Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2016.1150891

57 (2016) 25718–25728
November

Taylor & Francis
Taylor & Francis Group

Heavy metals removal using iminodiacetate chelating resin by batch and column techniques

D.A. Fadel[a,*], S.M. El-Bahy[b], Y.A. Abdelaziz[a]

[a]*Nuclear Research Center, Atomic Energy Authority, P.O. 13759 Inshas, Cairo, Egypt, Tel. +20 1066211706; email: Dalia_f_shaaban@yahoo.com (D.A. Fadel), Tel. +20 1065753428; email: yasser.abdelaziz27@yahoo.com (Y.A. Abdelaziz)*
[b]*Faculty of Medical and Applied Science, Chemistry Department, Taif University, Taif, Saudi Arabia, Tel. +966 531559921, +20 1005031728; email: Salah_bahy@yahoo.com*

Received 24 October 2015; Accepted 1 February 2016

ABSTRACT

Iminodiacetate chelating resin (IDAR) was prepared for removal of heavy metal ions from aqueous media. The prepared resin showed a powerful uptake behavior toward Cu(II), Ni(II), Hg(II), and Co(II). Different experimental parameters such as solution pH, metal ions concentration, contact time, and adsorption temperature were studied in batch method. The maximum adsorption capacity was found to be 1.79, 1.72, 0.96, and 1.26 mmol/g resin for Cu(II), Ni(II), Hg(II), and Co(II), respectively. The experimental data were analyzed by Langmuir, Freundlich, and Temkin isotherm models. Equilibrium studies showed that the data of metal ions adsorption followed the Langmuir model. Also, the kinetic and thermodynamic parameters of the adsorption process were estimated. These parameters showed that the adsorption process is spontaneous and followed the pseudo-second-order kinetics. Additionally, the removal of metal ions using (IDAR) chelating resin has been studied using column technique as well. Elution of chelating resin loaded with Cu(II), Ni(II), and Hg(II) was successfully performed with 0.2 M HNO_3 solutions and the resin could be reused for five sorption–desorption cycles with small loss of adsorption capacity. Co(II) was partially eluted under these conditions and penetrated throughout the length of the column.

Keywords: Chelating resin; Iminodiacetate; Kinetic models; Batch method; Column method; Heavy metal ions

1. Introduction

Environmental contamination with metal ions gained recently more concern because of their high persistence, and the nervous system damage, and even cancer, caused by their accumulation at certain levels. The most frequent metal ions found in industrial wastewater are copper, cadmium, nickel, mercury, and cobalt, which are toxic at high concentrations [1,2]. A difficult problem encountered in the removal of the heavy metals is that the target species are usually in low concentration and in complex mixtures. Various separation methods such as precipitation, chemical reduction, ion exchange, membrane separation, adsorption, and biological treatment have been used to remove metal ions from Industrial wastewater [3,4]. Among these methods, numerous researches concentrated on metal ion recovery using adsorbent, because they are reusable, easy separation, and have

---

*Corresponding author.

higher adsorption capacities and selectivity [5–12]. In our previous articles, chelating resins containing different chelating groups were synthesized for removal of metal ions from aqueous solution with high performance [13–15]. Chelating resins with iminodiacetic acid groups are commercially available and widely used. For example, the resins Chelex 100, Purolite S930, and Amberlite IRC-718 have been used to remove metal ions from wastewater discharged from printed circuit board manufacturing, which contains copper, nickel, mercury, and cobalt [16–24].

In the present work, iminodiacetate chelating resin was prepared and used to remove Cu(II), Ni(II), Hg (II), and Co(II) metal ions from aqueous medium using batch and fixed bed column methods. The effects of different controlling parameters like pH, metal ions concentration, equilibration time, and temperature on the adsorption capacity of the chelating resin for Cu(II), Ni(II), Hg(II), and Co(II) were examined by batch method. The experimental data were fitted to Langmuir, Freundlich, and Temkin isotherm models. Thermodynamic as well as kinetic properties of the removal process were also clarified. Breakthrough curves for the recovery of Cu(II), Ni(II), Hg(II), and Co(II) were also investigated by column method.

2. Materials and methods

2.1. Materials

Acrylamide (AM) and N,N-methylenebisacrylamide (MBA) were pure grade products of Merck Co., Germany. Ammonium persulfate (APS), sodium hydroxide, sodium carbonate, chloroacetic acid, ethylenediamine, and nitric acid purchased from Sigma-Aldrich. Metal salts $Cu(CH_3COO)_2 \cdot H_2O$, $Ni(CH_3COO)_2 \cdot 4H_2O$, $HgCl_2$, and $CoSO_4 \cdot H_2O$ were used as sources for Cu(II), Ni(II), Hg(II), and Co(II), respectively. All solvents used were of reagent grade and were purified by distillation before use.

2.2. Synthesis and characterization of iminodiacetate chelating resin (IDAR)

Iminodiacetate chelating resin (IDAR) beads were synthesized according to the method reported in our earlier work [14]. In brief, crosslinked polyacrylamide CPM beads were synthesized by suspension polymerization according to the method of Wang et al. [22]. Transamidation of CPM resin was carried out according to former study [14]. Iminodiacetate chelating resin IDAR beads were synthesized according to the method reported in our earlier work [14].

Fourier transform infrared spectra (FTIR) of the prepared resins were performed as previously shown [14].

Water regain factor, W %, represents the percentage of water absorbed by 1 g of the resin. Water regain was calculated according to the previously published method [25]. One gram of swollen resin is placed in a short column and centrifuged at 3,000 rpm for 5 min to remove excess water and then weighed. The resin was dried at 70–80°C until complete dryness, then the column is weighed again with and without the resin. To calculate water regain, Eq. (1) was used.

$$W\ \% = \frac{(W_w - W_d)}{W_w} \times 100 \tag{1}$$

where W_w and W_d are weights (g) of the swollen resin after centrifugation and dried resin, respectively.

2.3. Adsorption of metal ions

2.3.1. Uptake of metal ions using batch method

The optimum pH for metal ion uptake was determined by batch method. A sample of 100 ml of the single-metal ion solution (5.0 mmol/L) is shaken with 0.1 g of resin for a desired duration. The pH of metal ion solutions was adjusted. The adsorption value was calculated by determining the metal ion concentration before and after treatment. The concentration of the metal ions in the solution was determined using Hitachi atomic absorption Z-6100 polarized Zeeman. Experiments were carried out in triplicate. The quantity of metal ions adsorbed per gram of the resin was calculated using Eq. (2):

$$q = \frac{(C_o - C_e)V}{W} \tag{2}$$

where q is the adsorption capacity (mmol/g). C_o and C_e is the initial and the final concentrations of metal ions (mmol/L), respectively, V is the volume of metal ions solution (L), and W is the weight of dry resin (g).

To determine the optimum concentration of metal ion adsorption, 100 ml of metal ion solution under different concentrations over a range of (1–25 mmol/L) in a glass bottle (250 ml), after adjusting its pH to the optimum adsorption value, the 0.1 g of chelating resin was added to the bottle and shaken for a desired duration. The resin was filtered and the concentration of the residual metal ion in the solution was determined.

To determine the equilibration time for the metal under investigation, the metal ion solution and 0.1 g of resin at optimum adsorption pH and optimum concentration were sampled in glass bottles. The bottles were occasionally shaken and taken from the shaker at suitable time intervals. The time of equilibrium for all the metal ions was estimated in a similar method.

To determine the effect of temperature on metal ion adsorption, 0.1 g of dry resin in a series of glass bottles containing 100 ml of the metal ion solution (1 mmol/L) at optimum adsorption pH. The mixture was shaken under optimum shaking time while keeping the temperature at 25, 35, and 45˚C. After adsorption, solution was filtered and the remaining concentration of the metal ions was estimated.

2.3.2. Uptake of metal ions using column method

Chelating resin (1.0 g) was packed in glass column (1.0 cm diameter, 10 cm height). Single-metal ion solution (5–7.2 mmol/L) at optimum pH was passed through the resin at the flow rate 1.0 ml/min until the metal ions completely leaked through the column into the effluent. The remaining concentration of metal ions in the effluent was analyzed by Hitachi atomic absorption Z-6100 polarized Zeeman. Metal ions were removed from resin with 0.2 M HNO_3. After elution, the resin was carefully washed with water, 0.2 M NaOH solution, and finally with distilled water to make it ready for reuse. The sorption desorption cycle of metal ions was repeated five times.

The total metal ions adsorbed (m_{ads}, mmol) was equal to the area under the plot of the adsorbed ions concentration (C_{ads}) (mmol/L) vs. t (min) and can be calculated as the following [26,27]:

$$m_{\text{ads}} = \frac{Q}{1000} \int_{t=0}^{t=t_{\text{total}}} (C_{\text{ads}})\, dt \tag{3}$$

where Q is the flow rate (ml/min).

The value of q_e (mmol/g) is calculated as the follows:

$$q_e = \frac{m_{\text{ads}}}{M} \tag{4}$$

where M is the dose of adsorbent (g). The metal removal percentage can be calculated from the ratio of the amount of the metal adsorbed (m_{ads}, mmol) to the total amount of metal ions sent to the column (m_{total}, mmol) which can be calculated as follows:

$$R\,\% = \frac{m_{\text{ads}}}{m_{\text{total}}} \times 100 \tag{5}$$

$$m_{\text{total}} = \frac{C_o Q t_{\text{total}}}{1000} \tag{6}$$

The mass transfer zone Δt [28] is given by Eq. (7):

$$\Delta t = t_e - t_b \tag{7}$$

where t_b is the breakthrough time (time at which the concentration of metal ion in the effluent raised suddenly to an appreciable value) and t_e is the bed exhaustion time (time at which the concentration of metal ion in the effluent exceeded 99% of the influent concentration).

The length of mass transfer zone Z_m [29] is obtained from the breakthrough curve and is calculated from Eq. (8):

$$Z_m = Z\left(1 - \frac{t_b}{t_e}\right) \tag{8}$$

where Z is the bed height in cm.

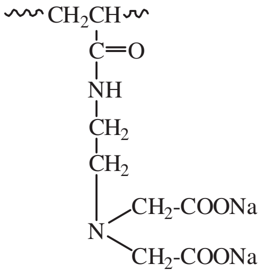
3. Results and discussion

3.1. Synthesis and characteristics of chelating resin containing iminodiacetate groups (IDAR)

The chelating resin (IDAR) with iminodiacetate groups employed in this work was synthesized according to the procedure previously presented [14]. In brief, chelating resin bearing iminodiacetate groups, derived from acrylamide—N,N-methylenebisacrylamide (CPM) copolymers, were prepared in two steps: first, anion exchangers with primary amine groups were obtained by the transamidation reaction of CPM resin with ethylenediamine, and second, the chelating resin (IDAR) was prepared by the reaction of the primary amine groups with sodium monochloroacetate. The structure of the chelating resin is presented in Fig. 1.

FTIR of the synthesized resins were performed as formerly shown [14].

The water regain for chelating resin was determined to be 31.6 mmol/g (W % = 57). This high value indicates the hydrophilic character of the resin which increases the uptake of metal ions.



IDAR

Fig. 1. Iminodiacetate chelating resin (IDAR).

3.2. Uptake of metal ions by batch technique

3.2.1. Optimum pH of metal ions uptake

The adsorption behavior of some metal ions on chelating resin containing iminodiacetate moieties at different pH values were examined by the batch technique and the results are shown in Fig. 2. At low pH value, high concentration of H^+ can react with carboxylate ions (COO–) and amine groups. That is, H^+ can compete with metal ions for adsorption sites and decrease the adsorption capacity. This article repeated the adsorption studies in the range of pH 1.0–6.6 because these metal ions could be precipitated by OH^- to form metal(II) hydroxide above natural pH. Additionally, no adsorption was observed at pH 1 because the concentration of H^+ was much greater than that of the metal ions, the adsorption capacities of metal ions being zero should be reasonable. As shown in Fig. 2, the sorption capacity increases with increasing the pH of the solution from pH 1 to 6.6. The optimum adsorption pH value (natural pH) at which the maximum adsorption capacity for metal being found at 5.5, 6.6, 5.0, and 6.0 for Cu(II), Ni(II), Hg(II), and Co(II), respectively. Therefore, for this work all the following experiments were performed at these optimum pH values.

3.2.2. Effect of initial concentration and equilibrium isotherm models

Adsorption isotherms are used to describe the relationship between the amount of adsorption and equilibrium concentration of metal ions at constant temperature. Fig. 3 shows the adsorption isotherms of the studied metal ions at optimum pH. Inspection of Fig. 3 reveals that the uptake increases with increasing equilibrium concentration until reaching the saturation value after which, the concentration no longer affects the uptake of the metal ion. The capacity of the resin is an important factor to determine how much resin is required to quantitatively remove a specific metal ion from the solution. The loading capacity was determined at optimum pH and the results expressed in (mmol/g resin) of the resin are presented in Table 1. The optimum concentration of metal ions for Cu(II), Ni(II), Co(II), and Hg(II) are 14, 12, 12, and 14 (mmol/L), respectively. It is observed in Fig. 5 that the maximum level of metal ion sorption was in the order of Cu(II) > Ni(II) > Co(II) > Hg(II). It is shown in Fig. 3 that the maximum uptake of metal ions was in the order of Cu(II) > Ni(II) > Co(II) > Hg(II). This order is maybe related to the difference in ionic radius of these ions. The ionic radius of the metal ions are in the order of Cu(II) (0.70 Å) < Ni(II) (0.72 Å) < Co(II) (0.74 Å) < Hg(II) (0.83 Å) [30,31]. A comparison of the present chelating resin with those of

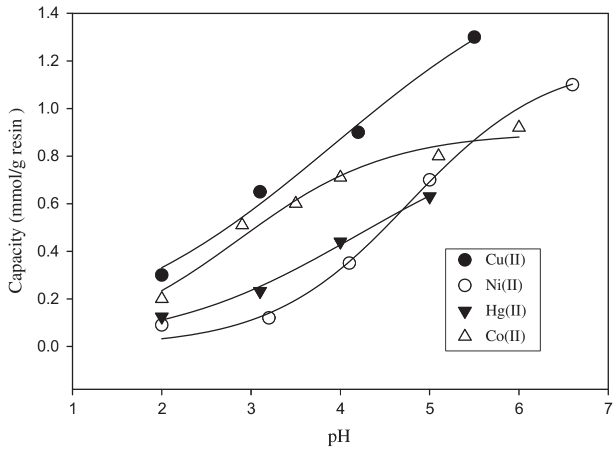


Fig. 2. Effect of pH on the uptake of metal ions; 25˚C, shaking time 4 h, and initial metal ion concentration of 5.0 mmol/L.

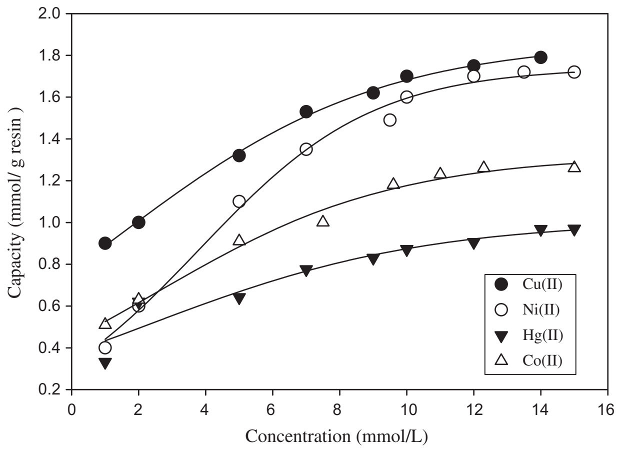


Fig. 3. Effect of initial metal ions concentration on the adsorption capacity of Cu(II), Ni(II), Hg(II), and Co(II); 25˚C, shaking time 4 h, and at optimum pH value.

different types of chelating resins in recent references is shown in Table 1. The data presented in Table 1 reveal that, generally, the prepared chelating resin in this work has a good advantage in metal ion adsorption more than the previously reported resins.

Various isotherm equations like Langmuir, Freundlich, and Temkin were used to describe the equilibrium characteristics of adsorption.

The Langmuir model presupposes that the resin surface has sites of identical energy and each metal ion located at a single site; it predicts the formation of adsorbate monolayer on the adsorption surface. The equation of Langmuir sorption model is formulated as follows [32]:

$$\frac{C_e}{q} = \frac{C_e}{Q_{\max}} + \frac{1}{KQ_{\max}} \tag{9}$$

where C_e is the equilibrium concentration of metal ions in solution (mmol/L), q is the equilibrium adsorption capacity (mmol/g), $Q_{\max}$ (mmol/g) and K (L/mmol) are the maximum adsorption capacity and Langmuir constant, respectively. The values of Langmuir equation parameters are reported in Table 2.

Langmuir isotherm model was expressed in terms of the dimensionless constant separation factor (R_L) [33] which is defined by Eq. (10):

$$R_L = \frac{1}{1 + KC_o} \tag{10}$$

where C_o is the initial concentration (mmol/L). The value of R_L indicates the shape of the isotherm to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) [34,35].

The variation of R_L with concentration of metal ion is shown in Fig. 4. R_L values were found to be between 0 and 1 for all the concentrations of Cu(II), Ni(II), Hg(II), and Co(II) which indicates that the adsorption of Cu(II), Ni(II), Hg(II), and Co(II) is favorable. It is shown that the R_L values decreased by the increasing metal ion concentration which indicates that removal process is more favorable for the higher concentration of metal ion than for the lower ones.

Freundlich isotherm is an equation which based on multilayer sorption (heterogeneous surfaces). The linearized form of Freundlich isotherm model is indicated as [36]:

$$\log q = N \log C_e + \log K_F \tag{11}$$

where q is the equilibrium adsorption capacity (mmol/g), C_e is the equilibrium concentration of metal ion (mmol/L) and K_F is the Freundlich constant (mmol/L); the term N is a measurement of effectiveness of adsorption. Values of K_F and N were calculated from the slopes and intercepts of the straight lines. The values of Freundlich equation parameters are reported in Table 2.

Similar to R_L values of Langmuir isotherm, the values of N parameter in the Freundlich model indicate

Table 1
Comparison of maximum adsorption capacity of the chelating resin with those of some other chelating resins reported in literature for the adsorption of Cu(II), Ni(II), Hg(II), and Co(II)

Chelating resin	Metal ions	Sorption capacity (mmol/g)	Conditions	Refs.
Cross-linked magnetic chitosan-isatin Schiff's base resin (CSIS)	Cu(II), Ni(II), and Co(II)	1.6, 0.68, and 0.9	pH 5.0, 28°C	[5]
Chelating fiber (PET-TSC)	Cu(II), Hg(II), and Co(II)	1.52, 0.59, and 1.32	pH 5.0, 30°C	[6]
Reduced size Dowex-50 (RDS-50)	Cu(II) and Ni(II)	1.31 and 1.21	pH 6.0, 25°C	[7]
Poly (GMA-co-MBA) containing amino group	Cu(II), Hg(II), and Co(II)	1.58, 3.35, and 1.1	pH 7.5, 10.0, 4.0, 25°C	[8]
Melamine–formaldehyde–diethylenetriaminepentaacetic acid (MF–DTPA)	Cu(II) and Co(II)	0.23 and 0.29	pH 6.5, 25°C	[9]
Crosslinked poly(glycidyl methacrylate-glycine) (PGLY)	Cu(II) and Ni(II)	1.22 and 1.07	pH 4, 25°C	[10]
Polydithiocarbamate chelating resin	Cu(II) and Ni(II)	0.55 and 0.63	pH 5, 30°C	[11]
Chitosan-grafted-poly(2-amino-4,5-pentamethylene-thiophene-3-carboxylicacid N-acryloyl-hydrazide)	Cu(II), Ni(II), and Co(II)	2.36, 0.9 and 2.15	pH 6, 30°C	[12]
Iminodiacetate chelating resin (IDAR)	Cu(II), Ni(II), Hg (II), and Co(II)	1.79, 1.72, 0.96, and 1.26	pH 5.5, 6.6, 5.0, 6.0, 25°C	This work

Table 2
Parameters of Langmuir, Freundlich, and Temkin isotherms for ion exchange of metals on the chelating resin

	Langmuir isotherm			Freundlich isotherm			Temkin isotherm		
Metal ion	$Q_{\max}$	K	R^2	N	K_F	R^2	K_T	B	R^2
Cu(II)	1.85	1.311	0.992	0.155	1.16	0.906	468.7	0.197	0.871
Ni(II)	2.18	0.297	0.991	0.496	1.89	0.987	3.19	0.467	0.981
Hg(II)	1.07	0.524	0.984	0.304	2.26	0.901	0.31	0.188	0.931
Co(II)	1.39	0.594	0.986	0.293	1.96	0.985	12.14	0.247	0.959

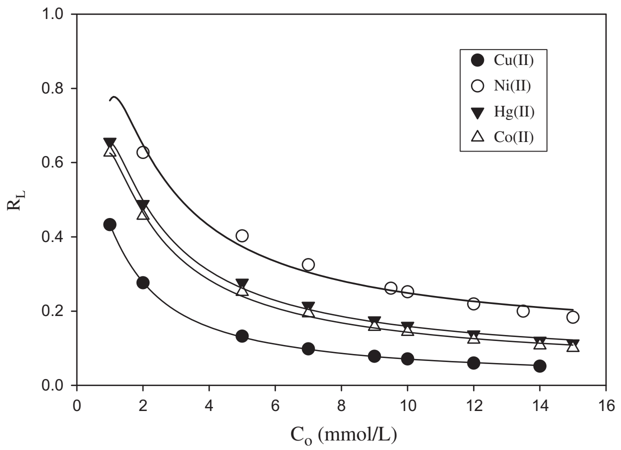


Fig. 4. Variation of adsorption intensity (R_L) with initial metal ion concentration (C_o).

the type of isotherm as follows: irreversible ($N = 0$), favorable ($0 < N < 1$), or unfavorable ($N > 1$). The Freundlich constants (N values) shown in Table 2 were smaller than 1.0 for all the metal ions indicating the facile adsorption process on the employed resin.

The linear form of Temkin isotherm model is indicated by the following equation [37]:

$$q = B \ln K_T + B \ln C_e \tag{12}$$

where B and K_T are Temkin constants which are related to the heat of adsorption and adsorbent/adsorbate interactions, respectively. The values of Temkin equation parameters are reported in Table 2.

The Langmuir, Freundlich, and Temkin sorption constants calculated from isotherms and their correlation coefficients are indicated in Table 3. From the better correlation coefficient, it can be concluded that the Langmuir sorption isotherm is more appropriate to explain the uptake of Cu(II), Ni(II), Hg(II), and Co(II) onto iminodiacetate chelating resin.

3.2.3. The effect of shaking time and sorption dynamics

Kinetic experiments were done at the optimum pH and optimum concentration of metal ions and the data are listed Fig. 5. As indicated in Fig. 5, equilibrium was attained within 35 min for Cu(II), Hg(II), and Co(II) and 25 min for Ni(II). The shaking for 10 min was found to give 58% sorption for Cu(II), 71% for Ni(II), 64% for Hg(II), and 54% for Co(II). This high initial rate indicates that the sorption of metal ions occurs mostly on the surface of the resin.

Three well-known kinetic models were applied to evaluate experimental data. For this purpose, Lagergren's pseudo-first-order kinetic model, pseudo-second-order kinetic model and intraparticle diffusion model were applied.

The linearized form of the first-order rate equation by Lagergren and Svenska [38] is given as:

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_{ads}}{2.303}\right)t \tag{13}$$

where q_e and q_t are the amounts of the metal ions adsorbed (mmol/g) at equilibrium and at time t (min), respectively, and K_{ads} is the sorption rate constant (1/min).

The experimental results were as well applied to the pseudo-second-order kinetic model [39] which is given by the following equation:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \left(\frac{1}{q_e}\right)t \tag{14}$$

where K_2 (1/gmmol min) is the rate constant of pseudo-second-order sorption reaction. The constants related to these plots are given in Table 3. As it can be seen from the results given in Table 3, correlation coefficients are higher compared to the results obtained from the first-order kinetics. So, it is possible to suggest that the sorption of Cu(II), Ni(II), Hg(II), and Co(II) onto chelating resin followed a second-order type reaction kinetics.

Table 3
First-order, second-order, and intraparticle diffusion rate constants

Equations	Parameters	Cu(II)	Ni(II)	Hg(II)	Co(II)
Pseudo-first-order kinetic equation	q (mmol/g)	1.75	3.94	1.24	1.57
	K_{ads} (1/min)	0.087	0.223	0.119	0.092
	R^2	0.991	0.894	0.932	0.891
Pseudo-second-order kinetics	q (mmol/g)	2.20	1.95	1.157	1.65
	K_2 (g/mmol/min)	0.046	0.0146	0.107	0.046
	R^2	0.995	0.991	0.995	0.986
Intraparticle diffusion equation	K_{id} (mmol/g/min$^{1/2}$)	0.219	0.170	0.110	0.174
	R^2	0.928	0.732	0.904	0.939

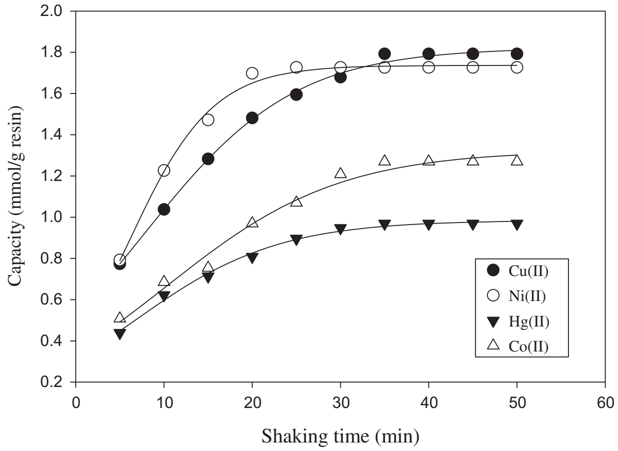


Fig. 5. Effect of shaking time on the adsorption capacity of Cu(II), Ni(II), Hg(II), and Co(II); at optimum pH, optimum concentration and at 25°C.

The intraparticle diffusion model is based on the theory projected by Weber and Morris can be indicated as [40]:

$$q_t = K_{id}\ t^{0.5} \tag{15}$$

where K_{id} is the intraparticle diffusion rate constant (1/mmol g min$^{0.5}$). The constants related to these plots are given in Table 3. According to Eq. (15), if the plot gives a straight line, then the uptake of metal ions is controlled only by the intraparticle diffusion, but if the uptake results give a multilinear plot it indicates that there are two or more stages relating in the uptake process.

As can be seen from Fig. 6, the uptake of metal ions was controlled by three different steps: (1) rapid external surface sorption; (2) gradual sorption where intraparticle diffusion is rate controlled and (3) final equilibrium stage due to the low concentration of metal ions, in addition to the low number of available sorption sites. Based on these data, it could be concluded that the intraparticle diffusion was not the only rate-controlling stage. Therefore, the sorption process may be a complex nature consisting of both surface sorption and intraparticle diffusion. Additionally, all of these propose that the sorption of metal ions on chelating resin could be controlled by external mass transfer followed by intraparticle diffusion.

3.2.4. Adsorption thermodynamics

The thermodynamic parameters for adsorption of metal ions were calculated at three different temperatures (25, 35, and 45°C). Hundred milliliters of metal ion solution with a concentration of (1 mmol/L) was allowed to equilibrate with 0.1 g of resin. The

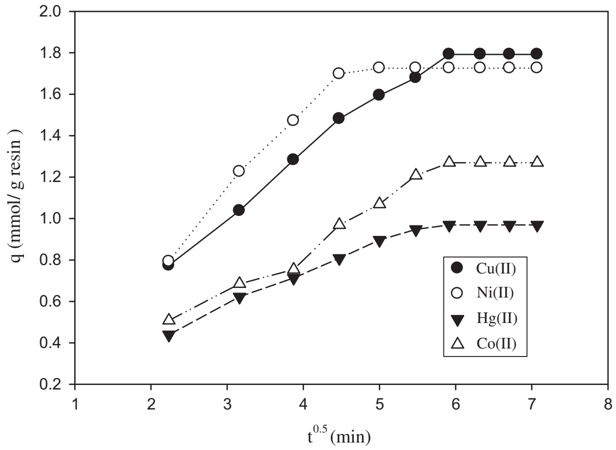


Fig. 6. Plot of Weber–Morris intraparticle diffusion model for the adsorption of metal ions on chelating resin.

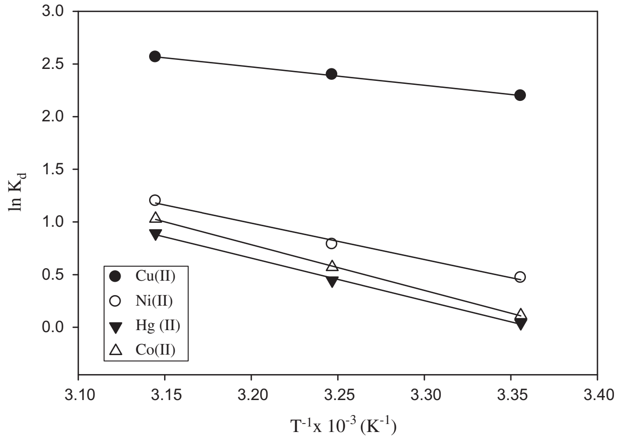


Fig. 7. Plot of $\ln K_d$ as a function of reciprocal of temperature ($1/T$) for the adsorption of metal ions on chelating resin.

distribution coefficient for the adsorption process, K_d, calculated with Eq. (16) [41]:

$$K_d = \frac{C_o - C}{C} \times \frac{V}{W} \tag{16}$$

where C_o and C are the initial and equilibrium concentration of the metal ions in aqueous phase, V is the total volume of the solution taken in liter and W is the weight of the resin used in grams.

To calculate the free energy of the adsorption (ΔG°_{ads}), Eq. (17) was applied:

$$\Delta G^\circ_{ads} = -RT \ln K_d \tag{17}$$

Eq. (18) allows calculating the enthalpy (ΔH°_{ads}) and entropy (ΔS°_{ads}) of the sorption by plotting $\ln K_d$ vs. $1/T$.

$$\ln K_d = \frac{\Delta S^\circ_{ads}}{R} - \frac{\Delta H^\circ_{ads}}{RT} \tag{18}$$

where R (8.314 J/mol K) is the gas constant. The values of the slope and the intercept from Fig. 7 give ΔH°_{ads} and ΔS°_{ads} for the adsorption of Cu(II), Ni(II), Hg (II), and Co(II) ions on the resin. The thermodynamic parameters were listed in Table 4. As shown in Table 4, positive values of ΔH°_{ads} indicates the endothermic natures of metal ions sorption [42,43]. The positive values of ΔS°_{ads} may be related to the increased randomness due to the liberation of water of hydration drying the adsorption of metal ions [42,43]. The negative values of G°_{ads} obtained indicate that the sorption reaction is spontaneous.

3.3. Adsorption of metal ions using column method

The prepared chelating resin (IDAR) was also found successful in removal of metal ions by column method. The breakthrough curves are indicated in Fig. 8. In the column technique, metal ion solutions (5–7.2 mmol/L) at optimum pH were allowed to flow gradually through the column with a flow rate of 1.0 mL/min at 25˚C. The obtained breakthrough curves show that using 1.0 mL/min flow rate of heavy metal ions, the solutions start to breakthrough at 70, 110, 90, and 110 mL of effluent for Cu(II), Ni(II), Hg (II), and Co(II), respectively. Uptake of metal ions were calculated and tabulated in Table 5.

Several models were applied to predict the breakthrough curve and also to calculate the column kinetic constants and the maximum adsorption capacity of a column. These models such as Thomas model that is the most general and widely used one. The data were fitted to the Thomas model [44] using nonlinear regression analysis, Eq. (19):

$$\frac{C_{eff}}{C_o} = \frac{1}{1 + \exp(((K_{Th} q_{Th} M)/Q) - ((K_{Th} C_o V_{eff})/Q))} \tag{19}$$

where C_{eff} is the effluent concentration (mmol/L), C_o the influent concentration (mmol/L), Q the flow rate (ml/min), V_{eff} the effluent volume (ml), M the mass of the adsorbent (g), and t the time (min), while K_{Th} is the Thomas rate constant (ml/mmol min), q_{Th} the maximum metal sorption capacity of the resin (mmol/g). The Thomas rate constant (K_{Th}), maximum metal

Table 4
Thermodynamic parameters for the adsorption of metal ions onto chelating resin

	$-\Delta G^\circ_{ads}$ (kJ/mol)					
Metal ion	298 K	308 K	318 K	ΔH°_{ads} (kJ/mol)	ΔS°_{ads} (J/mol)	R^2
Cu(II)	5.44	6.14	6.78	14.49	66.93	0.998
Ni(II)	1.16	2.01	2.90	24.75	86.96	0.999
Hg(II)	0.097	1.13	2.35	33.56	49.46	0.997
Co(II)	0.028	1.46	2.72	36.08	120.22	0.999

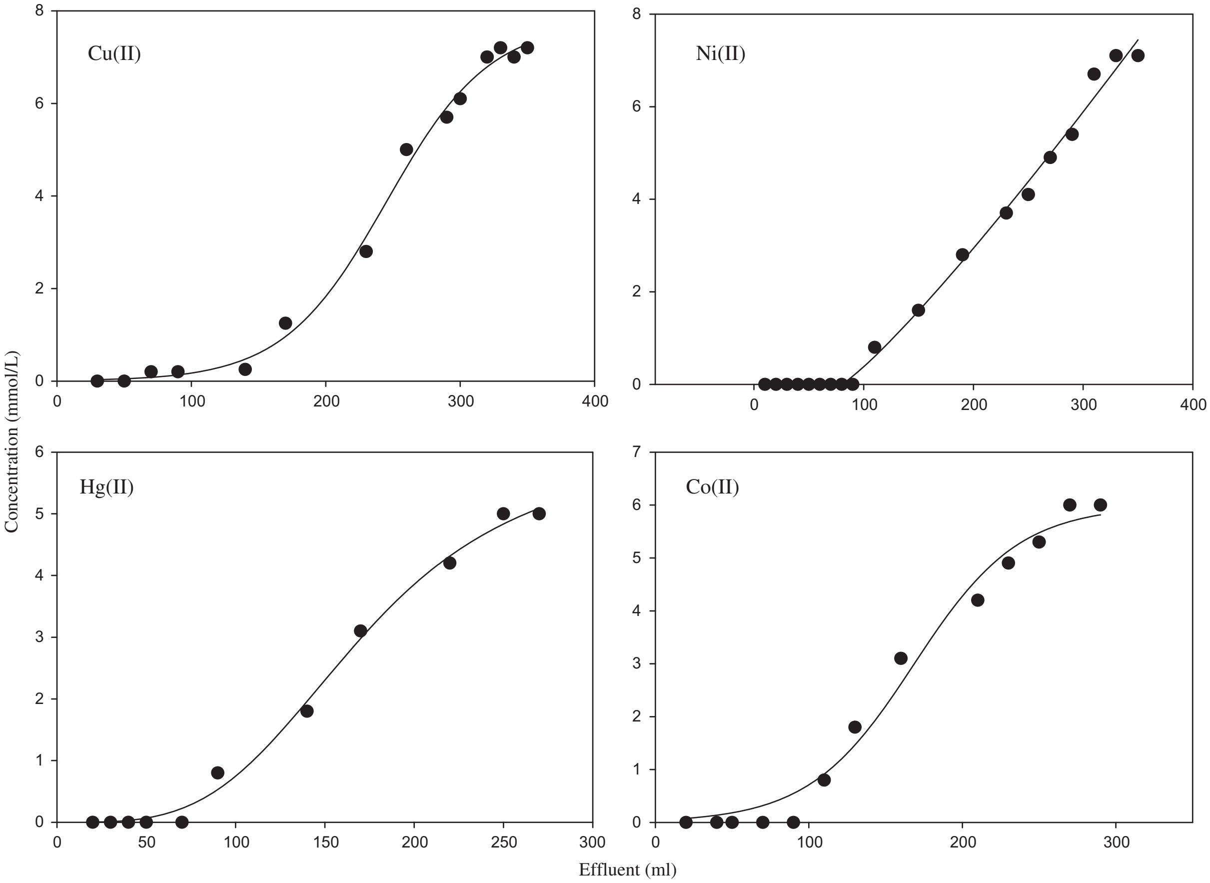


Fig. 8. Breakthrough curves for Cu(II), Ni(II), Hg(II), and Co(II); initial concentration is 7.2, 7.1, 5.0, and 6.0 mmol/L, respectively, flow rate is 1.0 ml/min at optimum pH and at 25˚C.

Table 5
The breakthrough parameters and Thomas constants for Cu(II), Ni(II), Hg(II), and Co(II) at flow rate of 1 ml/min and bed height column of 5 cm

		Breakthrough analysis						Thomas model		
Metal ion	C_o (mmol/L)	t_b (min)	t_e (min)	Δt (min)	Z_m (cm)	q_e (mmol/g)	R %	q_{Th} (mmol/g)	K_{Th} (mL/mmol/min)	R^2
Cu(II)	7.2	70	330	260	3.94	1.51	60	1.642	3.764	0.9445
Ni(II)	7.1	110	330	220	3.33	1.44	58	1.534	2.9014	0.9209
Hg(II)	5	90	250	160	3.2	0.64	47	0.78	5.2	0.9927
Co(II)	6	110	270	160	2.963	0.92	53	1.0212	4.2667	0.974

sorption capacity of the resin (q_{Th}), and correlation coefficient were calculated and presented in Table 5.

The chelating resin containing metal ions were subjected to regeneration using nitric acid (0.2 M). In order to examine the durability of the prepared chelating resin, successive sorption–elution cycles were repeated five times. From the sorption–elution process, it is clear that the sorption capacities showed a small decrease after five regeneration cycles. The adsorption capacity decreased to 85, 90, and 88% for Cu(II), Ni(II), and Hg(II), respectively, after five regeneration cycles as reported in Table 6. The elution of Co(II) still remained incomplete; this is most likely because Co(II) is partially oxidized on the chelating resin giving a much more stable (Co(III)–resin) complex [45]. Therefore, it is fulfilled that iminodiacetate chelating resin is a durable chelating resin for the removal of metal ions from aqueous media.

Table 6
The adsorption capacities (%) of the resin after repeated adsorption–desorption operations

	Capacity (mmol of M(II)/g resin) %					
Metal ion	Recycle 0	Recycle 1	Recycle 2	Recycle 3	Recycle 4	Recycle 5
Cu(II)	100[a]	98	96	91	88	85
Ni(II)	100[b]	99	98	96	93	90
Hg(II)	100[c]	98	97	95	90	88
Co(II)	100[d]	–	–	–	–	–

[a] Cu(II); sorption capacity of the original chelating resin was 1.51 mmol/g resin.

[b] Ni(II); sorption capacity of the original chelating resin was 1.44 mmol/g resin.

[c] Hg(II); sorption capacity of the original chelating resin was 0.64 mmol/g resin.

[d] Co(II); sorption capacity of the original chelating resin was 0.92 mmol/g resin.

4. Conclusion

According to this study, we can say that iminodiacetate chelating resin is an efficient for adsorption of Cu (II), Ni(II), Hg(II), and Co(II) from aqueous media. In batch technique, the optimum adsorption pH values of metal ions occur in the range of 5.0–6.6 depending on the metal ion used. Metal ions adsorption increases with increasing concentration of metal ions. The maximum uptake of iminodiacetate chelating resin followed the order Cu(II) > Ni(II) > Co(II) > Hg(II). Equilibrium isotherm data were treated using three different models. Among these models, Langmuir model is the best fitting model agreement with the experimental data with high R^2. Kinetic study showed that the pseudo-second-order model is suitable to explain the removal of metal ions. The sorption dependence of Cu(II), Ni(II), Hg(II), and Co(II) on temperature was studied and the thermodynamic parameters ΔG°, ΔH°, and ΔS° were evaluated. The results show a feasible, spontaneous, and endothermic adsorption process. Also the chelating resin was highly valuable for the sorption of metal ions by column technique. Elution of metal ions was done using nitric acid and the resin used repeatedly with small decrease in adsorption capacity. In conclusion, the outcomes from this investigation support the view that iminodiacetate chelating resin (IDAR) is an efficient resin for removal of metal ions from aqueous solutions.

References

[1] T. Vaughan, C.W. Seo, W.E. Marshall, Removal of selected metal ions from aqueous solution using modified corncobs, Bioresour. Technol. 78 (2001) 133–139.

[2] C.H. Xiong, Y. Li, G. Wang, L. Fang, S. Zhou, C. Yao, Q. Chen, X. Zheng, D. Qi, Y. Fu, Y. Zhu, Selective removal of Hg(II) with polyacrylonitrile-2-amino-1,3,4-thiadiazole chelating resin: Batch and column study, Chem. Eng. J. 259 (2015) 257–265.

[3] S.H. Lin, R.S. Juang, Heavy metal removal from water by sorption using surfactant-modified montmorillonite, J. Hazard. Mater. 92 (2002) 315–326.

[4] C. Xiong, Y. Zheng, Y. Feng, C. Yao, C. Ma, X. Zheng, J. Jiang, Preparation of a novel chloromethylated polystyrene-2-amino-1,3,4-thiadiazole chelating resin and its adsorption properties and mechanism for separation and recovery of Pt(iv) from aqueous solutions, J. Mater. Chem. A 2 (2014) 5379–5386.

[5] M. Monier, D.M. Ayad, Y. Wei, A.A. Sarhan, Adsorption of Cu(II), Co(II), and Ni(II) ions by modified magnetic chitosan chelating resin, J. Hazard. Mater. 177 (2010) 962–970.

[6] M. Monier, D.A. Abdel-Latif, Modification and characterization of PET fibers for fast removal of Hg(II), Cu(II) and Co(II) metal ions from aqueous solutions, J. Hazard. Mater. 250–251 (2013) 122–130.

[7] R. Kumar, M. Kumar, R. Ahmad, M.A. Barakat, l-Methionine modified Dowex-50 ion-exchanger of reduced size for the separation and removal of Cu(II) and Ni(II) from aqueous solution, Chem. Eng. J. 218 (2013) 32–38.

[8] N.M. Abd El-Moniem, M.R. El-Sourougy, D.A.F. Shaaban, Heavy metal ions removal by chelating resin, Pigm. Resin Technol. 34 (2005) 332–339.

[9] A. Baraka, P.J. Hall, M.J. Heslop, Preparation and characterization of melamine–formaldehyde–DTPA chelating resin and its use as an adsorbent for heavy metals removal from wastewater, React. Funct. Polym. 67 (2007) 585–600.

[10] C.Y. Chen, C.L. Chiang, C.R. Chen, Removal of heavy metal ions by a chelating resin containing glycine as chelating groups, Sep. Purif. Technol. 54 (2007) 396–403.

[11] P.K. Roy, A.S. Rawat, P.K. Rai, Synthesis, characterisation and evaluation of polydithiocarbamate resin supported on macroreticular styrene–divinylbenzene copolymer for the removal of trace and heavy metal ions, Talanta 59 (2003) 239–246.

[12] M.M. Bekheit, N. Nawar, A.W. Addison, D.A. Abdel-Latif, M. Monier, Preparation and characterization of chitosan-grafted-poly(2-amino-4,5-pentamethylene-thiophene-3-carboxylic acid N′-acryloyl-hydrazide) chelating resin for removal of Cu(II), Co(II) and Ni(II) metal ions from aqueous solutions, Int. J. Biol. Macromol. 48 (2011) 558–565.

[13] A.F. Shaaban, D.A. Fadel, A.A. Mahmoud, M.A. Elkomy, S.M. Elbahy, Synthesis of a new chelating resin bearing amidoxime group for adsorption of Cu (II), Ni(II) and Pb(II) by batch and fixed-bed column methods, J. Environ. Chem. Eng. 2 (2014) 632–641.

[14] A.F. Shaaban, D.A. Fadel, A.A. Mahmoud, M.A. Elkomy, S.M. Elbahy, Removal of Pb(II), Cd(II), Mn(II) and Zn(II) using iminodiacetate chelating resin by batch and fixed bed column methods, Desalin. Water Treat. 51 (2013) 5526–5536.

[15] A.F. Shaaban, D.A. Fadel, A.A. Mahmoud, M.A. Elkomy, S.M. Elbahy, Synthesis and characterization of dithiocarbamate chelating resin and its adsorption performance toward Hg(II), Cd(II) and Pb(II) by batch and fixed-bed column methods, J. Environ. Chem. Eng. 1 (2013) 208–217.

[16] M.V. Dinu, E.S. Dragan, Heavy metals adsorption on some iminodiacetate chelating resins as a function of the adsorption parameters, React. Funct. Polym. 68 (2008) 1346–1354.

[17] L.C. Lin, R.S. Juang, Ion-exchange equilibria of Cu(II) and Zn(II) from aqueous solutions with Chelex 100 and Amberlite IRC 748 resins, Chem. Eng. J. 112 (2005) 211–218.

[18] A. Agrawal, K. Sahu, Separation and recovery of lead from a mixture of some heavy metals using Amberlite IRC 718 chelating resin, J. Hazard. Mater. 133 (2006) 299–303.

[19] C. Xiong, C. Yao, Sorption behavior of iminodiacetic acid resin for indium, Rare Met. 27 (2008) 153–157.

[20] C. Xiong, C. Yao, H. Wang, Adsorption of iminodiacetic acid resin for lutetium, J. Rare Earth 22 (2004) 640–643.

[21] L.C. Lin, J.K. Li, R.S. Juang, Removal of Cu(II) and Ni(II) from aqueous solutions using batch and fixed-bed ion exchange processes, Desalination 225 (2008) 249–259.

[22] H. Wang, J. Ma, Y. Zhang, B. He, Adsorption of bilirubin on the polymeric β-cyclodextrin supported by partially aminated polyacrylamide gel, React. Funct. Polym. 32 (1997) 1–7.

[23] H. Mahdavi, A. Zirakzadeh, J. Amani, Modified cross-linked polyacrylamide supported palladium salts as a new heterogeneous catalyst for Heck reaction, React. Funct. Polym. 67 (2007) 716–722.

[24] K.Z. Elwakeel, M. Rekaby, Efficient removal of Reactive Black 5 from aqueous media using glycidyl methacrylate resin modified with tetraethelenepentamine, J. Hazard. Mater. 188 (2011) 10–18.

[25] S.M. El-Bahy, Z.M. El-Bahy, Synthesis and characterization of polyamidoxime chelating resin for adsorption of Cu(II), Mn(II) and Ni(II) by batch and column study, J. Environ. Chem. Eng. 4 (2016) 276–286.

[26] B. Preetha, T. Viruthagiri, Batch and continuous biosorption of chromium(VI) by *Rhizopus arrhizus*, Sep. Purif. Technol. 57 (2007) 126–133.

[27] S.H. Hasan, B.N. Bhattacharjee, P. Srivastava, Batch and continuous biosorption of Cu^{2+} by immobilized biomass of *Arthrobacter* sp., J. Environ. Manage. 90 (2009) 3313–3321.

[28] H. Kalavathy, B. Karthik, L.R. Miranda, Removal and recovery of Ni and Zn from aqueous solution using activated carbon from *Hevea brasiliensis*: Batch and column studies, Colloids Surf. B 78 (2010) 291–302.

[29] C.M. Futalan, C.C. Kan, M.L. Dalida, C. Pascua, M.W. Wan, Fixed-bed column studies on the removal of copper using chitosan immobilized on bentonite, Carbohydr. Polym. 83 (2011) 697–704.

[30] Ö. Yavuz, Y. Altunkaynak, F. Güzel, Removal of copper, nickel, cobalt and manganese from aqueous solution by kaolinite, Water Res. 37 (2003) 948–952.

[31] J.E. Huheey, Inorganic Chemistry Principles of Structure and Reactivity, second ed., Harper International Edition, Harper & Row, New York, NY, 1978.

[32] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.

[33] T.W. Weber, R.K. Chakravorti, Pore and solid diffusion models for fixed-bed adsorbers, AIChE J. 20 (1974) 228–238.

[34] A. Sari, M. Tuzen, D. Citak, M. Soylak, Equilibrium, kinetic and thermodynamic studies of adsorption of Pb(II) from aqueous solution onto Turkish kaolinite clay, J. Hazard. Mater. 149 (2007) 283–291.

[35] X.S. Wang, J. Huang, H.Q. Hu, J. Wang, Y. Qin, Determination of kinetic and equilibrium parameters of the batch adsorption of Ni(II) from aqueous solutions by Na-mordenite, J. Hazard. Mater. 142 (2007) 468–476.

[36] H. Freundlich, Adsorption in solution, Phys. Chem. Soc. 40 (1906) 1361–1368.

[37] M.J. Temkin, V. Phyzev, Recent modifications to Langmuir isotherms, Acta Physiochim, USSR 12 (1940) 217–222.

[38] S. Lagergren, B.K. Svenska, Zurtheorie der sogenannten adsorption geloesterstoffe, VeternskapsakadHandlingar 24 (1898) 1–39.

[39] Y.S. Ho, Second-order kinetic model for the sorption of cadmium onto tree fern: A comparison of linear and non-linear methods, Water Res. 40 (2006) 119–125.

[40] W.J. Weber, J.C. Morris, Equilibria and capacities for adsorption on carbon, J. Sanitary Eng. Div. 90 (1964) 79–91.

[41] A. Nilchi, R. Saberi, M. Moradi, H. Azizpour, R. Zarghami, Adsorption of cesium on copper hexacyanoferrate–PAN composite ion exchanger from aqueous solution, Chem. Eng. J. 172 (2011) 572–580.

[42] N. Unlu, M. Ersoz, Removal of heavy metal ions by using dithiocarbamated-sporopollenin, Sep. Purif. Technol. 52 (2007) 461–469.

[43] A.H. Bandegharaei, M.S. Hosseini, Y. Jalalabadi, M. Sarwghadi, M. Nedaie, A. Taherian, A. Ghaznavi, A. Eftekhari, Removal of Hg(II) from aqueous solutions using a novel impregnated resin containing 1-(2-thiazolylazo)-2-naphthol (TAN), Chem. Eng. J. 168 (2011) 1163–1173.

[44] H.C. Thomas, Heterogeneous ion exchange in a flowing system, J. Am. Chem. Soc. 66 (1944) 1664–1666.

[45] F.D. Mendes, A.H. Martins, Recovery of nickel and cobalt from organic acid complexes: Adsorption mechanisms of metal-organic complexes onto aminophosphonate chelating resin, J. Hazard. Mater. 137 (2006) 925–933.