

# Evaluation of Amberjet 1500H, Amberjet 1300H and Amberlite IRC 86 Ion-Exchange Resins for the Removal of Toxic Nickel Ions from Aqueous Solution

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**Abstract:** A gel resins containing Sulfonic and carboxylic acid groups were investigated in this study for its sorption properties towards nickel metal ions. The use of selective ion exchange to recover nickel metal ions from aqueous solution has been studied. The ion exchange behavior of nickel metal ions on three resins, depending on adsorbate amount, adsorbent amount, acidity, temperature, and contact time, as well as the adsorption isotherms and kinetics were systematically investigated. Experimental measurements have been made on the batch sorption of toxic nickel ions from aqueous solutions using cation exchange resins. The precision of the method was examined at under optimum conditions. The data obtained show that the maximum nickel metal ions uptake was increased in the series: Amberjet 1500H (74.58%) > Amberjet 1300H (69.73%) > Amberlite IRC 86 (10.54%). The equilibrium ion exchange capacity of resin for metal ions was measured and explored by using adsorption isotherms. The thermodynamic parameters ( $\Delta H^{\circ}$ ,  $\Delta S^{\circ}$ ,  $\Delta G^{\circ}$  and  $E_a$  values) were also determined at different temperatures.

**Keywords:** Sorption; Ion exchange; Nickel; Kinetics and thermodynamics

## 1. Introduction

Heavy metal released in the environment has been increasing continuously as a result of industrial activities and technological developments and poses a threat to human health [1]. In this case, one of the common methods for removing metals is ion exchange technique. Ion exchange onto low cost media such as synthetic resins offers an attractive and inexpensive option for the removal of dissolved metals. There has been growing concern over the effect of heavy metals on humans and aquatic ecosystems. There are many different applications of ion exchanges in the industry. Recoveries of inorganic substances on heavy metal cations from wastewater are examples of their application. Many separation techniques have been proposed for the identification of metals in various environmental samples, including solvent extraction, ion exchange, co-precipitation, membrane processes and sorption [2]-[3]. Among these methods, ion exchange is highly popular and has been widely practiced in industrial wastewater treatment processes.

## 2. Experimental

### Materials and Equilibrium studies

Analytical grade reagents were used. Solutions of certain molarities of test metals were prepared by dilution of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  from Sigma Co. with double distilled water. Synthetic Amberjet 1500H, Amberjet 1300H and Amberlite IRC 86 ion exchange resins ( $\text{H}^+$  - form) were obtained from Rohm and Hass Co. Procedures

During batch operation, resins and solution dumped into a vessel and after mixing, the solution and the resin allowed for equilibrium for 6 h in the shaker. The nickel solution was measured using complexometric technique. The batch ion exchange experiments were performed in a wide variety of conditions. Equilibrium data for nickel ions were determined at 5.98 mmol/l of the nickel ion at a desired temperature.

## 3. Results and Discussion

### 3.1. Effect of contact time and adsorption kinetics

The obtained data for the Ni(II) removal from aqueous solution using the Amberjet 1500H, Amberjet 1300H and Amberlite IRC 86 ion-exchange resins are presented in Fig.1. The adsorption of Ni(II) from aqueous solution onto the three resins was rapid at the start of the experiment and then the rate of adsorption become slow down. The maximum amount of Ni(II) from aqueous solutions was adsorbed onto the three resins within 240 min. and then no significant change was observed. Thus, the time of equilibrium for the Ni(II) adsorption onto the resins from aqueous solutions was 240 min. The probable reason for rapid adsorption of Ni(II) from aqueous solution may be more available active sites in the resins for adsorption. In addition, the sulphonic and carboxylic groups on the ion-exchange resin were responsible for the complex formation between metal ions Ni(II) and functional groups ( $-\text{SO}_3\text{H}$  and  $-\text{COOH}$ ) [4]-[5]. However the more active sites may not be available in the resins for further metal ions adsorption with progress of contact time.

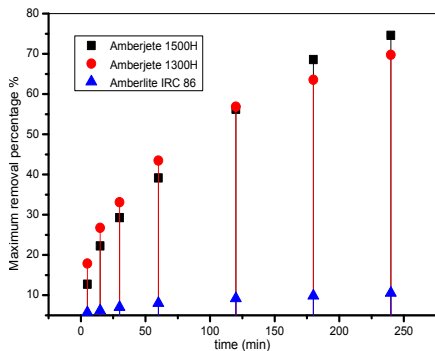


Fig. 1 Effect of contact time of nickel removal onto the three resins

The pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models were applied to determine the adsorption rate of Ni(II) onto the ion-exchange resins. The linear equation for pseudo-first-order kinetic model can be expressed as [6]:

$$\log \frac{q_e}{q_t} = \log q_{e,1} - \frac{k_1}{2.303} t$$

where  $k_1$  is the pseudo-first-order rate constant ( $\text{min}^{-1}$ ) and  $q_e$  ( $\text{mmol g}^{-1}$ ) is the adsorption capacity at equilibrium, and  $q_t$  ( $\text{mmol g}^{-1}$ ) is the adsorbed amount of metal ion after time  $t$  (min). The linear equation for pseudo-second-order kinetic model can be expressed as [7]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e,2}^2} + \frac{t}{q_{e,2}}$$

where  $k_2$  is the pseudo-second-order rate constant ( $\text{g mmol}^{-1} \text{min}^{-1}$ ). The  $q_e$ ,  $k_1$  and  $k_2$  values for different temperatures of Ni(II) solution were calculated from their respected plots, which are not included here. The obtained  $q_e$ ,  $k_1$ ,  $k_2$  and correlation coefficient ( $R^2$ ) values are tabulated in Table 1. The  $R^2$  values for pseudo-first-order kinetic model are relatively higher than pseudo-second-order kinetic model for the Ni(II) adsorption onto the Amberjet 1500H, Amberjet 1300H ion-exchange resins. These results implied that the adsorption of Ni(II) onto both obeyed first order model kinetic model [5]-[8]. Whereas the  $R^2$  values for pseudo-second-order kinetic model is relatively higher than pseudo-first-order kinetic model for the Ni(II) adsorption onto Amberlite IRC 86. However, the experimental  $q_e$  values are very close to the calculated  $q_e$  values for pseudo-second-order kinetic model. These results implied that the adsorption of Ni(II) onto the Amberlite IRC 86 ion-exchange resin obeyed second order model kinetic model [5]-[8]. The diffusion of metal ions cannot be explained on the basis of pseudo-first-order and pseudo-second-order kinetic model only. Due to this reason, intraparticle diffusion model was applied to estimate the diffusion of Ni(II) in the resins using Weber-Morris intraparticle diffusion model [9]:

$$q_t = k_{id} t^{0.5} + C$$

where  $k_{id}$  is the intraparticle diffusion rate coefficient ( $\text{g mmol}^{-1} \text{min}^{-0.5}$ ) and  $C$  provides an idea about the thickness of the boundary layer [10]. The plot of  $q_t$  vs.  $t^{0.5}$  (Fig. and date are not shown) shows the intercept values for Ni(II) is 0.0186, 0.0682 and 0.0294 mmol/g for Amberjet 1500H, Amberjet 1300H and Amberlite IRC 86 ion-exchange resins, respectively. The obtained values indicated that adsorption of Ni(II) onto the three resins was not only controlled through a boundary layer effect.

**Table 1:** Adsorption kinetics models

kinetics models	Name of the resins		
	1500H	1300H	ICR 86
Lagergren			
$q_{e,1}$ (mmol/g)	0.4090	0.3179	0.0302
$k_1$ ( $\text{min}^{-1}$ )	0.0126	0.0119	0.0112
$R^2$	0.9726	0.9988	0.9822
Second order			
$q_{e,2}$ (mmol/g)	0.5226	0.4559	0.0646
$k_2$ ( $\text{g}/\text{mmol min}$ )	0.0368	0.0675	1.1187
$R^2$	0.9653	0.9836	0.9934

### 3.2. Adsorption Isotherm Models

The surface property and affinity of ion-exchange resins for Ni(II) removal can be determined using the different adsorption isotherm models. The obtained equilibrium data from the adsorption of Ni(II) onto the ion-exchange resins fitted to the linear equation of Langmuir [11], Freundlich [12]. The linear equation for Langmuir and Freundlich isotherm models are expressed as follows:

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

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

where  $q_e$  ( $\text{mmol/g}$ ) is the adsorbed amount of Ni(II) at equilibrium,  $C_e$  ( $\text{mmol/l}$ ) is the equilibrium concentration of Ni(II),  $q_m$  ( $\text{mmol/g}$ ) and  $b$  ( $\text{L}/\text{mmol}$ ) are Langmuir constants.  $K_F$  and  $n$  are Freundlich constants, which indicate the capacity and intensity of adsorption. The obtained values of applied adsorption isotherm parameters are reported in Table 2.  $R^2$  values indicated that the Langmuir isotherm model for the Ni(II) adsorption onto both Amberjet 1500H and Amberjet 1300H was best fitted in comparison with Freundlich isotherm model.

Whereas  $R^2$  values indicated that Freundlich isotherm model for the Ni(II) adsorption onto Amberlite IRC 86 ion-exchange resin was best fitted in comparison with Langmuir isotherm model. The  $n$  values were found to be 6.296, 5.316 and 0.6417 for the Ni(II) adsorption onto the Amberjet 1500H, Amberjet 1300H and Amberlite IRC 86 ion-exchange resins, respectively, from aqueous solution. The obtained results for the Ni(II) adsorption are similar to the reported adsorbent by Özbay [13] and Monier et al., groups [14]. The adsorption data are tabulated in Table 2.

**Table 2:** Adsorption Isotherm Models

Isotherm models	Name of the resins		
	1500H	1300H	ICR 86
Freundlich			
$n$	6.2964	5.3160	0.6417
$K_F$ ( $\text{mmol g}^{-1}$ )	0.4854	0.4782	0.8617
$R^2$	0.9540	0.7769	0.9996
Langmuir			
$q_m$ ( $\text{mmol g}^{-1}$ )	0.4166	0.3879	0.0469
$b$ ( $\text{L}/\text{mmol}$ )	8.3350	6.2530	0.7309
$R_L$	0.0205	0.0275	0.2966
$R^2$	0.9982	0.9912	0.9989

### 3.3 Thermodynamics of Ni(II) adsorption

The effect of temperature on the adsorption of Ni(II) from aqueous solution onto the three ion-exchange resins was performed to evaluate the influence of metal ion adsorption capacity. The removal percentage of the Amberjet 1500H, Amberjet 1300H and Amberlite IRC 86 ion-exchange resins was raised from 74.58 to 93.65%, 69.73 to 92.98% and 10.54 to 75.25% for the three resins respectively, with increase in temperature (293 to 318 K). This may be due to the formation of new active sites in the ion-exchange resins to increase in temperature. Thermodynamic studies were performed in detail to find out the nature of adsorption process. Thermodynamic parameters such as standard free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) were calculated using the following equations:

$$\Delta G^\circ = -RT \ln(K_D)$$

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

where  $K_D$  is the distribution coefficient,  $T$  is the temperature (K) and  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ). The  $\Delta H^\circ$  and  $\Delta S^\circ$  values were obtained from the slope and intercept of  $\ln K_D$  vs.  $T^{-1}$  plot for the Ni(II) adsorption from aqueous solution onto the resins at various temperature. The obtained values are tabulated in Table 3. The negative  $\Delta G^\circ$  values suggested that the adsorption of Ni(II) from aqueous solution onto both Amberjet 1500H and Amberjete 1300H resins was spontaneous in nature at higher temperature (318 K). The positive  $\Delta H^\circ$  values confirmed the endothermic nature of Ni(II) adsorption. Moreover, the positive  $\Delta S^\circ$  value showed increases in affinity of Ni(II) onto the ion-exchange resins. A linear relationship can be seen with a regression coefficient  $R^2$ , 0.841, 0.787 and 0.776 for Amberjet 1500H, Amberjet 1300H and Amberlite IRC 86 resins, respectively. As well as,  $E_a$  values for the Amberjet 1500H, Amberjete 1300H and Amberlite IRC 86 resins are observed to be 41.281, 43.207 and 41.871 kJ/mol, respectively in Table 3. These results indicate that the adsorption has a low potential barrier and assigned to a physisorption.  $\Delta H^\circ$  values obtained from adsorption of Ni(II) onto both Amberjet 1500H and Amberjet 1300H are lower than that of Amberlite IRC 86. This result gives clear evidence that the interactions between Ni(II) and the surface sulphonic groups of both resins may be weak. On the other hand, the positive values of  $E_a$ ,  $\Delta G^\circ$ , and  $\Delta H^\circ$  indicate the presence of an energy barrier in the adsorption process. The positive values for these parameters are quite common because the activated complex in the transition state is in an excited form [15].

**Table 3:** Thermodynamic parameters

Parameters	Name of the resins		
	1500H	1300H	ICR 86
$\Delta H$ , KJ/Mol	48.271	51.999	14.953
$\Delta S$ , J/Mol	153.813	164.335	18.193
$E_a$ , KJ/Mol	41.280	43.206	41.870
$S^*$	$1.21 \times 10^{-8}$	$6.67 \times 10^{-9}$	$2.76 \times 10^{-8}$
Temp., K	$\Delta G$ , KJ/Mol		
293 K	2986.896	3576.041	10820.032
308 K	1497.846	2137.875	3273.628
318 K	-1025.195	-741.636	3147.637

In order to further support the assertion that physical adsorption is the predominant mechanism, the values of the activation energy ( $E_a$ ) and sticking probability ( $S^*$ ) were estimated from the experimental data. They were calculated using a modified Arrhenius type equation related to surface coverage as expressed in equations:

$$\theta = 1 - \frac{C_e}{C_0}$$

$$S^* = (1 - \theta) \exp\left(-\frac{E_a}{RT}\right)$$

The sticking probability,  $S^*$ , is a function of the adsorbate/adsorbent system under consideration and is dependent on the temperature of the system. The parameter  $S^*$  indicates the measure of the potential of an adsorbate to remain on the adsorbent indefinitely. It can be expressed as in Table 3.

The effect of temperature on the sticking probability was evaluated throughout the temperature range from 293 to 318 K by calculating the surface coverage at the various temperatures. Table 3 also (the results) indicated that the values of  $S^* \leq 1$  for both 1500H and 1300H, hence the sticking probability of the Ni(II) onto the two resins systems are very high, while for ICR 86 system  $S^*$  was  $\geq 1$ , hence the nickel ions unsticking to ICR 86 surface – no sorption.

The apparent activation energy ( $E_a$ ) and the sticking probability ( $S^*$ ) are estimated from the plot (the fig. not shown). The positive values of the apparent activation energy ( $E_a$ ) indicated that the higher solution temperature favors the adsorption process and also the adsorption process is endothermic in nature [16].

### 3.4 Effect of adsorbent dosage

The adsorbent dose is an important parameter in the adsorption studies because it determines the capacity of the adsorbent for a given initial concentration of metal ion solution. The effect of adsorbent dose on Ni(II) removal percentage is shown in Fig. 2. It was observed that the removal percentage increased rapidly with the increase in the adsorbent dose till 6.0 g Amberjet 1300H, 8.0 g Amberlit IRC 86 and after the critical dose, the removal percentage reached almost a constant value. This can be attributed to the increase in the adsorbent surface area and availability of more active adsorption sites on the resin surface with increasing the dosage of the adsorbent [17]. On the other hand, the removal percentage of Ni(II) show increase till 4.0 g Amberjet 1500H then decreased with the increase in the adsorbent dosage, as a result of aggregation of the adsorbent particles.

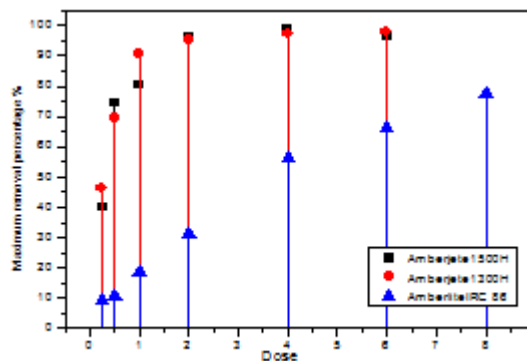


Fig. 2 Effect of resins dose on nickel removal percentage

### 3.5 Effect of nickel concentration and adsorption isotherm

The effect of initial nickel concentration on the efficiency of its adsorption onto the three resins was investigated in the initial concentration range of 2.06 - 9.88 mmol/l and the results are shown in Fig. 3. By increasing the initial nickel concentration, the percentage amount of nickel removal decreased onto both Amberjet 1300H and Amberlite IRC 86. At a constant amount of resin, the decrease in the adsorption percentage is probably due to the saturation of the active binding sites on the resin surface at higher nickel concentrations. On the other hand, by increasing the initial nickel concentration the actual amount of nickel adsorbed per unit mass of the resins increased. The higher initial concentration of nickel provides an important driving force to overcome the mass transfer resistance for nickel transfer between the solution and the surface of the resins [18]. It was also observed that the amount of nickel adsorbed per unit mass of the Amberjet 1500H ion-exchange resin increased with a rise in concentration of Ni(II) up to 3.94 mmol/l then sudden decreased at higher concentrations. In the process, the nickel molecules primarily encounter the boundary layer effect and then diffuse from boundary layer film onto adsorbent surface and finally diffuse into the porous structure of the adsorbent, which will take relatively longer contact time. Thus, the ion-exchange resins can be efficiently used for the removal of low concentration Ni(II) from aqueous solutions.

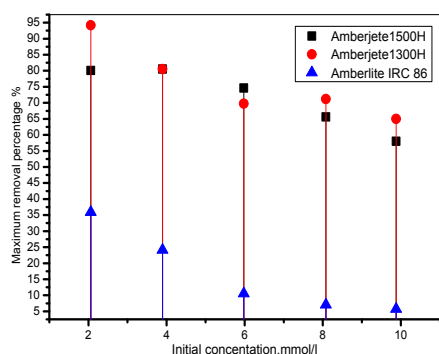


Fig. 3 Effect of different concentrations on nickel removal

### 3.6 Effect of solution Acidity

Acidity of solution is one of the dominant parameters to control the adsorption process. The obtained data for the Ni(II) adsorption from aqueous solution of different acidity in the range (0.001 - 2.0 M HCl) is presented in Fig. 4.

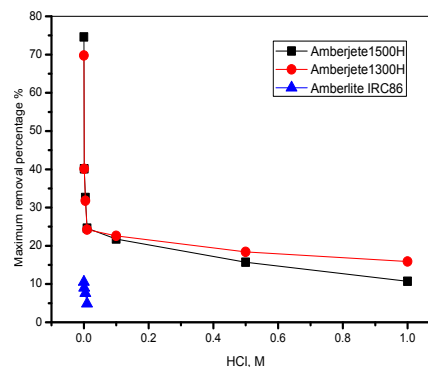


Fig.4 Effect of HCl concentrations on nickel removal

The adsorption of the Ni(II) onto the ion-exchange resins decreased by increasing concentration of HCl. The adsorption of the Ni(II) onto the ion-exchange resins in highly acidic medium (2.0 M HCl) is very low because  $H^+$  competes with metal ions during the adsorption process [18]. Due to this reason the adsorption of Ni(II) from aqueous solution onto the three ion-exchange resins became slow in the highly acidic medium. However, the adsorption of Ni(II) from aqueous solution onto the ion-exchange resins was enhanced to increase in pH from acidic to neutral medium because anionic sites are generated onto the adsorbent after the formation of the water layer through reaction between  $H^+$  and  $OH^-$  [19]-[20].

## 4. Conclusion

Both strong cation exchange resins (Amberjet 1500H and 1300H containing sulfonic functional groups) and weak cation exchange resin (Amberlite IRC86 containing carboxylic functional groups) for removing target pollutant Ni(II) from aqueous solutions are evaluated and focus on the binding equilibrium and batch studies of metal ions. The adsorption of the Ni(II) ions was determined at different temperatures by using the three resins. Based on the efficient removal of nickel ion from aqueous waste at 293 K and 5.98 mmol/l on 1500H (74.58%) is larger than that of 1300H (69.73%) due to the intrinsic ion exchange capacity. While the adsorption capacities of Amberlite IRC86 (10.54%) are very weak compared to the above resins. In addition, the favorable temperature will be 318 K where the removal percentage for 1500H, 1300H and IRC86 was 93.65, 92.98 and 75.25% respectively. Also, we conclude that ion exchange resins could be exploited for applications in the treatment of potable waters, industrial effluents as well as it can be applied for the treatment of coolant water in the nuclear power plants. Detailed studies will be needed to further evaluate ion exchange resins in the treatment of coolant water in the nuclear power plant.

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