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Removal of divalent heavy metal ions from aqueous solutions by Dowex HCR-S synthetic resin

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Ion exchange technology is currently the best way to remove heavy metals from water and wastewater. In this study, we investigated heavy metal ions as cadmium (Cd^{2+}), nickel (Ni^{2+}) and zinc (Zn^{2+}) removal from aqueous solutions using synthetic resin. Batch experiments on the removal efficiency of heavy metal ions at under different conditions such as initial solution pH, stirring speeds, temperatures, initial concentrations and resin dosages of synthetic wastewater solutions were carried out. The maximal exchange levels attained were as follows: 99.76% Cd^{2+}, 93.66% Ni^{2+} and 83.10% Zn^{2+} onto Dowex HCR-S synthetic resin at 293 K, 250 mg L^{-1} initial metal concentration, ion exchange time of 60 min, 400 rpm stirring speed, pH: 6.0 and 2 g resin dosage.

Keywords: zinc; cadmium; nickel; heavy metals; ion exchange; Dowex HCR-S

INTRODUCTION

Fast industrialization has affected to rise up disposal of heavy metals into the environment. The exceeding increase in the use of the heavy metals over the past few decades has unavoidable consequence in an increased flow of metallic substances in the aquatic environment.

Toxic heavy metal ions get introduced to wastewater through various industrial activities such as mining, refining ores, fertilizer industries, tanneries, batteries, paper industries, pesticides etc. [1]. Heavy metals are not biodegradable and tend to be accumulated in living organism, causing various diseases and disorders; therefore, they must be removed before discharge to natural resources [2, 3].

A number of technologies have been developed over the years to remove heavy metals from industrial wastewater. The most important technology includes coagulation/flocculation [4], chemical precipitation [5], adsorption [6], ion-exchange [7], biosorption [8], electrochemical processes [9] and membrane technology [10].

Ion exchange can be used to remove heavy metals from wastewater using an ion exchange resins as synthetic ones derived from guaran [11], Chelex 100 [12], clinoptilolite [13], Amberlite (IR 120, 200, and 252 ZU) [14], Dowex M-4195 [15], Lewatit [16], indion BSR [17], Amberlite IR-96 and Dowex 1x8 [18], and Dowex 50W [19].

In the present study, ion exchange of Cd^{2+}, Ni^{2+} and Zn^{2+} on Dowex HCR S/H strongly acidic cation exchanger resin is examined. The purpose of this study, is examine the interest for different heavy metals of the resin. The parameters that influence adsorption such as initial nickel concentration, stirring speed, resin dosage, temperature, pH and contact time were investigated.

2. MATERIALS AND METHODS

Synthetic Dowex HCR S/H in hydrogen form was obtained from Fluka Co. The properties of Dowex HCR S/H are given in Table 1. The heavy metal solutions of Zn (II), Ni (II) and Cd (II) chloride (analytical grade from Sigma Co) were prepared in double-distilled water.

To study the effect of important parameters like contact time, stirring speed, resin amount, pH, initial metal concentration and temperature on the removal of Cd (II), Ni (II) and Zn (II) by Dowex HCR S/H, experiments were conducted at room temperature except those in which the effect of temperature. The parameters chosen in the experiments were given in Table 2.

A batch system was used for removing by the exchange reaction of heavy metal ions from wastewater. Experimental period was determined as 60 min result of the preliminary tests. The temperature of the reactor was controlled with a HAAKE D8 thermostat connected to reactor. The experimental set up is shown in Figure 1 [20].

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Table 1. Properties of Dowex HCR-S resin

Parameters	Value
Type	Strong acid cation
Change capacity	1.8 meq/ml
Particul size	300 µm – 1200 µm
pH	0 – 14
Max. operating temperature	100 °C
Ionic form	H^+
Ionic density	1.22 g/cm^3
Physical form	Uniform particle size, spherical beads

Table 2. Experimental parameters

Parameter	Studied ratio
Initial metal concentration mg/L	25,50, 100, 250, 500 and 1000
Adsorbent dosage (g/500 ml)	0.25, 0.50, 1.00, 1.50 and 2.00
pH	3.0, 4.0, 5.0 and 6.0
Stirring speed (rpm)	200, 300, 400, 500 and 600
Solution temperature (K)	293, 313, 333 and 353

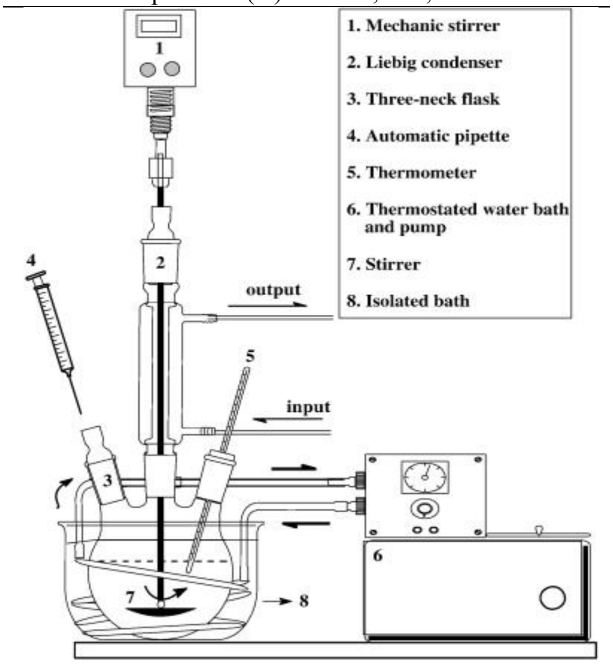

Fig. 1. Experimental set up.

Kinetic experiments were made by using 500 ml of heavy metal solutions (Cd^{2+}, Ni^{2+} and Zn^{2+}) of various concentrations. Samples were taken at different time intervals and remaining metal concentrations were analyzed. The remaining metal concentration in solution with atomic absorption spectrometers (AAS – 6800) device was decided. The amount of metal removal onto Dowex HCR S/H was calculated from the percent efficiency equation as follows:

$$\%efficiency = \left(\frac{C_0 - C_t}{C_0}\right) \times 100 \tag{1}$$

where C_o (mg L^{-1}) is the initial metal concentration, C_t (mg L^{-1}) is the concentration of metal ions in solution at time t.

3. RESULTS AND DISCUSSION

3.1 Effect of pH on ion exchange process

In order to establish the effect of pH on the ion exchange of zinc (II), cadmium (II) and nickel (II) ions on to synthetic resin, the batch equilibrium

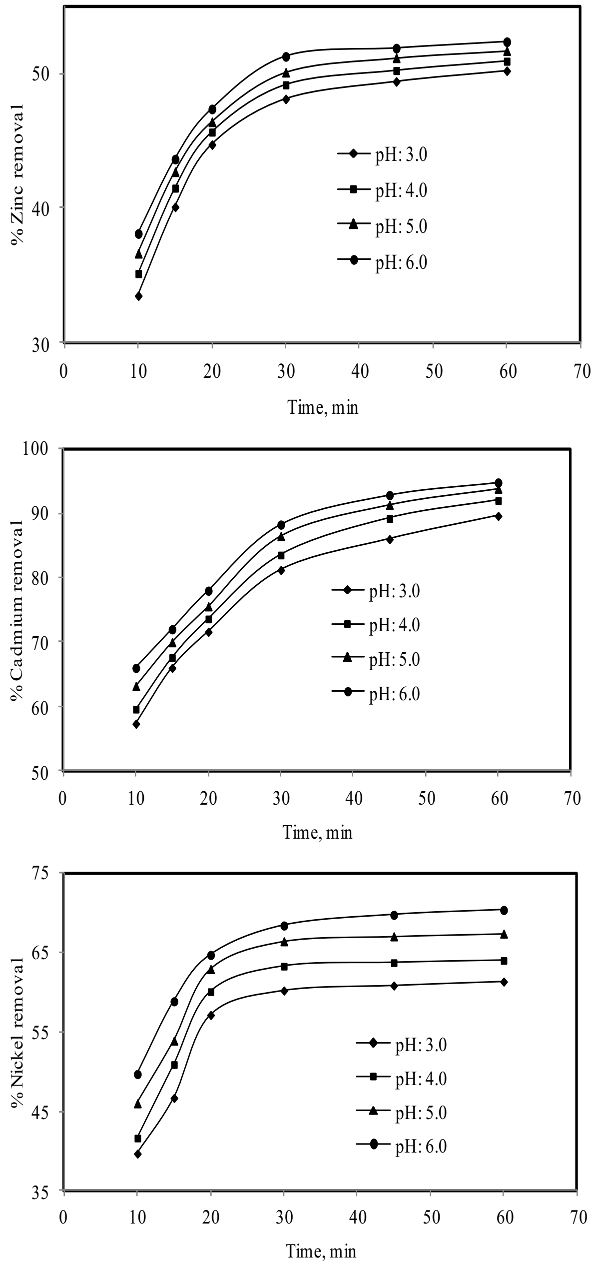

Fig. 2. The effect of initial pH on removal efficiency for the here metal ions (250 mg L^{-1} initial metal concentration, 293 K solution temperature, 400 rpm stirring speed, 1 g/500 ml resin dosage).

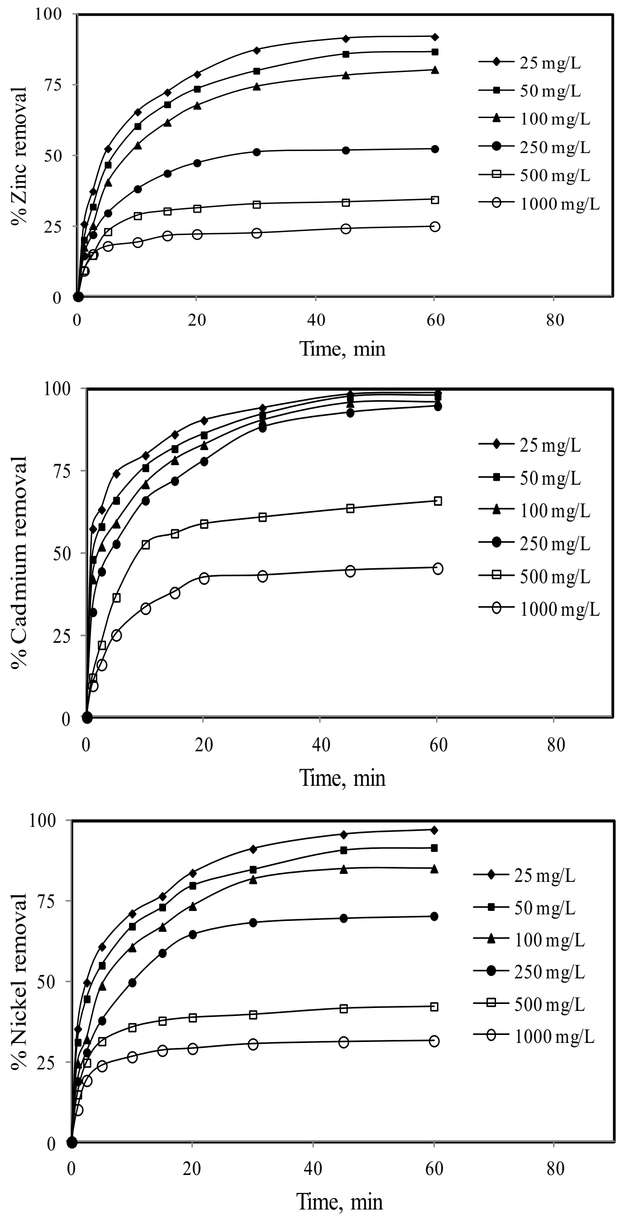

Fig. 3. The effect of initial metal concentration on removal efficiency (pH 6.0, 293 K solution temperature, 400 rpm stirring speed, 1 g/500 ml resin dosage).

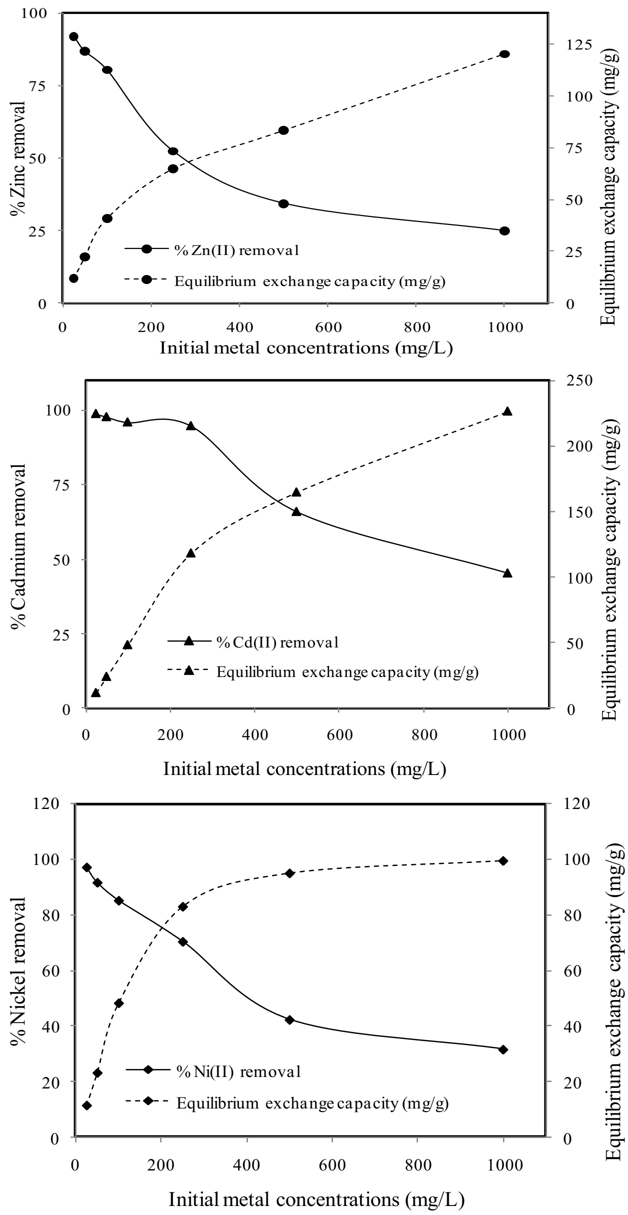

Fig. 3a. The effect of initial metal concentration on removal efficiency and exchange capacity (pH 6.0, 293 K solution temperature, 400 rpm stirring speed, 1 g/500 ml resin dosage).

studies at different pH values were carried out in the range of 3.0 – 6.0 for a constant resin amount of 1 g/L and initial metal concentrations of 250 mg/L at 293 K (Fig. 2). Because of precipitation of heavy metal ions, high values of pH were not studied. Fig. 2 shows the change in metal uptake by synthetic resin at different initial pH levels. It can be seen from Fig. 2 that the pH of the aqueous solution is an important control parameter in the ion exchange process [12]. The percentage of removal metals increased with pH from 3 to 6 with maximum binding occurring pH 6. At pH 6, 52.336% for zinc, 94.777% for cadmium and 70.359% for nickel.

3.2 Effect of initial metal concretions on ion exchange process

Half litre of each of the three metal solutions (Zn^{2+}, Cd^{2+} and Ni^{2+}) of different concentrations ranging from 25 to 1000 mg/L with 1 g of synthetic resin was stirred at 400 rpm and ambient temperature (293 K) for a contact period of 1 h. The results obtained are shown in Fig. 3 and Fig. 3a and indicate that all the curves have the same shape.

It was also realized that the capacity of metal removal by Dowex HCR S/H at the equilibrium increased with the initial concentration of metal but the percent removal decreased with the increase in initial metal concentration from 92.09% for 25 mg/L of Zn to 24.849% for 1000 mg/L of Zn, from 98.842% for 25 mg/L of Cd to 45.338% for 1000 mg/L of Cd and from 97.167% for 25 mg/L of Ni to 31.500% for 1000 mg/L of Ni. Similar results were obtained for Ni (II) on Lewatit resin [16] and Cd (II) on Duolite ES 467 resin [21]. Apparently, the initial heavy metal concentrations played an important role in affecting the capacity of metal exchange onto synthetic resin. The higher the heavy metal concentrations, the stronger the driving forces of the concentration gradient, and therefore the higher the adsorption capacity. In general, the percentage of metal removal increased rapidly up to approximately 10 min and thereafter, rose slowly before attaining a saturation value.

3.3 Effect of solution temperature on ion exchange process

The effect of solution temperatures onto heavy metal removal is shown in Fig. 4. The removal of heavy metal ions as Zn^{2+}, Cd^{2+} and Ni^{2+} increased slightly increasing temperature from 293 K to 353 K. It is seen from Fig. 4 that when synthetic resin for Zn (II) was used with an increase in temperature from 293 to 353 K, the ion exchange efficiency capacity increased from 52.366% to 59.280% for the initial metal concentration of 250 mg L^{-1}; in the case of Cd (II) and Ni (II), the efficiency increased from 94.777% to 98.719% and from 70.359% to 74.680 for the same initial metal concentrations and pH 6.0. This indicated that the exchange reaction was endothermic in nature and ions exchange mechanism favors higher temperatures [7]. An increase in the removal with the rise in temperature may be explained by active site onto synthetic resin being more active at high temperatures. Additionally, an increase in temperature results for mobility of the ions being increased and a decrease in the retarding forces acting on the adsorption ions [22].

3.4 Effect of resin dosage on ion exchange process

The percentage efficiency of each of the three heavy metal ions at different doses of Dowex HCR S/H strongly acidic resin is shown in Fig. 5 and Fig. 5a. The degree (%) of removal efficiency increased as the resin dose was increased. It might be concluded that by increasing the resin dose, the removal efficiency of heavy metal ions increased, while ion exchange density decreased with increase in resin dose. The decrease in ion exchange density may be due to the fact that some adsorption sites may remain unsaturated during the adsorption process whereas the number of sites available for adsorption increases by increasing the resin doses and that results in the increase of removal efficiency [23]. It could be seen from Fig. 5 when increased resin dosage from 0.25 to 2.00 g, removal efficiency increased from 22.143% to 88.099% for Zn (II), from 42.625% to 99.757% for Cd (II) and from 27.591% to 93.665% for Ni (II).

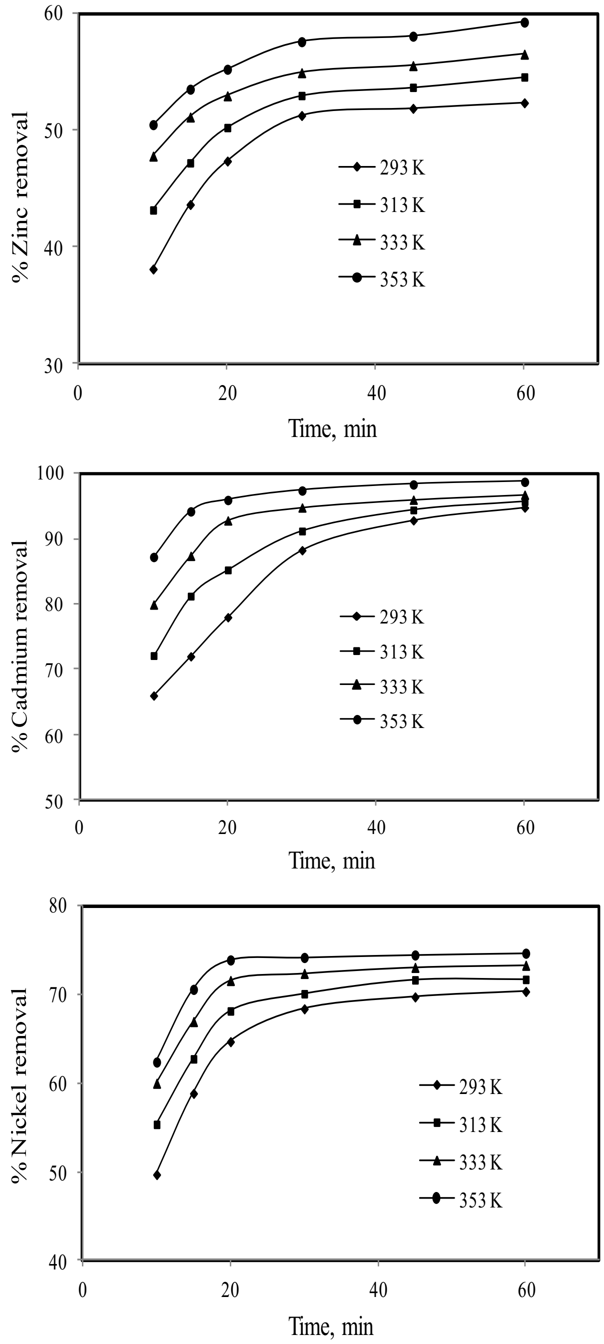

Fig. 4. The effect of solution temperature on removal efficiency (pH 6.0, 1 g/500 ml resin dosage, 400 rpm stirring speed and 250 mg L^{-1} initial metal concentrations).

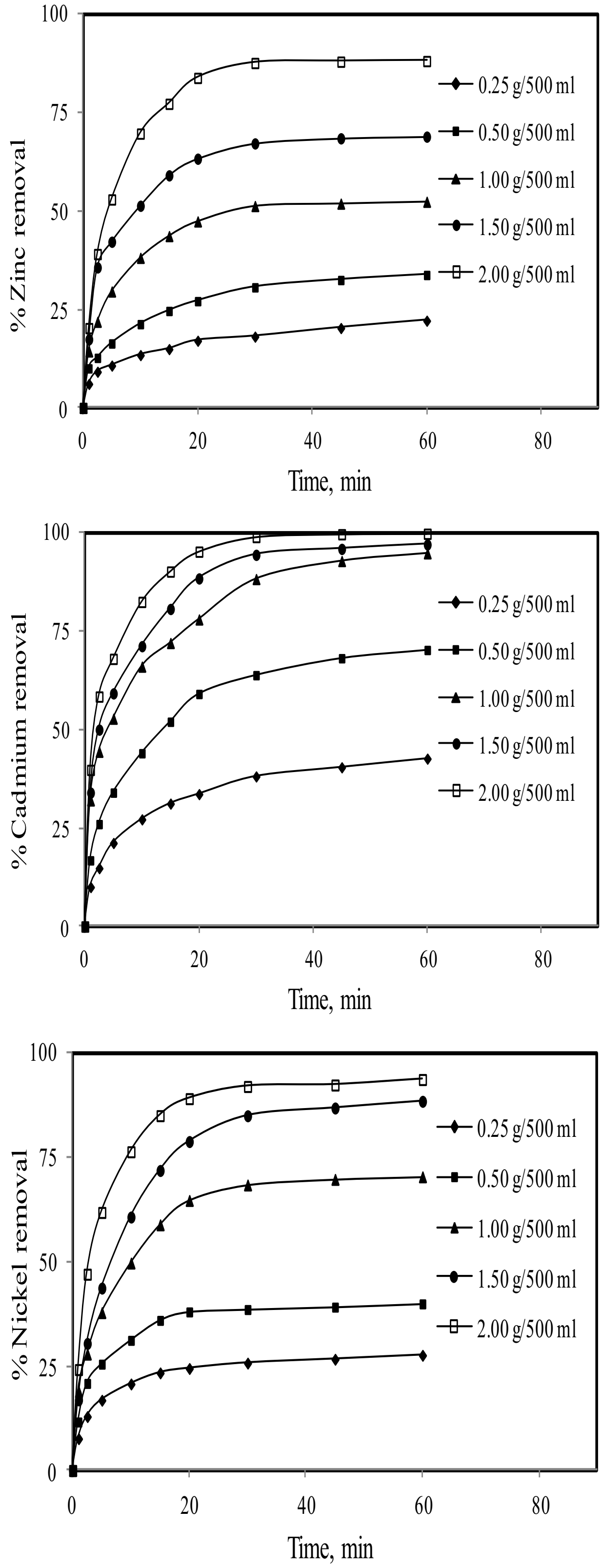

Fig. 5. The effect of resin dosage on removal efficiency (pH 6.0, 293 K solution temperature, 400 rpm stirring speed and 250 mg L^{-1} initial metal concentrations).

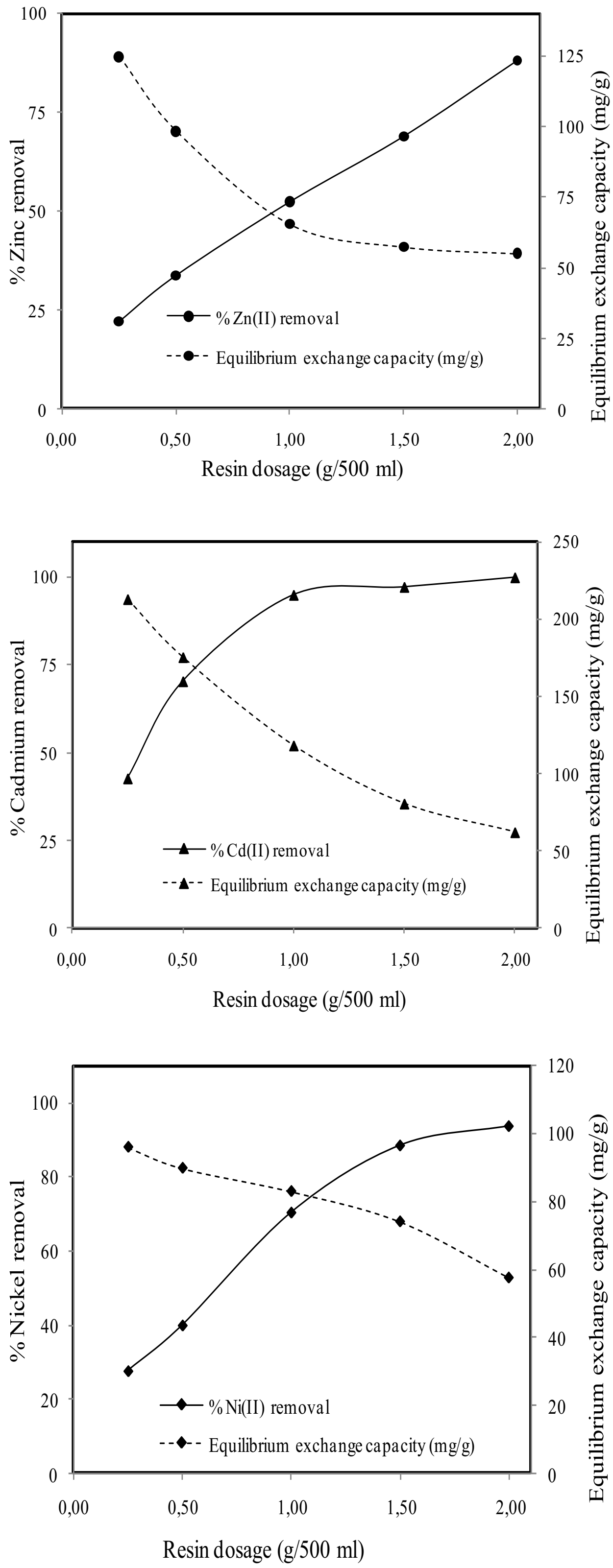

Fig. 5a. The effect of resin dosage on removal efficiency and exchange capacity (pH 6.0, 293 K solution temperature, 400 rpm stirring speed and 250 mg L^{-1} initial metal concentrations).

3.5 Effect of stirring speed on ion exchange process

Experimental results regarding the effect of agitation speed (200, 300, 400, 500 and 600 rpm) were presented. It is clear that stirring is found to be appropriate for maximum exchange of metal ion from the synthetic wastewater. The removal of metal ions using Dowex HCR S/H reaches 56.622% for Zn (II), 98% for Cd (II) and 73.805% for Ni (II) at 600 rpm, (Fig. 6). The effect of the

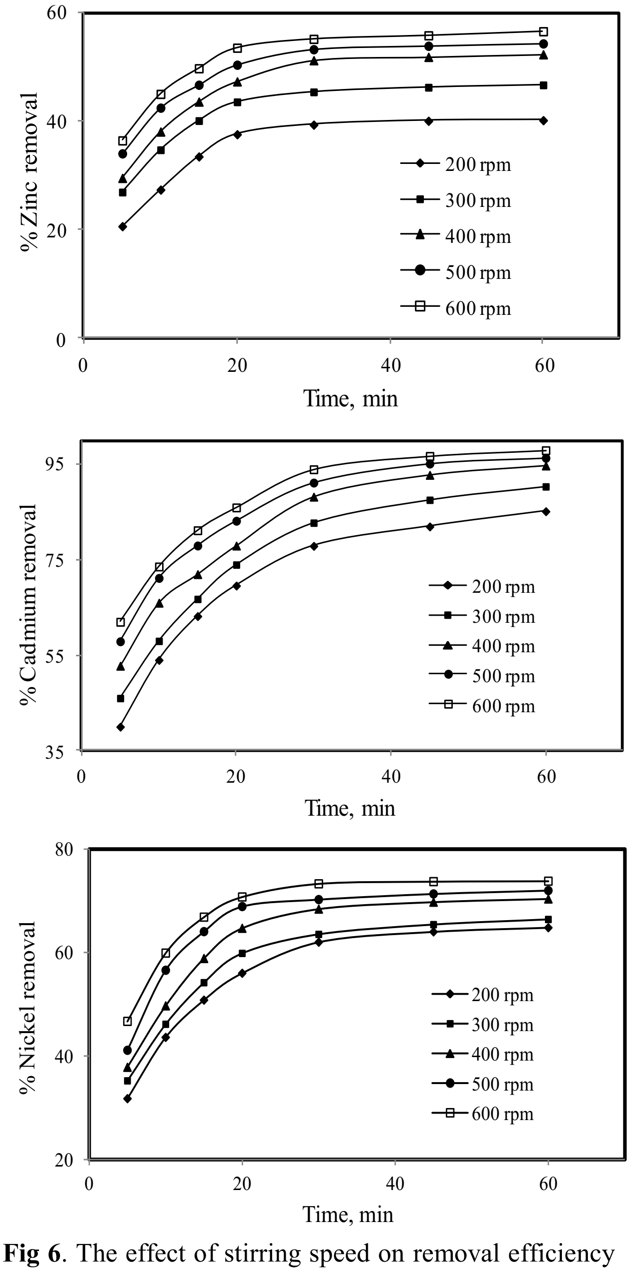

Fig 6. The effect of stirring speed on removal efficiency (pH 6.0, 1 g/500 ml resin dosage, 293 K solution temperature and 250 mg L^{-1} initial metal concentration).

Agitation speed was examined at agitation speeds of range of 200–600 rpm. Stirring speeds higher than 600 rpm were not studied due to the effect of centrifugal forces on the system will increase. It is obvious that agitation increased metal removal from aqueous solutions. This is due to the fact that metal ions, through their transportation to the solid phase, come on resistance at the liquid phase, through the boundary layer. The moving induced by the stirring of suspensions during experiments leads to a reducing of the boundary layer thickness and to a consequent decrease of the transportation resistance of metal ions. This increases the transfer rate of the ions and, thus, the ion exchange rate of the Zn (II), Cd (II) and Ni (II) ions [21].

CONCLUSION

The batch experiments presented in this study revealed that the Dowex HCR-S strongly acidic cationic synthetic resin could be effectively used as adsorbent for removing heavy metals. Treatment of heavy metal ions from aqueous solution was found to increase by increasing the resin dosage, stirring speed, temperature and solution pH. Increase of initial metal concentration decreases removal efficiency but the percent removal decreases with the increase in initial metal concentration. According to the heavy metal removal studies by using Dowex HCR-S strongly acidic cationic synthetic resin, the selectivity sequence could be given as Cd (II) > Ni(II) > Zn(II) at all studying parameters such as initial solution pH, stirring speeds, temperatures, initial concentrations and resin dosages of synthetic wastewater solutions.

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ОТСТРАНЯВАНЕ НА ДВУВАЛЕНТНИ ЙОНИ НА ТЕЖКИ МЕТАЛИ ОТ ВОДНИ РАЗТВОРИ СЪС СИНТЕТИЧНА ЙОНООБМЕННА СМОЛА DOWEX HCR-S

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(Резюме)

В момента йонообменните технологии предоставят най-добрия начин за отстраняване на тежки метали от водата и отпадъчните води. В тази работа ние изследваме отстраняването на йоните на тежки метали като кадмий (Cd^{2+}), никел (Ni^{2+}) и цинк (Zn^{2+}) от водни разтвори с помощта на синтетична йонообменна смола. Проведени са в периодични условия експерименти върху ефективността на отстраняване на металните йони от синтетични отпадъчни води при различни условия – начална стойност на pH, скорост на разбъркване, температура, начални концентрации и количество смола. Максимални степени на извличане се постигат както следва: 99.76% Cd^{2+}, 93.66% Ni^{2+} и 83.10% Zn^{2+} върху Dowex HCR-S при 293 K, начална концентрация на металните йони 250 mg L^{-1}, контактно време от 60 минути, скорост на разбъркване 400 об/мин, pH 6.0 и 2 г смола/500 мл.