations of solutes at the initial and equilibrium time t, respectively. V (L) is the volume of solution and W (g) is the mass of dry adsorbent.

The effect of initial pH on the removal of Ni(II) ions from aqueous solution was studied in the range of 2 to 9 pH , which was adjusted using 0.01 N HCI and 0.01 N NaOH solutions. For these experiments 50 ml of (20mg /L and 50 mg/L) Ni(II) solution was agitated with 0.1 g of resin for a period of 60 minutes.

The influence of resin dosage on Ni(II) removal was studied with various resin dosage (0.05 to 0.2 g/L) for 50 mg/L Ni(II) solution.

Various isotherm models such as Langmuir, Freundlich, and Redlich-Peterson were investigated. Reaction-based kinetic models such as Lagergren pseudo- first order and Ho pseudo - second order models were studied. The efficiency of both the resins on Ni(II) removal was compared and tabulated.

Desorption studies: After adsorption experiments with 50 mg/L solution of Ni(II) and 100 mg of adsorbent, the Ni(II) laden resins were separated out by filtration and the filtrate was discarded. The resins were given a gentle wash with double distilled water to remove the unabsorbed metal ions. Desorption studies were carried out using several such samples. They were agitated with 50 ml of HCl of various strengths (0.5–2.5 M). The desorbed metal ions in the solution were separated and analyzed as before.

Results and Discussion

Effect of agitation time, adsorbent dose and initial pH on the adsorption of Ni(II) ions from aqueous solution: The removal amount of Ni(II) increased as the contact time elapsed. The equilibrium time was reached within 100 minutes for all the concentrations studied (10 to 50 mg/L) for both weak acid and strong acid resins. The kinetic curves are single, smooth and continuous, indicating the possible monolayer coverage of metal ions on the surface of the resin[11]. Adsorption increased with increase in resin dose and agitation time. Optimum resin dosage was fixed as 0.1g for both the resins. The effect of pH on the sorption of Ni(II) ions was tested at different pH values (2.0-9.0). The results indicated that the maximum uptake of Ni(II) ions occurred at initial pH of 5.0 for both the resins. The adsorption capacity of both the resins increased with increase in pH of the aqueous solution. This can be explained on the basis of decrease in competition between protons (H^+ ions)/ (Na^+) and metal cations (Ni^{2+} ions) for the same functional groups ($-COO^-$) for the weak acid resin and ($-SO_3^-$) for the strong acid resin, resulting in a lower electrostatic repulsion between the surface of the adsorbent and Ni(II) ions[12].

Adsorption Isotherms: Sorption isotherms describe the partition of metal ions in solid and liquid phase at equilibrium. Sorption equilibrium study provides fundamental physicochemical results to evaluate the applicability of sorption processes as a unit operation[13]. Various isotherm models and their parameters are presented in table-4. The Langmuir equation (figure-1) assumes that the solid surface presents a finite number of identical sites which are energetically uniform and a monolayer is formed when the solid surface reaches saturation[14]. The Freundlich expression is an empirical equation based on sorption on a heterogeneous surface suggesting that binding sites are not equivalent[15]. Redlich-Peterson isotherm is a combination of Langmuir and Freundlich models and the equilibrium adsorption data fitted well into Redlich-Peterson isotherm model[16] also (figure-2).

Table-4
Isotherm parameters for removal of Ni(II) by Amberlite-IRC86 and Amberlite200C

Isotherm models	Constants	Value	
		Amberlite -IRC86	Amberlite 200C
Langmuir[13] $C_e/q_e = 1/Q_o b + C_e/Q_o$ (2)	Q_0 (mg/g)	37.927	43.113
	b (L/mg)	0.1399	0.1059
	R^2	0.9760	0.9898
Freundlich[3] $\log q_e = \log K_f + 1/n \log C_e$ (3)	K_F (mg/g)	6.845	6.749
	n	3.547	2.899
	R^2	0.9899	0.9645
Redlich-Peterson[14] $q_e = K_R C_e / 1 + a_R C e^{\beta}$ (4)	K_R (L/g)	5.311	4.786
	a_R (L/mg)	0.1404	0.1454
	R^2	0.9761	0.9900

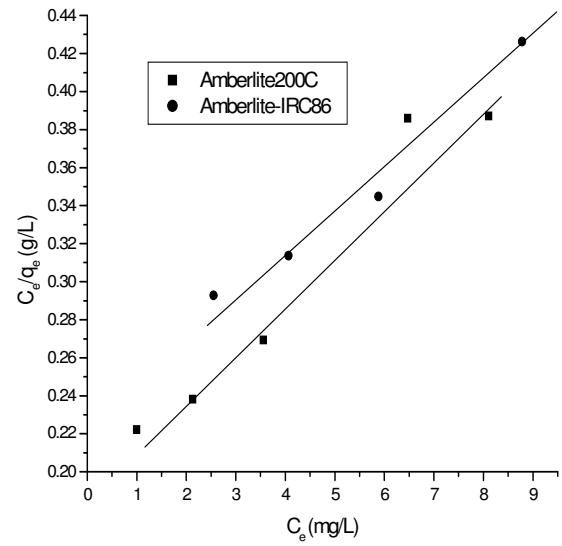

Figure-1
Langmuir isotherm

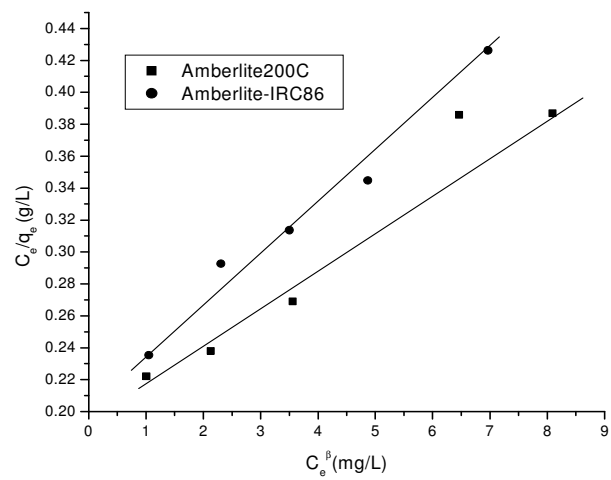

Figure-2
Redlich Peterson isotherm

The maximum adsorption capacity of Amberlite-IRC86, weak acid cation exchange resin was found to be 37.92 mg/g and for Amberlite200C, strong acid cation exchange resin, the maximum adsorption capacity was found to be 43.11 mg/g respectively.

Adsorption Kinetics: Lagergren Pseudo - first order kinetic model: The rate constant of adsorption was determined from Lagergren Pseudo - first order equation (figure 3a, 3b) which is generally expressed as[9],

$$\log(q_e - q_t) = \log q_t - K_1 t / 2.303 \quad (5)$$

where, q_e and q_t are the adsorption capacity (mg/g) at equilibrium and at time t, respectively and K_1 is the rate constant for pseudo - first order adsorption.

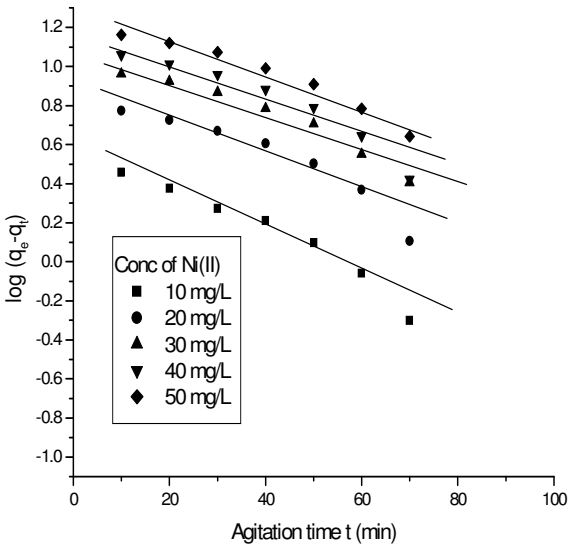

Figure-3a
Pseudo firsr order for Amberlite-IRC86

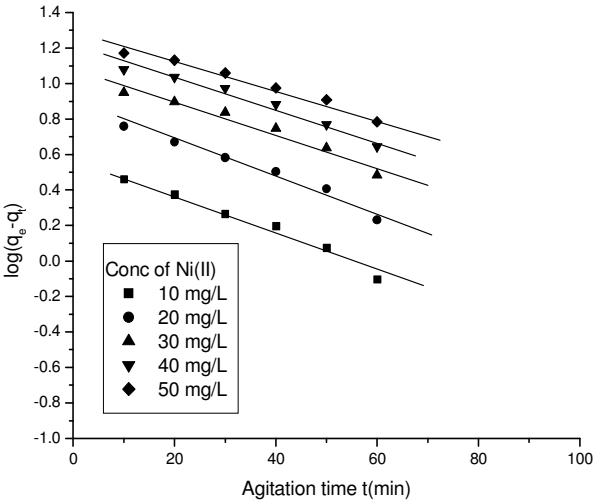

Figure-3b
Pseudo first order for Amberlite200C

Ho Pseudo - second order kinetic model: The linear form of Ho pseudo - second order kinetic model (figure 4a, 4b) is expressed as[17]

$$t/q_t = 1/K_2 q_e^2 + t/q_e \quad (6)$$

where, K_2 is the rate constant of second order adsorption (g/mg/min).

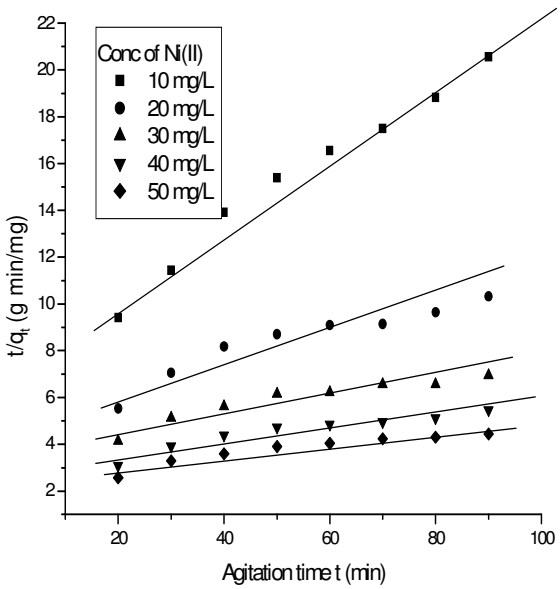

Figure-4a
Pseudo second order for Amberlite-IRC86

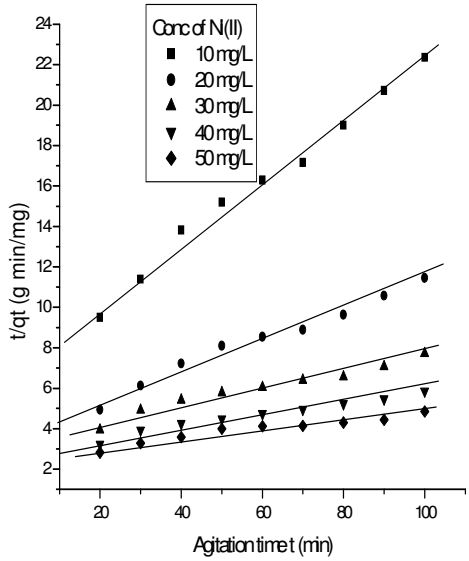

Figure-4b
Pseudo second order for Amberlite200C

Kinetic parameters for the removal of Ni(II) by both the resins are given in table-5.

Treatment of electroplating effluent: The waste water from the electroplating industry was agitated with varying dosages of the adsorbents for 180 min. When the adsorbent dosage increases, the removal of Ni(II) also increases and attains 93.6% removal for the weak acid resin at a dose of 300mg/50ml of wastewater and 98.7% for the strong acid resin at a dose of 300mg/50ml of the effluent.

Table-5
Kinetic parameters for the removal of Ni(II) by Amberlite-IRC86 and Amberlite200C

Conc Of Ni(II) (mg/L)	Pseudo-first-order model K_1 x10^{-2} (1/min)		Pseudo-second-order model K_2 x10^{-2}(g/ mg min)	
	Amberlite-IRC86	Amberlite 200C	Amberlite -IRC86	Amberlite 200C
10	0.376	3.787	0.4413	0.0444
20	3.807	4.005	0.1261	0.1992
30	3.891	4.045	0.0653	0.0881
40	4.031	3.403	0.0573	0.0529
50	3.314	3.922	0.0437	0.0358

Desorption studies: A desorption study is important because it is useful in the regeneration of the resin and recovery of heavy metals. 97.8% desorption could be achieved with 0.25N HCl for 50mg/L concentration of Ni(II) for the strong acid resin. Similarly 95.5% desorption was achieved with 0.25N HCl. This is due to the fact that in acidic conditions, H^+ ions protonate the adsorbent surface by replacing the metal ions on the adsorbent surface, leading to desorption of the positively charged metal ion species. Therefore it is clear that Ni(II) is adsorbed on the adsobent surface through the ion-exchangeable sites present in the resin[18].

Conclusion

Based on the present study, it is clearly shown that both Amberlite200C and Amberlite-IRC86 are found to be effective adsorbents for the removal of Ni(II) from aqueous solution and industrial effluent. The maximum adsorption capacity of Amberlite-IRC86, weak acid cation exchange resin was found to be 37.92 mg/g and for Amberlite 200C, strong acid cation exchange resin, the maximum adsorption capacity was found to be 43.11 mg/g respectively. The adsorption process is strongly affected by parameters such as agitation time, pH and adsorbent dosage. The percentage removal of Ni(II) increased with the increase in contact time and adsorbent dosage. The overall adsorption rate was analyzed with both pseudo-first order and pseudo-second order kinetic models. The data obtained from this study was excellently described by Langmuir, Freundlich and Redlich-Peterson models. Desorption studies showed that both the resins can be regenerated and reused. Overall, it can be concluded that both the strong acid cation exchange resin, Amberlite200C and the weak acid cation exchange resin, Amberlite-IRC86 can be effectively employed in the removal of Ni(II) from aqueous solution and effluent. Moreover, the strong acid resin, Amberlite200C was found to have a slightly higher adsorption capacity than the weak acid resin and can be successfully used in wastewater treatment plants.

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