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Kinetics and equilibrium studies for the removal of nickel and zinc from aqueous solutions by ion exchange resins

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ABSTRACT

Removal of heavy metals from wastewater is obligatory in order to avoid water pollution. In the present study, performance of Dowex HCR S/S cation exchange resin was evaluated for removal of nickel and zinc from aqueous solutions. Batch shaking adsorption experiments were performed in order to examine the effects of pH, dosage of resin and contact time on removal process. It was observed that more than 98% removal efficiency was achieved under optimal conditions for nickel and zinc. The experimental equilibrium data were tested for the Langmuir, Freundlich and Temkin isotherms. Correlation coefficients indicate the following order to fit isotherms: Langmuir > Freundlich > Temkin for both nickel and zinc ions. Pseudo-first- and -second-order kinetic models were used for describing kinetic data. It was determined that removal of Ni^{2+} and Zn^{2+} was well-fitted by second-order reaction kinetic. Furthermore, separation factors and distribution coefficients of nickel and zinc for Dowex HCR S/S were calculated.

1. Introduction

The release of large quantities of heavy metals into the natural environment has resulted in a number of environmental problems. Toxic metals can be distinguished from other pollutants, since they are not biodegradable and can be accumulated in nature. They also cause various diseases and disorders when exceed specific limits [1,2]. Zinc is one of the most important pollutants for surface and ground water. Because of its acute toxicity and non-biodegradability, zinc-containing liquid and solid wastes are considered as hazardous wastes [3,4]. The nickel ion, compared with other heavy metals, is a more recalcitrant pollutant [5]. As it is widely used in many industrial processes, removal of nickel from wastewaters gains importance. Metal treatment industries containing nickel in discharged waters, frequently use nickel in its sulfate form [6]. This affects the decision of treatment method used for removal of nickel from wastewaters.

Classical techniques of heavy metal removal from solutions include the following processes: precipitation, electrolytic methods, ion exchange, evaporation and adsorption [7]. Among these methods ion exchange receives considerable interest with high efficiency and low operational costs. The main advantages of ion exchange over chemical precipitation are recovery of metal value, selectivity, less sludge volume produced and the meeting of strict discharge specifications [8].

Among the materials used in ion exchange processes, synthetic resins are commonly preferred as they are effective and inexpensive [9]. Cation exchange resins generally contain sulfonic acid groups. These groups can also be carboxylic, phosphonic or phosphinic. Certain general rules for cation exchange are: (i) the exchanger prefers ions of high charge, (ii) ions of small hydrated volume are preferred and (iii) ions, which interacts strongly with the functional groups of the exchangers are preferred [10,11].

In literature, there have been various investigations about removal of heavy metals by ion exchange resins. Halle et al. observed that macroporous carboxylic cation exchanger Wofatit CA-20 in the sodium form exhibites high removal efficieny for treatment of Ni(II) ions from washings formed during the nickel plating [12]. Cu(II) ions are effectively removed from sea and river water by Amberlyst A-27 and Diaion PA-318, strongly basic anion exchangers and batocuproinodisulphonate as a chelating agent [13]. Also, Dowex HCR S/S and Dowex Marathon C resins provided adsorption capacities of 26.27 mg/g and 46.55 mg/g for copper removal [14]. Macroporous strongly basic anion exchanger-Lewatit MP-500A is characterized by high selectivity for Cr(VI) ions [15].

Dowex HCR S/S type resins are in sodium form and due to their high cation exchange capacities they reduce the residual concentration of heavy metals below the discharge limits. They are also widely available as they are commercially produced. Furthermore their regeneration properties supply economical benefits. Due to

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Nomenclature

A	Temkin isotherm constant
B	constant related with adsorption heat
C	total ion concentration in solution
C_e	equilibrium concentration of solution
C_o	initial heavy metal concentration
C_t	metal concentration at time t
$C_{M^{2+}}$	concentration of metal ions in solution
C_{Na^+}	concentration Na^+ ions in solution
D	distribution coefficient
m	amount of the resin
M	Ni^{2+} or Zn^{2+} ions exchanging with Na^+ ions in the solution phase
k	equilibrium constant of Langmuir isotherm
k_1	rate constant of pseudo-first-order adsorption kinetic
k_2	rate constant of pseudo-second-order adsorption kinetic
K_f	Freundlich isotherm constant
K_{M^{2+}/Na^+}	preference factor of metal ions for ion exchange process
n	adsorption intensity
R^2	correlation coefficients
t	time
x_{Na^+}	equivalence ratio of Na^+ ions in solution
V	solution volume
V_m	monolayer capacity for Langmuir isotherm
y_{Na^+}	equivalence ratio of Na^+ ions in resin
q_e	amount of adsorbed heavy metal per unit resin mass
$q_{M^{2+}}$	concentration of metal ions in resin
q_{Na^+}	concentration of Na^+ ions in resin
q	total ion exchange capacity
$q_{e,calculated}$	calculated value for amount of adsorbed heavy metal per unit resin mass
$q_{e,experimental}$	experimental value for amount of adsorbed heavy metal per unit resin mass
q_t	amount of heavy metal adsorbed at time t
α	separation factor for nickel and zinc removal

mentioned properties, in this study Dowex HCR S/S resin has been preferred.

Batch technique was used in order to determine the equilibrium data. After defining optimum reaction conditions (pH, resin dosage, contact time), experimental results were applied to Langmuir, Freundlich and Temkin isotherms. First- and second-order reaction kinetics were calculated for determination of adsorption mechanisms. Distrubution coefficients and separation factors of nickel and zinc were also found for Dowex HCR S/S. It is thought that results of this study can be useful for treatment processes of sectors containing heavy metal in their wastewaters.

2. Experimental

2.1. Materials

Analytical grade reagents were used in experimental studies. Nitrate salts of test metals ($Zn(NO_3)_2{\cdot}6H_2O$ and $Ni(NO_3)_2{\cdot}6H_2O$ from Merck) were used for preparing certain concentrations of synthetic solutions. pH adjustments were carried out by using 0.1N HCl and 0.1N NaOH.

Dowex HCR S/S cation exchange resin was preferred as dowex-type ion exchangers are durable, insoluble and compatible. The structural polymeric backbone of the resin is styrene cross-linked with divinyl benzene functionalized with a sulfonic acid functional group as the ion exchange site [16].

Table 1
Characteristics of tested Dowex HCR S/S.

Type	Strong acid cation
Matrix	Styrene-DVB, gel
Functional group	Sulfonic acid
Physical form	Uniform particle size spherical beads
Shipping weight	800 g/L
Total exchange capacity	Minimum 1.9 eq/L
Particle size	0.3–1.2 mm: 90% minimum, <0.3 mm: 1% maximum
Particle density	1.30 g/mL
Whole beads	90% minimum
Ionic form as shipped	Na^+

Pysical and chemical properties of Dowex HCR S/S are given in Table 1.

2.2. Apparatus

HACH DR 2000 spectrophotometer was used for the determination of remaining metal concentrations in solutions. Used methods were 1-(2 Pyridylazo)-2-Naphthol (PAN) Method (Method no: 8150) and Zincon Method (Method no: 8009) for nickel and zinc analyses, respectively. Batch experiments were carried out in *NUVE* shaker. *Testo* pH-meter was used for pH measurements.

2.3. Equilibrium studies

The batch ion exchange experiments were performed in a wide variety of conditions including different pH, various resin dosages and agitation periods. Effects of each factor were determined keeping other variables constant. In the experiments 100 ml of synthetic solutions containing 100 mg/L of Ni(II) and Zn(II) were added into flasks with different amounts of resin varying between 0.05 and 0.7 g. pH adjustments were made by using 0.1N sodium hydroxide and 0.1N hydrochloric acid. Solutions were shaked at 200 rpm for a predetermined period. Temparature was kept constant at 23 °C during batch tests. At the end of agitation time resins were filtered and metal contents of solutions were analyzed by spectrophotometer.

2.4. Isotherm studies

The adsorption capacity was calculated using following formula:

$$q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

where q_e (mg/g) is the equilibrium adsorption capacity, C_o and C_e (mg/L) are the initial and equilibrium concentration of metal ions in solution, V (L) is the volume, and m (g) is the amount of the resin.

By using this formula q_e values for different metal concentrations were calculated. Relationship of q_e versus C_e is shown in Fig. 1.

Adsorption isotherm studies were carried out in a series of 250 mL reaction bottles. 100 mL of metal solutions were adjusted to 100 mg/L concentration. Resin amounts were kept constant at 0.2 and 0.3 g for nickel and zinc solutions. After reaching equilibrium, solutions were separated and analyzed.

2.5. Kinetic studies

Kinetic experiments were made by using 100 mL of nickel and zinc solutions of various concentrations (50, 100, 150 mg/L). Samples were taken at different time intervals (0–300 min) and remaining metal concentrations were analyzed. The rate constants were calculated using conventional rate expressions. Following for-

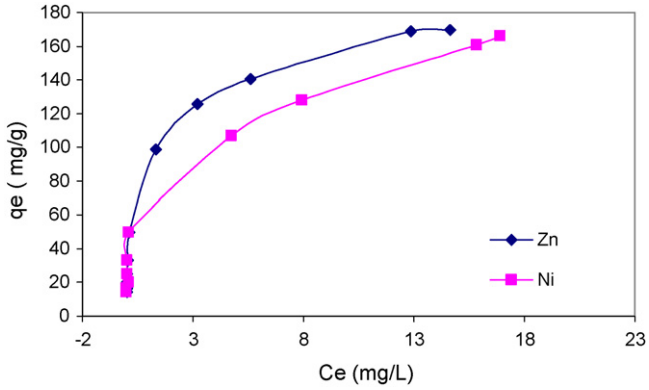

Fig. 1. Relationship between equilibrium concentration and adsorption capacity.

mula was used to determine adsorbed metal concentration q_t:

$$q_t = \frac{(C_o - C_t)V}{m} \quad (2)$$

where q_t (mg/g) is the adsorption capacity at time t, C_o (mg/L) is the initial metal concentration, C_t (mg/L) is the concentration of metal ions in solution at time t, V (L) is the volume, and m (g) is the amount of the resin.

3. Results and discussion

3.1. Effect of pH

Hydronium ion concentration is an important parameter affecting the ion-exchange process. This is partly because hydrogen ions themselves are strongly competing adsorbate and the solution pH influences the ionization of surface functional groups.

In order to investigate the effect of pH on removal of nickel and zinc by Dowex HCR S/S 100 ml of 100 mg/L metal solutions were used. Experiments were performed in the pH range 2–9. Constant resin amount (0.2 g) was added to all reaction bottles and solutions were agitated for 2 h at 200 rpm speed.

Effect of pH on removal efficiency is shown in Fig. 2.

As seen from Fig. 2. optimal uptake of Ni^{2+} and Zn^{2+} occurred at pH 4 and 6, respectively. At high pH values, decrease in removal efficiency achieved by resins can be described with formation of $Ni(OH)_2$ and $Zn(OH)_2$ during reaction of Ni^{2+} and Zn^{2+} ions with OH^-. In this state, hydrolysis accompanied by precipitation of metal hydroxides may occur [14].

In order to examine the effects of pH on precipitation, experiments without resin dosage were carried out. As seen from Fig. 3,

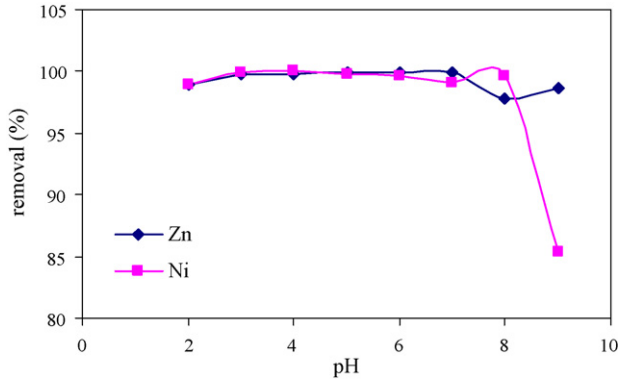

Fig. 2. Effect of pH on removal of nickel and zinc by Dowex HCR S/S cation exchange resin. (Initial metal concentration 100 mg/L, resin dosage 0.2 g/100 mL, agitation period 2 h).

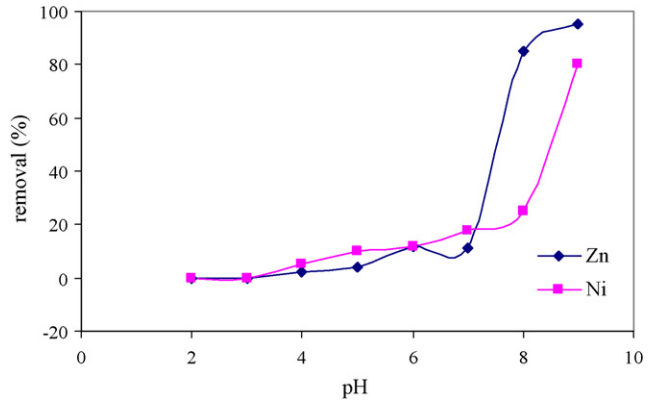

Fig. 3. Effect of pH on precipitation of metal hydroxides (Initial metal concentration 100 mg/L, without resin dosage, agitation period 2 h).

at high pH values metal ions precipitate due to formation of metal hydroxides.

3.2. Effect of resin dosage

The resin amount is also one of the important parameters to obtain the quantitative uptake of metal ion. The dependence of metal sorption on resin input amount was studied by varying the amount of Dowex HCR S/S (0.05–0.7 g), while the other parameters such as pH (pH 6 and 4 for nickel and zinc, respectively), initial metal concentration (100 mg/L) and stirring speed (200 rpm) remained constant.

It was apparent that the adsorption percentage of metal ions increased with higher resin dosages and the removal efficiency of 99% was achieved by using 0.2–0.3 g/100 mL resin dosage for nickel and zinc (Fig. 4). This result proved that increasing the amount of adsorbent provides higher removal due to formation of greater adsorption sites.

3.3. Effect of agitation time

Predetermined optimal values of pH and resin dosage were used for analyzing effects of time on removal process. Fig. 5 shows the dependence of removal efficiency with agitation time. The removal increases with time and attains equilibrium in 90 min for nickel and in 120 min for zinc with initial concentrations of 100 mg/L. It is clear that complete removal of nickel ions requires less residence time compared to zinc.

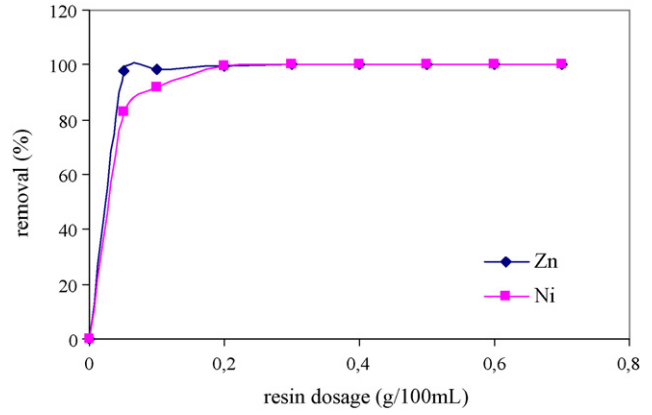

Fig. 4. Effect of resin dosage on removal of nickel and zinc by Dowex HCR S/S cation exchange resin. (Initial metal concentration 100 mg/L, pH 4 and 6, agitation period 2 h).

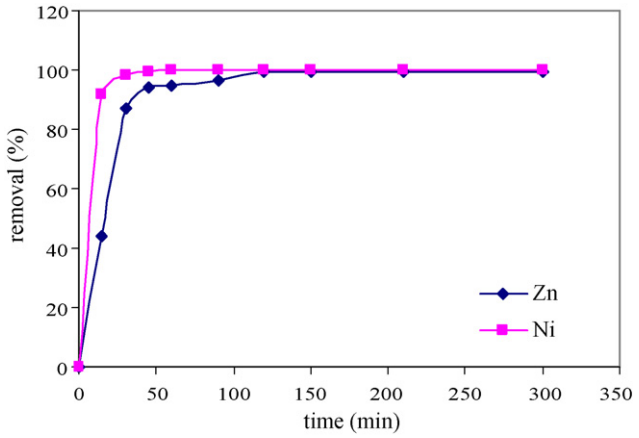

Fig. 5. Effect of contact time on removal of nickel and zinc by Dowex HCR S/S cation exchange resin. (Initial metal concentration 100 mg/L, pH 4 and 6, resin dosage 0.2 and 0.3 g).

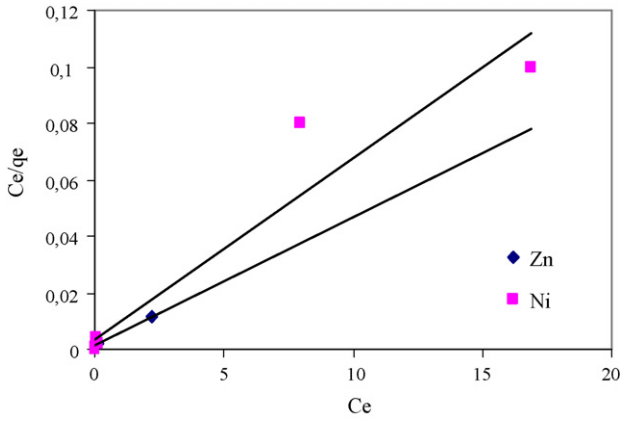

Fig. 6. Langmuir adsorption isotherm for removal of nickel and zinc on Dowex HCR S/S.

3.4. Distribution coefficients and separation factors

In order to calculate distribution coefficients and separation factors, batch experiments were carried out at optimal conditions (pH 4 and 6; resin dosage 0.2 and 0.3 g, respectively for nickel and zinc) by using 100 mL of 150 mg/L metal solutions.

Distribution coefficients were determined by the formula given below [17]:

$$D = \frac{\text{amount on resin}}{\text{amount in solution}} \times \frac{\text{mL of solution}}{\text{g of dry resin}} \quad (3)$$

Calculated distribution coefficients were quite high for both nickel (5.80×10^4) and zinc (2.25×10^4) ions.

Exchanging ions of unequal charge as in the case with the exchange of Na^+ with the solution phase Ni^{2+} or Zn^{2+} (represented with M^{2+}) can be expressed as:

$$M_s^{2+} + 2Na_r^+ \rightarrow M_r^{2+} + 2Na_s^+ \quad (4)$$

where subscripts s and r refer to "solution" and "resin" phases, respectively. In ion exchange processes, selectivity can be quantified in terms of the separation factor (α) [18]:

$$\alpha_{M^{2+}/Na^+} = K_{M^{2+}/Na^+} \frac{(q/c)}{y_{Na^+}/x_{Na^+}} \quad (5)$$

Here, K_{M^{2+}/Na^+} is the preference factor and is given by the formula

$$K_{M^{2+}/Na^+} = \frac{q_{M^{2+}}}{C_{M^{2+}}} \left(\frac{C_{Na^+}}{q_{Na^+}} \right)^2 \quad (6)$$

where, q total ion exchange capacity (eq/L); C total ion concentration in solution (eq/L); y_{Na^+} equivalence ratio of Na^+ ions in resin x_{Na^+} equivalence ratio of Na^+ ions in solution; $q_{M^{2+}}$ concentration of metal ions in resin (eq/L); $C_{M^{2+}}$ concentration of metal ions in solution (eq/L); C_{Na^+} concentration Na^+ ions in solution (eq/L); q_{Na^+} concentration of Na^+ ions in resin (eq/L)

In this study separation factors (α) were calculated as 0.577 and 0.1029 for nickel and zinc removal. According to these values, it was concluded that in removal processes using HCR S/S resins, adsorption tendencies of both ions are satisfying.

3.5. Adsorption isotherms

Results obtained for the adsorption of Ni^{2+} and Zn^{2+} ions were analyzed with well-known adsorption models such as Langmuir, Freundlich and Temkin.

3.5.1. Langmuir model

The Langmuir isotherm is a commonly applied model for adsorption on a completely homogenous surface with negligible interaction between adsorbed molecules [19]. The model assumes uniform adsorption energies onto the surface and maximum adsorption depends on saturation level of monolayer.

Langmuir model can be represented with the following linear equation:

$$\frac{C_e}{q_e} = \frac{1}{kV_m} + \frac{C_e}{V_m} \quad (7)$$

where q_e represents the mass of adsorbed heavy metal per unit resin (mg/g), V_m is the monolayer capacity, k is the equilibrium constant and C_e is the equilibrium concentration of the solution (mg/L). k and V_m were determined from the slope, intercept of the Langmuir plot (Fig. 6).

3.5.2. Freundlich model

The Freundlich model is known as earliest empirical equation and is shown to be consistent with exponential distribution of active centers, characteristic of heterogeneous surfaces [20,21].

Freundlich equation is:

$$\log\ q_e = \log K_f + \frac{1}{n} \log C_e \quad (8)$$

where K_f and n represent adsorption capacity and intensity, respectively. K_f is an important constant used as relative measure for adsorption efficiency. The magnitude of the n shows an indication of the favorability of adsorption. Values of n larger than 1 show the favorable nature of adsorption [22].

The plot of log q_e against log C_e, shows data for adsorption of Ni^{2+} and Zn^{2+}onto HCR S/S cation exchange resin is fitting well to the Freundlich isotherm (Fig. 7).

3.5.3. Temkin model

Temkin adsorption isotherm is expressed as:

$$q_e = B \ln\ A + B \ln\ C_e \quad (9)$$

where A is Temkin constant representing adsorbat–adsorbat interactions and B is another constant related with adsorption heat [23].

Temkin isotherm takes into account the adsorbing species–adsorbent interactions. Isotherm constants A and B can be determined from plot of qe versus ln C_e (Fig. 8).

From Table 2 it is seen that value of A is larger for Ni^{2+} than Zn^{2+}. This means in cation exchange processes by using HCR S/S, adsorbate/adsorbate interactions are more effective for nickel comparing with zinc.

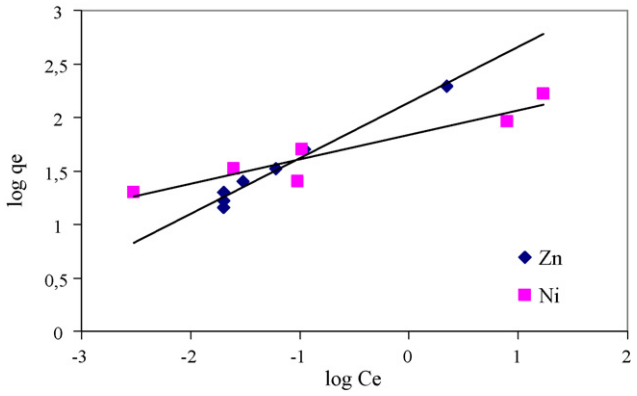

Fig. 7. Freundlich adsorption isotherm for removal of nickel and zinc on Dowex HCR S/S.

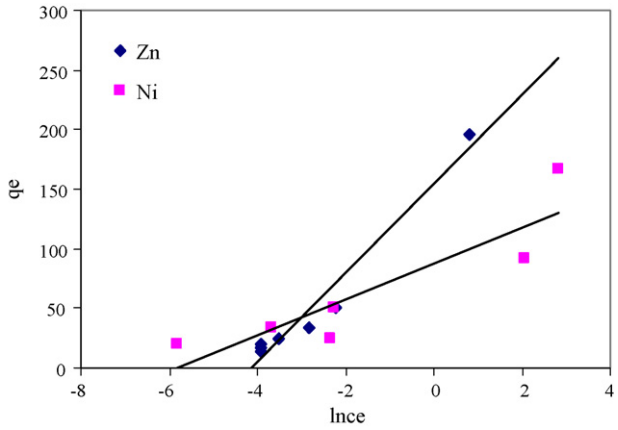

Fig. 8. Temkin adsorption isotherm for removal of nickel and zinc on Dowex HCR S/S.

All constants determined from Langmuir, Freundlich and Temkin isotherms are given in Table 2.

3.6. Kinetics of adsorpiton

Adsorption kinetics provide valuable information about the mechanism of adsorption [24]. Rate of adsorbate uptake, which is required for selecting optimum operating conditions for the full-scale batch process, can be described with adsorption kinetics [25].

Kinetic studies for nickel and zinc were performed by using different concentrations (50,100,150 mg/L). Optimum conditions were used during these experiments. pH was adjusted to 4 and 6 and resin mass was 0.2 and 0.3 g for nickel and zinc. Samples were taken with different time intervals ranging between 5 and 300 min. Plots of heavy metal concentration against time are in Fig. 9(a) and (b).

As seen from Fig. 9(a and b), maximum amount of nickel and zinc ions were adsorbed within the first 90 and 120 min, respectively. After these periods adsorption processes exhibit slower rate and reach equilibrium.

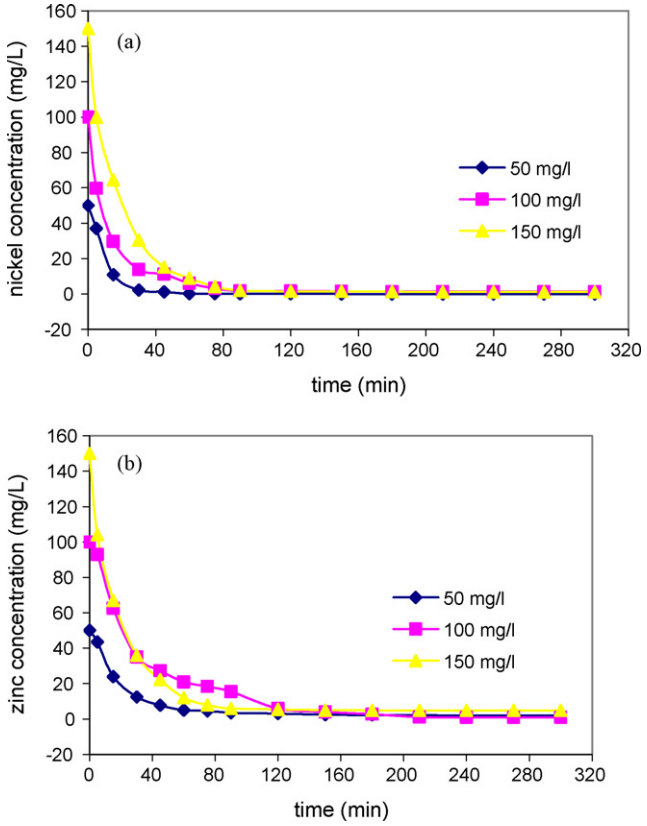

Fig. 9. Kinetics of adsorption of zinc (a) and nickel (b) onto Dowex HCR S/S cation exchange resin.

Chemical sorption mechanism for nickel and zinc can be expressed with the following reactions:

$$Ni^{2+} + 2RNa \rightarrow R_2Ni + 2Na^+ \quad (10)$$

$$Zn^{2+} + 2RNa \rightarrow R_2Zn + 2Na^+ \quad (11)$$

Rate constants (k_1 and k_2) of pseudo-first- and -second-order kinetics were calculated from experimental data obtained from related reactions.

3.6.1. Pseudo-first-order reaction kinetic

Simple linear equation for pseudo-first-order reaction kinetic is given below [26]:

$$\ln(q_e - q_t) = \ln\ q_e - k_1 t \quad (12)$$

where k_1 is the rate constant of the first-order adsorption, q_t is the amount of heavy metal adsorbed at time 't' (mg/g) and q_e is the amount of heavy metal adsorbed at saturation (mg/g). Plot of $\ln(q_e - q_t)$ versus t allows calculation of the rate constant k_1 and q_e for nickel and zinc removal (Fig. 10(a) and (b)).

Table 2
Isotherm parameters calculated for nickel and zinc removal on Dowex HCR S/S.

Metals	Langmuir isotherm constants			Feundlich isotherm constants			Temkin isotherm constants		
	V_m	k	R^2	K_f	n	R^2	A	B	R^2
Ni^{2+}	156.25	2	0.93	68.51	4.38	0.89	337.58	15.02	0.80
Zn^{2+}	222.22	4.5	0.99	138.48	1.92	0.98	62.82	37.30	0.95

Table 3
Comparison of adsorption rate constants, experimental and calculated q_e values for the pseudo-first- and -second-order reaction kinetics of removal of nickel and zinc by Dowex HCR S/S.

Metals	Initial metal concentration (mg/L)	$q_{e,experimental}$ (mg/g)	Pseudo-first-order			Pseudo-second-order		
			k_1 (1/min)	$q_{e,calculated}$ (mg/g)	R^2	k_2 (g/mg min)	$q_{e,calculated}$ (mg/g)	R^2
Ni^{2+}	50	16.66	4.99×10^{-2}	8.15	0.8843	3.29×10^{-2}	16.80	0.9978
	100	32.88	3.90×10^{-2}	17.63	0.9624	7.3×10^{-3}	33.44	0.9996
	150	49.56	4.80×10^{-2}	38.83	0.9797	3.46×10^{-2}	50.76	0.9991
Zn^{2+}	50	24.00	2.59×10^{-2}	13.00	0.9458	3.56×10^{-2}	25.18	0.9949
	100	49.56	2.51×10^{-2}	49.21	0.9596	6.6×10^{-3}	55.24	0.9783
	150	72.55	4.79×10^{-2}	64.16	0.9919	2.0×10^{-4}	74.62	0.999

3.6.2. *Pseudo-second-order reaction kinetic*

Pseudo-second-order reaction kinetic can be expressed as [27]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (13)$$

where k_2 (g/mg h) is the pseudo-second-order rate constant, q_e the amount adsorbed at equilibrium and q_t is the amount of metal adsorbed at time 't'.

Similar to the pseudo-first-order reaction kinetic, q_e and k_2 can be determined from the slope and intercepts of plot t/q_t versus t (Fig. 11(a) and (b)).

Calculated rate constants (k_1 and k_2), adsorbed amounts of heavy metals per unit resin mass (q_e) and linear regression correlation coefficients (R^2) for pseudo-first- and -second-order reaction kinetics are summarized in Table 3. In pseudo-second-order reaction kinetic, calculated values of q_e are closer to experimental values for both nickel and zinc. Furthermore as seen from Table 3, correlation coefficients are higher for second order kinetic studies.

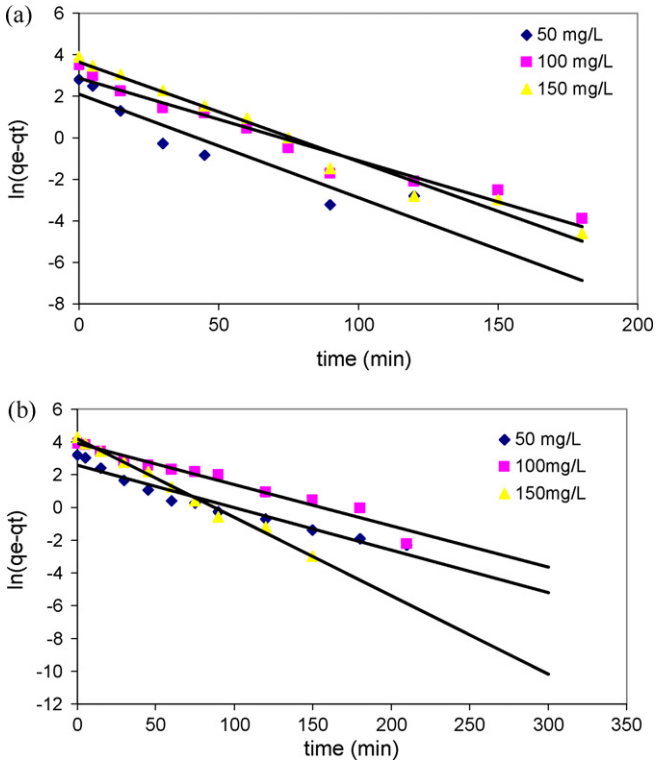

Fig. 10. Pseudo-first-order reaction kinetics for the adsorption of nickel (a) and zinc (b) onto Dowex HCR S/S cation exchange resin.

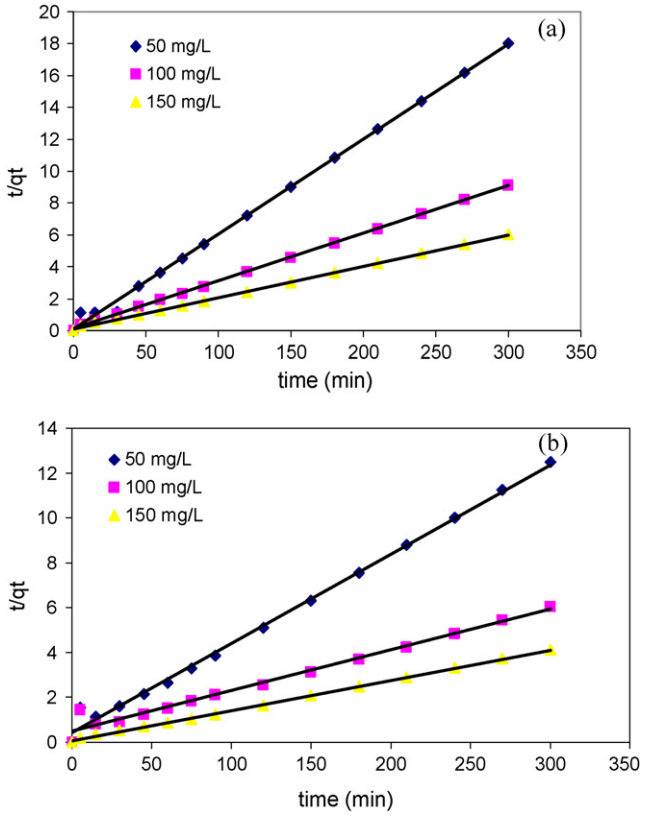

Fig. 11. Pseudo-second order reaction kinetics for the adsorption of nickel (a) and zinc (b) onto Dowex HCR S/S cation exchange resin.

4. Conclusions

The aim of this work was to investigate removal of nickel and zinc from aqueous solutions by using Dowex HCR S/S cation exchange resin. Optimal removal conditions for both metals were determined with batch experiments. Ion exchange process was pH-dependent and optimal removal efficiencies for nickel and zinc were obtained at pH 4 and 6, respectively. Adsorption of nickel ions reached equilibrium faster (within 90 min) comparing with zinc ions (within 120 min). Equilibrium distribution coefficients (D) were calculated as 5.80×10^4 and 2.25×10^4 whereas separation factors α were 0.577 and 0.1029 for nickel and zinc removal.

Experimental results were evaluated with Langmuir, Freundich and Temkin isotherms. In addition to higher values of correlation coefficients, monolayer capacities (V_m) determined from Langmuir isotherm and adsorption intensities (n) determined from Freundlich isotherm indicate appropriateness of Langmuir and Freundlich isotherms for both metals. In Temkin isotherm, it was stated

that adsorbate/adsorbate interactions are weaker for zinc removal due to smaller values of Temkin constant (A).

Pseudo-second-order reaction kinetic has provided a realistic description for removal of Ni^{2+} and Zn^{2+} with closer experimental and calculated values of q_e. Also correlation coefficients are higher in pseudo-second-order kinetics.

Experimental and theoretical results of this study demonstrate that Dowex HCR S/S cation exchange resin is suitable for adsorption of nickel and zinc from aqueous solutions.

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