Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2012.758059

51 (2013) 5526–5536
August

Taylor & Francis
Taylor & Francis Group

Removal of Pb(II), Cd(II), Mn(II), and Zn(II) using iminodiacetate chelating resin by batch and fixed-bed column methods

A.F. Shaaban[a,*], D.A. Fadel[b], A.A. Mahmoud[a], M.A. Elkomy[c], S.M. Elbahy[a]

[a]*Chemistry Department, Faculty of Science, Benha University, Benha, Egypt*
Tel. +20 1222358241; email: afshaaban@hotmail.com
[b]*Nuclear Research Center, Atomic Energy Authority, P.O. Box 13759 Inshas, Cairo, Egypt*
[c]*Faculty of Engineering (Shoubra), Benha University, Shoubra, Egypt*

Received 21 September 2012; Accepted 28 November 2012

ABSTRACT

Chelating resin bearing iminodiacetate function was prepared through subsequent treatment of poly(acrylamide-co-N,N´-methylenebisacrylamide) by ethylenediamine and sodium chloroacetate, respectively. The prepared resins were characterized using Fourier transform infrared spectroscopy. The different factors affecting the metal ions adsorption of this chelating resin such as solution pH, metal ions concentration, contact time, and adsorption temperature were studied in batch method. The prepared chelating resin showed a significant uptake performance towards Pb(II), Zn(II), Mn(II), and Cd(II) ions. Sorption capacities were found to be 1.7, 1.5, 1.6, and 1.77 mmol/g resin for Pb(II), Zn(II), Mn(II), and Cd(II), respectively. Equilibrium data were analyzed using the Langmuir, Freundlich, and Temkin isotherms. The results showed that the adsorption process was well described by Langmuir isotherm model. The kinetic and thermodynamic parameters of the adsorption process were estimated. These data indicated that the adsorption process is spontaneous and followed the pseudo-second-order kinetics. Also, the removal of metal ions from aqueous solutions using iminodiacetate chelating resin in fixed-bed column was studied. Regeneration of chelating resin loaded with metal ions was successfully performed and the resin could be used repeatedly for five times with a small decrease in adsorption capacity.

Keywords: Chelating resin; Iminodiacetate; Polyacrylamide; Heavy metals

1. Introduction

Heavy metal pollution problem gained lately much concern because of its high persistence, headache, irritability, abdominal pain, and various symptoms related to the nervous system, caused by their accumulation at certain levels. The most common metals found in wastewater are copper, cadmium, nickel, manganese, mercury, lead, and zinc which are toxic at high levels [1–3]. Many water treatment techniques for toxic ions removal are available such as precipitation, reverse osmosis, ion exchange, membrane separation, and adsorption of metal ions with chelating resins. Among these technologies, the adsorption technique showed an effective separation of the toxic metal ions since chelating resins are easy-to-use, reusable, and have higher selectivity with high adsorption capacity [4–6]. The use of chelating resins for removal of heavy metals from wastewater or aqueous solutions has been extensively studied [5–19]. Carboxylated

---

*Corresponding author.

resins with iminodiacetic acid functional group such as Amberlite IRC 718, Lewatit TP 207, Chelex 100, and Purolite S930 were mainly applied because of their high selectivity and low manufacturing cost [20–26]. Dino and Dragan prepared chelating resins having iminodiacetate groups derived from acrylonitrile–divinylbenzene copolymers for heavy metal ions removal from aqueous solutions [20]. In addition, chelating resins containing hydroxy and iminodiacetate groups showed good adsorption selectivity for Cu(II) in the presence of Pb(II) and Cd(II) [27].

In this study, new chelating resin bearing iminodiacetate groups was synthesized and used to remove Pb(II), Zn(II), Mn(II), and Cd(II) metal ions from aqueous solution using batch and fixed-bed column methods. The different factors affecting the adsorption behavior such as pH value, metal ion concentration, contact time, and the effect of temperature were studied. Equilibrium data were analyzed using three models: Langmuir, Freundlich, and Temkin. Thermodynamic and kinetic models of the removal process were also clarified. Moreover, fixed-bed column method was used for removal of metal ions from aqueous solution by synthesized chelating resin.

2. Materials and methods

2.1. Materials

Acrylamide (AAM) and N,N´-methylenebisacrylamide (MBA) were pure grade products of Merck Co., Germany and were used directly. Ammonium persulfate [$(NH_4)_2S_2O_8$], ethylenediamine, chloroacetic acid, sodium carbonate, and nitric acid were purchased from Sigma–Aldrich Co., USA. Metal salts $Pb(NO_3)_2$, $Zn(CH_3COO)_2·2H_2O$, Mn $(CH_3COO)_2·4H_2O$, and $CdCl_2$ were used as sources for Pb(II), Zn(II), Mn(II), and Cd(II), respectively. All other reagents were used as received.

2.2. Synthesis of poly(acrylamide-co-N,N´-methylenebisacrylamide) (I)

A cross-linked polyacrylamide (I) beads were synthesized according to the method of Wang et al. [28]—by suspension polymerization method, using a 2-L three-necked round-bottom flask equipped with a condenser and an over-head stirrer. The predetermined amounts of co-monomer mixtures of AAM (98 g, 1.38 mol) and MBA (2 g, 0.013 mol) were mixed with ammonium persulfate [$(NH_4)_2S_2O_8$] (1 mol/100 mol of comonomer mixture), and suspended into a mixture of 100 mL chlorobenzene and 100 mL toluene. The employed solution was de-aerated by Nitrogen gas with flow rate 10 mL/min. Suitable stirring rate was adjusted (250 rpm) and the polymerization process performed at 80˚C for 30 min. After completing the reaction, the mixture was allowed to cool for about 3 h. The resin was filtered off, washed with water and then with methanol, air-dried, and sieved. The 250–400 μm fraction was used for the further synthesis with a yield of 85%.

2.3. Synthesis of cross-linked polyacrylamide bearing amino group via transamidation (II)

Transamidation of cross-linking polyacrylamide (I) was carried out according to the method of Mahdavi et al. [29]. Ethylenediamine (70 mL) was mixed with 5 g of AAM-MBA copolymer (I) and the mixture was stirred and heated at 100˚C for 24 h. The reaction mixture was poured into water (1,000 mL) containing crushed ice. The resin was filtered and washed with NaCl solution (0.2 M) until the filtrate was free from ethylenediamine, as indicated by the absence of any blue coloration with ninhydrin reagent. The resin was washed with water (to remove NaCl) and then with methanol, and finally, it was dried at 70˚C.

2.4. Synthesis of chelating resin bearing iminodiacetate groups (III)

A mixture of sodium monochloroacetate (30 g) in 150 mL of water and 3 g of aminated cross-linked polyacrylamide (II) was heated at 70˚C for 48 h. The resin was filtered off, washed with water, acetone, and finally air-dried. Fourier transform infrared spectra (FTIR) of the prepared resins were recorded using FTIR spectrometer (8201 PC Shimadzu) in the range of 400–4,000 cm^{-1}.

2.5. Uptake of metal ions using batch method

The optimum pH for sorption of metal ions was determined by batch method at 25˚C. Briefly, 0.1 g of the prepared resin was placed in a series of glass bottles containing 100 mL of 5 mmol/L of metal ion solution during shaking for 4 h. The pH of the medium was adjusted with 0.1 M HNO_3 and 0.1 M NaOH solutions. The sorption of metal ions in basic medium was avoided due to precipitation of metal hydroxides. The concentration of the metal ions in the solution was measured using Hitachi atomic absorption Z-6100 polarized Zeeman spectrometer before and after treatment to determine the adsorbed amounts of metal ions. The adsorption capacity of the resin (metal uptake) at equilibrium was calculated using Eq. (1).

$$Q = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where Q is the equilibrium adsorption capacity of the chelating resin in mmol/g resin, C_0 is the initial concentration in mmol/L, and C_e is the concentration at equilibrium of metal ions in mmol/L, V is the volume in L of metal ions solution, and W is the weight in g of chelating resin. Metal ion evaluation was repeated three times and the mean values were calculated and reported.

Experiments of adsorption isotherms were carried out at 25℃. A sample of 0.1 g of chelating resin was added to 100 mL metal ion solutions using different initial concentrations in the range of 1–25 mmol/L and at the optimum pH value. After 4 h shaking of the mixture, the resin was filtered and the residual metal ion concentration in the aqueous phase was determined.

To carry out the kinetic studies of the adsorption process, 0.1 g of chelating resin was added to a glass bottle containing 100 mL of optimum concentration of aqueous metal ion solutions during shaking at 25℃ and optimum pH value. The bottles containing the mixtures were withdrawn at suitable time intervals to determine the metal ion concentration and the time of equilibrium.

The adsorption of metal ion by the chelating resin as a function of temperature was studied in the temperature range of 298–318 K. A quantity of 0.1 g of chelating resin was shaken with 100 mL of aqueous solutions (1.0 mmol/L) containing metal ion at the optimum pH value. After adsorption, the solution was filtered and the residual concentration of the metal ions was determined.

2.6. Uptake of metal ions using column method

A quantity of 1.0 g of chelating resin was placed in glass column of 1.0 cm diameter and 10 cm height. Solutions of metal ions Pb(II), Zn(II), Mn(II), and Cd(II) having an initial concentration of 7.5, 5, 8, and 6.4 mmol/L at optimum pH value and 25℃ were allowed to flow gradually through the column at the flow rate of 1.0 mL/min until the metal ions completely leaked through the column into the effluent.

Elution and regeneration of the resin was carried out using 0.2 M HNO_3 after which, the resin was carefully washed with water, 0.2 M NaOH solution, and finally with distilled water to become ready for reuse. The sorption–desorption cycle of metal ions was repeated five times.

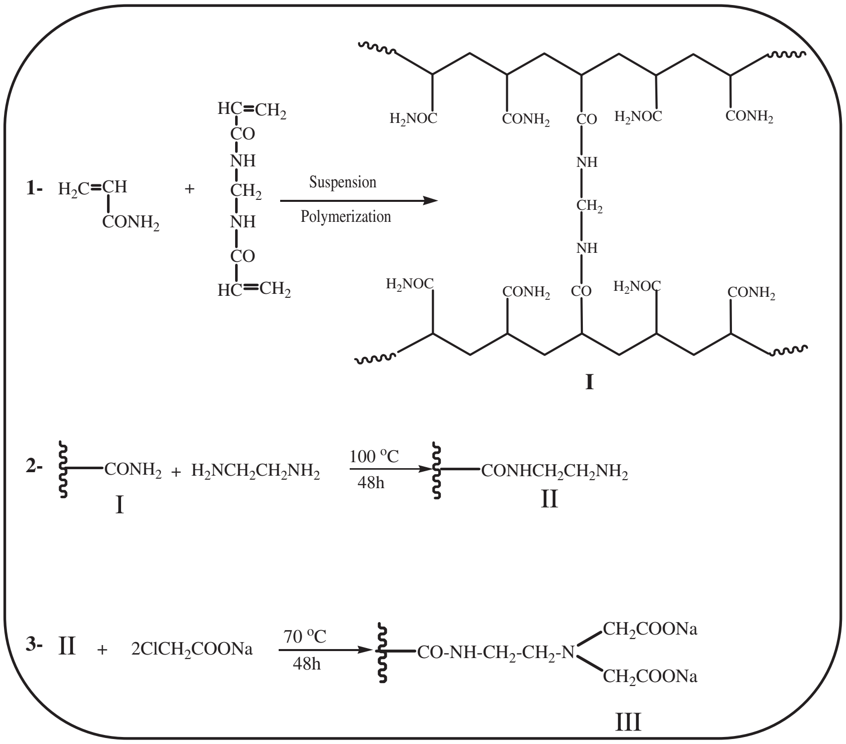

Fig. 1. Schematic illustration of preparation process of iminodiacetate chelating resin.

3. Results and discussion

3.1. Synthesis and characterization of chelating resin containing iminodiacetate groups (III)

Chelating resin (III) was synthesized from the grain size of 250–400 µm cross-linked polyacrylamide copolymer beads (I) through the steps shown in Fig. 1. Cross-linked polyacrylamide (I) with 2%wt MBA was synthesized by suspension polymerization [28]. In transamidation reaction of cross-linked polyacrylamide (I), ethylenediamine itself was used as a solvent as well as transamidation reagent [29]. The reaction was carried out at 100℃. The amino functions were detected using the semi quantitative ninhydrin reaction [29]. Chelating resin bearing iminodiacetate group (III) was prepared by the reaction of aminated cross-linked polyacrylamide (II) with sodium salt of chloroacetic acid. The FTIR spectrum of the cross-linked polyacrylamide (I) showed the characteristic absorptions of amide (N–H) and amide carbonyl (C=O) at 3,395 and 1,669 cm^{-1}, respectively. In iminodiacetic acid resin, the carboxylate groups absorb strongly near 1,672 cm^{-1}. Also, the new bands at 1,455 and 1,397 cm^{-1}, assigned to carboxylic groups, were observed in the FTIR spectra of the iminodiacetic acid resin [30].

3.2. Uptake of metal ions by batch technique:

3.2.1. Optimum pH of metal ions uptake:

The effect of the pH of the metal ion on the metal adsorption was studied by batch technique at 25℃ in the pH range of 1.0–6.2 and the results are shown in Fig. 2. At low pH value, H^+ reacts with carboxylate ions (COO^-) and tertiary amine $(-\underset{|}{N}-)$. The H^+ ions compete with the metal ions for the adsorption sites and therefore, the resin will have low adsorption capacity. Moreover, no adsorption of metal ion was observed at pH = 1.0 because, at this pH level, H^+ concentration was greater than metal ion concentration; and for this reason, the adsorption capacity of metal ion being zero should be acceptable. Similar results were also obtained in previous studies [20,31]. By increasing pH value, the adsorption capacity increases until it was maximum (optimum) at natural pH of 5.6, 6.2, 6, and 6 for Pb(II), Zn(II), Mn(II), and Cd(II), respectively. Above the natural pH for all metal ions, metal (II) hydroxide precipitate is formed ($M^{2+} + 2OH^- \rightarrow M(OH)_2\downarrow$) and adsorption data cannot be measured.

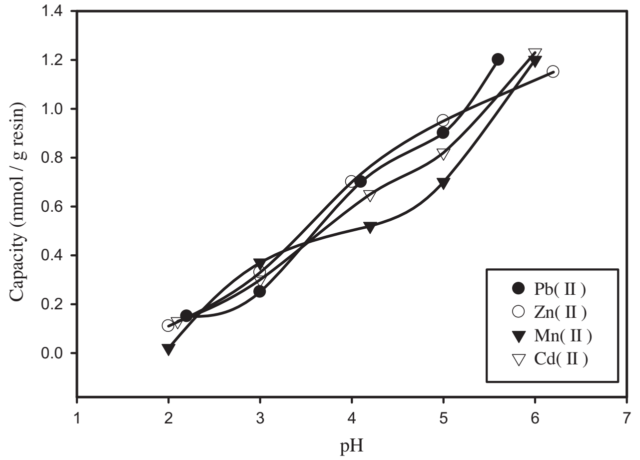

Fig. 2. Effect of pH on the uptake of metal ions; 25℃, shaking time 4 h and initial metal ion concentration of 5.0 mmol/L.

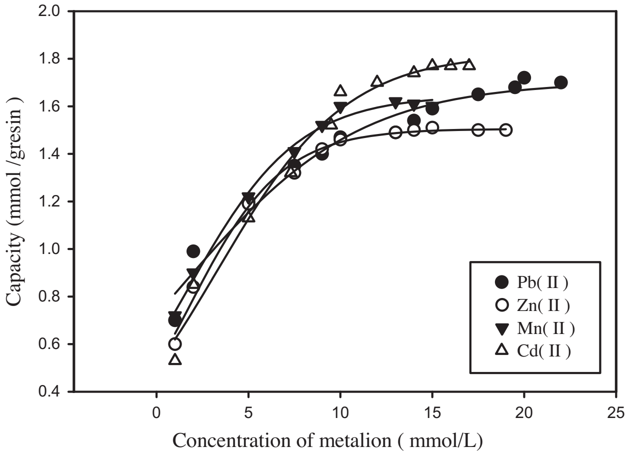

Fig. 3. Effect of initial metal ions concentration on the adsorption capacity of Pb(II), Zn(II), Mn(II), and Cd(II); 25℃, shaking time 4 h and at optimum pH value.

3.2.2. Effect of initial concentration and equilibrium isotherm models

The effect of the initial concentrations of metal ions on adsorption capacities is presented in Fig. 3. The data shown in Fig. 3 shows that the adsorption capacity increases with increasing initial metal concentration until reaching the saturation value. After saturation level, the change of the initial concentration no longer affects the capacity of metal ion adsorption. The loading capacity (mmol/g) was determined at optimum pH of each metal ion and at 25℃, Table 1. The optimum concentration of metal ions for Pb(II), Zn(II), Mn(II), and Cd(II) are 22, 14, 10, and 15 mmol/L, respectively. It is noteworthy to mention that, the

Table 1
Comparison of maximum adsorption capacity and kinetic model of iminodiacetate resin with those of some other chelating resins reported in literature for the adsorption of Pb(II), Zn(II), Mn(II), and Cd(II)

Chelating resin	Metal ions	Sorption capacity (mmol/g)	Kinetic model	Conditions	Ref.
AAM/MBA iminodiacetate	Pb(II), Zn(II), Mn (II), and Cd(II)	1.7, 1.5, 1.6, and 1.77	Second-order	pH = 5.6, 6.2, 6, and 6, 25°C	This work
GMA/DVB iminodiacetate	Pb(II), Zn(II), and Cd(II)	1.0, 1.1, and 1.3	–	pH = 6, 6.5, and 6.6, 28°C	[32]
(Iminodiacetic acid) (NJC-702)	Pb(II) and Cd(II)	1.3 and 0.65	Second-order	pH = 5, 40°C	[33]
(Iminodiacetic acid) (NDC-702)	Pb(II) and Cd(II)	1.28 and 0.82	Second-order	pH = 5, 30°C	[34]
(Iminodiacetic acid) (IRC748)	Pb(II) and Cd(II)	1.18 and 0.8	Second-order	pH = 5, 30°C	[34]
(Iminodiacetic acid) (IDA)	Pb(II) and Cd(II)	1.27 and 0.65	Second-order	pH = 5, 30°C	[35]
Salicylic acid type chelate adsorbent	Pb(II), Zn(II), and Cd(II)	0.31, 0.35, and 0.4	–	pH = 5, 35°C	[36]
Fe3O4@APS@AA-co-CA MNPs	Pb(II), Zn(II), and Cd(II)	0.8, 0.66, and 0.4	Second-order	pH = 5.5, 25°C	[37]
Cross-linked magnetic chitosan-phenylthiourea CSTU	Zn(II) and Cd(II)	0.79 and 1.07	Second-order	pH = 5, 30°C	[38]
Bis[2-(2-benzothiazolylthioethyl)sulfoxide	Pb(II), Zn(II), Mn (II), and Cd(II)	0.37, 0.11, 0, and 0.36	–	pH = 6, 30°C	[39]
Poly(triethylenetetramine bis (methylenephosphonic acid) SG-Cl-T-P	Zn(II), Mn(II), and Cd(II)	0.26, 0.19, and 0.35	–	pH = 5, 25°C	[40]

saturation level of sorption of metal ions was in the order of Cd(II) > Pb(II) > Mn(II) > Zn(II). A comparison of the present (AAM/MBA iminodiacetate) chelating resin with those of different types of chelating resins in recent references is shown in Table 1. The data presented in Table 1 reveals that, generally, the prepared chelating resin in this work has a good advantage in metal ion adsorption more than the previously reported resins. The capacity of the present chelating resin is 13.6, 8.4, 5.6, and 5 times more than Bis (2-2-benzothiazolylthioethyl sulfoxide) [39], SG-Cl-T-P [40], Salicylic acid type chelate adsorbent [36] and SG-Cl-T-P [40] with respect to Zn(II), Mn(II), Pb(II), and Cd(II), respectively.

The adsorption isotherms provide information about the distribution of the adsorbate molecules between the liquid phase and solid phase, when the adsorption process reaches an equilibrium state. Isotherm models of Langmuir, Freundlich, and Temkin were used to describe the equilibrium characteristics of adsorption.

Langmuir adsorption isotherm is based on the monolayer adsorption of metal ions on the surface of the resin. The Langmuir isotherm is expressed as [41]:

$$\frac{C_e}{q} = \frac{C_e}{Q_{\max}} + \frac{1}{K\,Q_{\max}} \tag{2}$$

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

Langmuir model was expressed by Weber and Chakravot [42] in terms of a dimensionless constant, known as separation factor (R_L) which is calculated by the following equation:

$$R_L = \frac{1}{1 + K\,C_o} \tag{3}$$

where K is the Langmuir constant (L/mmol) and C_0 is the initial concentration (mmol/L). The value of R_L indicates the nature of the isotherm to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) [43,44]. The variation of R_L with concentration of metal ion is shown in Fig. 4. R_L values

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

Metal ion	Langmuir isotherm			Freundlich isotherm			Temkin isotherm		
	$Q_{\max}$	K	R^2	N	K_F	R^2	K_T	B	R^2
Pb(II)	1.79	0.66	0.991	0.21	0.93	0.989	45.36	0.24	0.980
Zn(II)	1.60	1.02	0.998	0.25	0.81	0.966	26.27	0.26	0.980
Mn(II)	1.72	1.03	0.994	0.23	0.93	0.982	44.70	0.23	0.963
Cd(II)	2.01	0.47	0.983	0.34	0.74	0.980	7.79	0.37	0.970

were found to be between zero and one for all the concentrations of Pb(II), Zn(II), Mn(II), and Cd(II) which indicates that the ion exchange of Pb(II), Zn(II), Mn(II), and Cd(II) is favorable. It is observed that the R_L values decreased with the increase of metal ion concentration which implies that the ion exchange process is more favorable for the higher concentration of metal ion than for the lower ones.

Freundlich isotherm is based on multilayer adsorption and adsorption on heterogeneous surfaces. The Freundlich isotherm model is expressed as [45]:

$$\log q = N \log C_e + \log K_F \tag{4}$$

where q is the amount of metal ions adsorbed, C_e is the metal ion concentration at equilibrium, and K_F is the Freundlich constant, which indicates to the amount of metal ion per gram of resin at the equilibrium concentration; N is a measurement of the nature and strength of the adsorption process and of the distribution of active sites. The values of Freundlich equation parameters are given in Table 2. Similar to R_L values of Langmuir isotherm, the values of N parameter in the Freundlich model indicate 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 Temkin isotherm model is expressed in linearized form as follows [46]:

$$q = B \ln K_T + B \ln C_e \tag{5}$$

where K_T is the Temkin constant which is related with adsorbent/adsorbate interactions and B is another constant related to the heat of adsorption. The values of Temkin equation parameters are given in Table 2.

The Langmuir, Freundlich, and Temkin adsorption constants calculated by using isotherms and their correlation coefficients are presented in Table 2. The correlation coefficients values indicate that adsorption of Pb(II), Zn(II), Mn(II), and Cd(II) onto iminodiacetate chelating resin is fitted better by the Langmuir model ($R^2 = 0.983$–0.998) than the Freundlich and Temkin models ($R^2 = 0.966$–0.989) and ($R^2 = 0.963$–0.980), respectively.

3.2.3. Adsorption kinetics

Kinetic experiments were carried out using the optimum pH and optimum initial concentration of adsorption for each metal ion at 25°C and the results are shown in Fig. 5. As shown in Fig. 5, equilibrium was attained within 25 min for Cd(II), Zn(II) ions and 35 min for each of Mn(II) and Pb(II) ions. The sorption capacity after shaking the solution for 10 min was 67, 63, 53, and 50% for Cd(II), Zn(II), Mn(II), and Pb(II), respectively. The high initial rate suggests that the adsorption occurs mainly on the surface of chelating resin [47].

It is known that adsorption kinetics is dependent on various factors like mass transfer, diffusion control, chemical reactions, and particle diffusion. In order to clarify the kinetic characteristics of the adsorption of metal ions, three types of sorption kinetic models namely 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 [48] is given as:

$$\log(q - q_t) = \log q - \left(\frac{K_{\mathrm{ads}}}{2.303}\right)t \tag{6}$$

where q and q_t are the amounts of the adsorbed metal ions (mmol/g) at equilibrium and at time t (min), respectively. K_{ads} is the first-order rate constant (min^{-1}) of the adsorption. Lagergren's constants are given in Table 3.

The experimental data were also analyzed according to pseudo-second-order kinetic model [49] as in the following relation.

$$\frac{t}{q_t} = \frac{1}{K_2 q^2} + \left(\frac{1}{q}\right)t \tag{7}$$

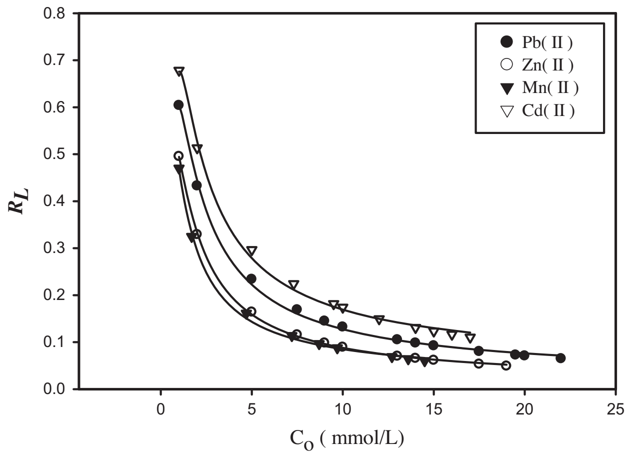

Fig. 4. Variation of adsorption intensity (R_L) with initial metal ion concentration (C_0).

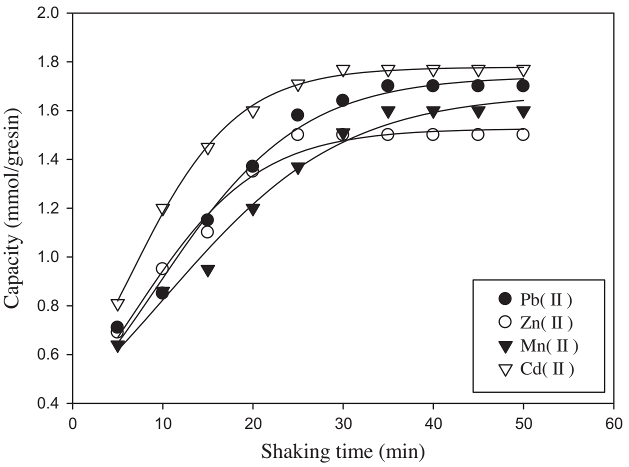

Fig. 5. Effect of shaking time on the adsorption capacity of Pb(II), Zn(II), Mn(II), and Cd(II) at optimum pH, optimum concentration and at 25˚C.

where K_2 ($\mathrm{g\,mmol^{-1}\,min^{-1}}$) is the rate constant of pseudo-second-order adsorption reaction. The constants of the second-order kinetic model plots are given in Table 3. As it can be seen from the results given in Table 3, correlation coefficients are higher than the results obtained from the first-order kinetics. So, it is possible to suggest that the sorption of Pb(II), Zn(II), Mn(II), and Cd(II) onto chelating resin obeys the second-order kinetics. This is in agreement with the data obtained from other previous reports as shown in Table 1.

With respect to Weber and Morris intraparticle diffusion, the adsorbate molecules can be transferred from the solution phase over an adsorbent in three consecutive steps [50] as: (a) external film diffusion; (b) intraparticle diffusion and (c) Adsorption of the adsorbate molecules on the interior surface of the adsorbent. Intraparticle diffusion was explored by Weber and Morris using the following expression [51]:

$$q_t = K_{\mathrm{id}} t^{0.5} \tag{8}$$

where K_{id} is the intraparticle diffusion rate constant ($\mathrm{mmolg^{-1}/min^{0.5}}$). The intraparticle diffusion rate (K_{id}) and correlation coefficient was determined from the plots of q_t against $t^{0.5}$. The constants of these plots are given in Table 3. According to Eq. (8), if the plot gives a straight line, the adsorption will be controlled only by the intraparticle diffusion, but a multilinear plot is formed which represents two or more steps involved in the adsorption process [52].

As can be seen from Fig. 6, the adsorption process was controlled by three stages: (1) Fast external surface adsorption; (2) gradual adsorption where intraparticle diffusion is a rate-controlled step; and (3) final equilibrium stage due to reduction of metal ions concentration in solution in addition to less number of adsorption sites are available.

From foregoing results, it is concluded that the intraparticle diffusion is not the only rate-limiting step. Thus, the adsorption process may be a complex nature and consists of both surface adsorption and intraparticle diffusion. Hence, it is suggested that the adsorption of heavy metal ions on chelating resin may be controlled by external mass transfer followed by intraparticle diffusion.

3.2.4. Adsorption thermodynamics

Thermodynamic parameters of the metal ion adsorption on the chelating resin were evaluated by carrying out the adsorption experiments at different temperatures (298, 308, and 318 K). 100 mL of 1.0 mmol/L metal ion solution were allowed to equilibrate with 0.1 g of resin at optimum pH value.

The distribution coefficient for the adsorption process, K_{d}, was calculated by Eq. (9) [53].

$$K_{\mathrm{d}} = \frac{C_0 - C_{\mathrm{e}}}{C_{\mathrm{e}}} \times \frac{V}{W} \tag{9}$$

where C_0 and C_{e} are the initial and equilibrium concentration of the metal ions in aqueous phase (mmol/L), V is the total volume of the solution in (L), and W is the weight of the chelating resin used in grams.

To calculate the free energy of the adsorption ($\Delta G^0_{\mathrm{ads}}$), Eq. (10) was employed:

$$\Delta G^0_{\mathrm{ads}} = -RT \ln K_{\mathrm{d}} \tag{10}$$

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

Equations	Parameters	Pb(II)	Zn(II)	Mn(II)	Cd(II)
Pseudo-first-order kinetic equation	q (mmol/g)	2.466	1.549	1.923	2.138
	K_{ads} (1/min)	0.115	0.106	0.089	0.115
	R^2	0.945	0.926	0.914	0.978
Pseudo-second-order kinetics	q (mmol/g)	2.188	1.776	2.118	2.044
	K_2 (g mmol^{-1} min^{-1})	0.038	0.077	0.034	0.079
	R^2	0.981	0.989	0.978	0.994
Intraparticle diffusion equation	K_{id} (mmolg^{-1}min$^{-1/2}$)	0.227	0.169	0.220	0.186
	R^2	0.903	0.834	0.941	0.823

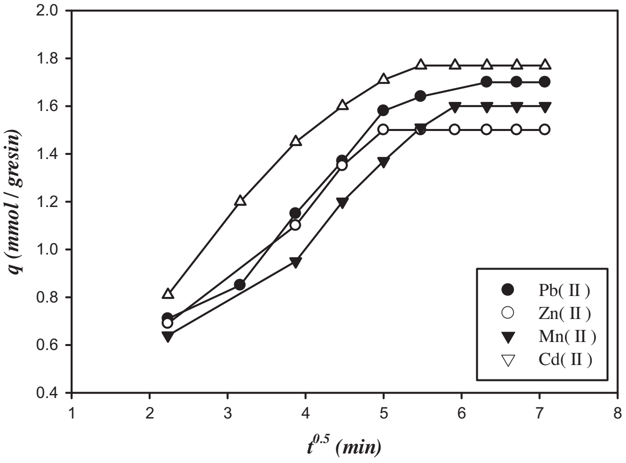

Fig. 6. Plot of Weber–Morris intraparticle diffusion model for the adsorption of metal ions on chelating resin.

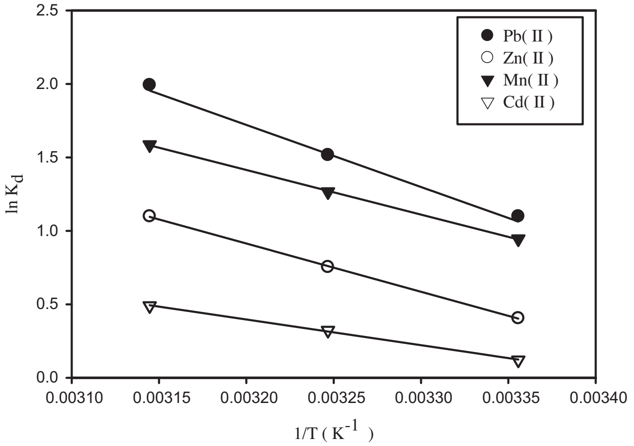

Fig. 7. Plot of $\ln K_d$ as a function of reciprocal of temperature ($1/T$) for the adsorption of metal ions on chelating resin.

The standard enthalpy (ΔH^0_{ads}) and entropy (ΔS^0_{ads}) of the adsorption were calculated by plotting ln K_d vs. $1/T$ in Eq. (11).

$$\ln K_d = \frac{\Delta S^0_{ads}}{R} - \frac{\Delta H^0_{ads}}{RT} \tag{11}$$

where R is the universal gas constant (8.314 J/mol K). The values of the slope ($-\Delta H^0_{ads}/R$) and the intercept ($\Delta S^0_{ads}/R$) (Fig. 7) give ΔH^0_{ads} and ΔS^0_{ads}, respectively. The values of ΔG^0_{ads}, ΔH^0_{ads}, and ΔS^0_{ads} for the adsorption of the metal ions on the chelating resin were collected in Table 4. The positive values of ΔH^0_{ads} indicate that the metal adsorption is an endothermic process [54,55]. Moreover, the positive values of ΔS^0_{ads} may be related to the increased randomness due to the liberation of water of hydration drying the adsorption of metal ions [54,55]. Finally, the thermodynamic parameters pointed to the spontaneity of the adsorption process which is indicated by negative values of ΔG^0_{ads}.

3.3. Uptake of metal ions using column techniques

Iminodiacetate chelating resin (III) was also found effective in column method for the removal of Pb(II), Zn(II), Mn(II), and Cd(II). The break-through curves are presented in Fig. 8. The solution was allowed to flow downward through the column at 25℃ with a flow rate of 1.0 mL/min. The obtained break-through curves indicate that using 1.0 mL/min flow rate of metal ions, solutions start to break-through at 70, 90, 110, and 80 mL of effluent for Pb(II), Zn(II), Mn(II), and Cd(II), respectively. Sorption capacities of the metal ions were calculated and illustrated in Table 5.

3.3.1. Elution and regeneration cycles

The used resin samples containing metal ions were subjected to elution using 0.2 M HNO_3 solution at 25°C. It was previously mentioned that, the adsorption capacities of the metal ions were zero or close to zero at pH ⩽ 1. This indicates that 0.1 M H^+ could prevent

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

Metal ion	$-\Delta G^0_{\text{ads}}$ (kJ/mol)			ΔH^0_{ads} (kJ/mol)	ΔS^0_{ads} (J/mol)	R^2
	298 K	308 K	318 K			
Pb(II)	2.72	3.88	5.27	35.17	127.03	0.996
Zn(II)	1.00	1.93	2.90	27.29	94.94	0.999
Mn(II)	2.34	3.24	4.19	25.25	92.53	0.999
Cd(II)	0.29	0.83	1.29	14.55	49.88	0.998

Table 5
The adsorption capacities (%) of the resin after repeated adsorption–desorption operations

Metal ion	Capacity (mmol of M^{2+}/g resin) %					
	Recycle 0	Recycle 1	Recycle 2	Recycle 3	Recycle 4	Recycle 5
Pb(II)	100[a]	97	97	87	86	85
Zn(II)	100[b]	100	90	86	90	83
Mn(II)	100[c]	99	91	87	91	81
Cd(II)	100[d]	100	98	92	90	91

[a] Pb(II); sorption capacity of the original chelating resin was 1.31 mmol/g resin.

[b] Zn(II); sorption capacity of the original chelating resin was 1.01 mmol/g resin.

[c] Mn(II); sorption capacity of the original chelating resin was 1.33 mmol/g resin.

[d] Cd(II); sorption capacity of the original chelating resin was 1.20 mmol/g resin.

the adsorptions of the metal ions. Thus, to improve the desorption efficiency 0.2 M H^+ was used. In order to inspect the reusability of iminodiacetate chelating resin, consecutive adsorption–desorption cycles were repeated five times. From the adsorption–desorption process, it is clear that the adsorption capacities showed a little decrease after five regeneration cycles. The sorption capacity decreased to 85, 83, 81, and 91% for Pb(II), Zn(II), Mn(II), and Cd(II), respectively after five regeneration cycles. Consequently, it is concluded that iminodiacetate chelating resin is a durable sorbent in removal of the metal ions under study from their single-metal ion solutions. After passing HNO_3 solution through the column to release metal ions from resin–metal ion complexes, H^+ could replace the metal ions adsorbed by (–COONa) groups within the chelating resin to form carboxylic acids (–COOH) and quaternary ammonium salts $\underset{|}{(\text{–NH}^+\text{–})}$, respectively. If this resin was used to adsorb metal ions in the previous adsorption conditions, only 30–40% of initial uptake value would be observed. Whereas, when the resin was neutralized with NaOH solution to form carboxylate salt (–COONa) and tertiary amine $\underset{|}{(\text{–N–})}$, the re-adsorption capacities could attain 81–91% of the first adsorption step (Table 5).

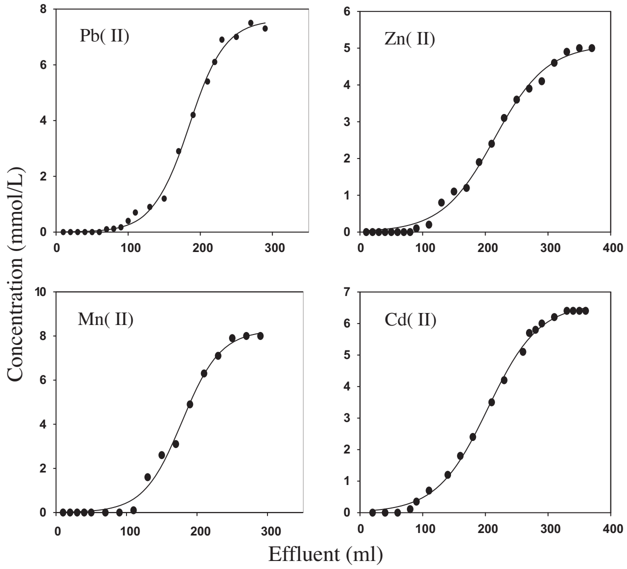

Fig. 8. Break-through curves for Pb(II), Zn(II), Mn(II), and Cd(II); initial concentration is 7.5, 5.0, 8.0, and 6.4 mmol/L, respectively, flow rate is 1.0 mL/min at optimum pH and at 25˚C.

4. Conclusions

Based on the present work, it can be concluded that chelating resin bearing iminodiacetate groups based on cross-linked polyacrylamide is an effective for removal of Pb(II), Zn(II), Mn(II), and Cd(II) from their aqueous solution. In batch-mode adsorption studies, the optimum adsorption pH of metal ions was in the range of 5.6–6.2 depending on the metal ion used. The adsorption of metal ions increases with increasing the initial concentration of metal ions. Equilibrium isotherm data were fitted using three different parameter models. Among these models, Langmuir model is the best fitting model with the experimental data with high R^2 value. Kinetic study showed that the pseudo-second-order model is appropriate to describe the adsorption process. The adsorption dependence of Pb(II), Zn(II), Mn(II), and Cd(II) on temperature was investigated and the thermodynamic parameters ΔG^0, ΔH^0, and ΔS^0 were calculated. The results show a feasible, spontaneous, and endothermic adsorption process. Iminodiacetate chelating resin was highly efficient for the adsorption of metal ions by batch and column methods. Metal ions are easily eluted with 0.2 M HNO_3 and the resin could be used repeatedly for five times with more than 80% of initial adsorption capacities.

References

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

[2] A.M. Donia, A.A. Atia, K.Z. Elwakeel, Selective separation of mercury(II) using magnetic chitosan resin modified with Schiff's base derived from thiourea and glutaraldehyde, J. Hazard. Mater. 151 (2008) 372–379.

[3] Z. Zainol, M. Nicol, Ion-exchange equilibria of Ni(II), Co(II), Mn(II) and Mg(II) with iminodiacetic acid chelating resin Amberlite IRC 748, Hydrometallurgy 99 (2009) 175–180.

[4] W.S. Wan Ngah, C.S. Endud, R. Mayanar, Removal of copper (II) ions from aqueous solution onto chitosan and cross-linked chitosan bead, React. Funt. Polym. 50 (2002) 181–190.

[5] A. Dabrowski, Z. Hubicki, P. Podkościelny, E. Robens, Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method, Chemosphere 56 (2004) 91–106.

[6] C.V. Diniza, F.M. Doylea, V.T. Ciminellia, Effect of pH on the adsorption of selected heavy metal ions from concentrated chloride solutions by the chelating resin, Dowex M-4195, Sep. Sci. Technol. 37 (2002) 3169–3185.

[7] H. Eccles, H. Greenwood, Chelate ion-exchangers: The past and future application, a user's view, Solvent Extr. Ion Exch. 10 (1992) 713–727.

[8] A.A. Zagorodnia, D.N. Muiravievab, M. Muhammedab, The separation of Zn and Cu using chelating ion exchangers and temperature variations, Sep. Sci. Technol. 32 (1997) 413–429.

[9] Haas V. Tare, Application of ion exchangers to recovery of metals from semiconductor wastes, React. Polym. 2 (1984) 61–70.

[10] T.H. Karppinen, A.Y. Pentti, Evaluation of selective ion exchange for nickel and cadmium uptake from the rinse water of a plating shop, Sep. Sci. Technol. 35 (2000) 1619–1633.

[11] R. Shah, S. Devi, Chelating resin containing s-bonded dithizone for the separation of copper(II), nickel(II) and zinc(II), Talanta 45 (1998) 1089–1096.

[12] F. Gode, E. Pehlivan, A comparative study of two chelating ion-exchange resins for the removal of chromium(III) from aqueous solution, J. Hazard Mater. 100 (2003) 231–243.

[13] M.E. Malla, M.B. Alvarez, D.A. Batistoni, Evaluation of sorption and desorption characteristics of cadmium, lead and zinc on Amberlite IRC-718 iminodiacetate chelating ion exchanger, Talanta 57 (2002) 277–287.

[14] K.S. Rao, D. Sarangi, P.K. Dash, G.R. Chaudhury, Treatment of wastewater containing copper, zinc, nickel and cobalt using Duolite ES-467, J. Chem. Technol. Biotechnol. 77 (2002) 1107–1113.

[15] F. Mijangos, M. Diaz, Metal-proton equilibrium relations in a chelating iminodiacetic resin, Ind. Chem. Eng. Res. 31 (1992) 2524–2532.

[16] R. Shah, S. Devi, Preconcentration and separation of palladium(II) and platinum(IV) on a dithizone anchored poly (vinylpyridine)-based chelating resin, Anal. Chim. Acta. 341 (1997) 217–224.

[17] V. Tare, S. Karra, C. Haas, Kinetics of metal removal by chelating resin from a complex synthetic wastewater, Water Air Soil Pollut. 22 (1984) 429–439.

[18] J. Yang, A. Renken, Heavy metal adsorption to a chelating resin in a binary solid fluidized bed, Chem. Eng. Technol. 23 (2000) 1007–1012.

[19] J. Lehto, A. Paajanen, R. Harjula, H. Leinonen, Hydrolysis and H^+/Na^+ exchange by Chelex 100 chelating resin, React. Polym. 23 (1994) 135–140.

[20] 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.

[21] L.C. Lin, R.S. Juang, Ion-exchange equilibria of Cu(II) and Zn(II) from aqueous solutions with Chelex100 and Amberlite IRC 748 resins, Chem. Eng. J. 112 (2005) 211–218.

[22] A. Agrawal, K. Sahu, Separation and recovery of lead from a mixture of some heavy metals using Amberlite IRC718 chelating resin, J. Hazard. Mater. 133 (2006) 299–303.

[23] Z. Yu, T. Qi, J. Qu, L. Wang, J. Chu, Removal of Ca(II) and Mg(II) from potassium chromate solution on Amberlite IRC 748 synthetic resin by ion exchange, J. Hazard. Mater. 167 (2009) 406–412.

[24] A. Deepatana, M. Valix, Comparative adsorption isotherms and modeling of nickel and cobalt citrate complexes onto chelating resins, Desalination 218 (2008) 334–342.

[25] 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.

[26] S. Şahan, U. Şahin, An automated on-line minicolumn preconcentration cold vapour atomic absorption spectrometer: Application to determination of cadmium in water samples, Talanta 88 (2012) 701–706.

[27] C.Y. Chen, C.L. Chiang, P.C. Huang, Adsorptions of heavy metal ions by a magnetic chelating resin containing hydroxy and iminodiacetate groups, Sep. Pur. Technol. 50 (2006) 15–21.

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

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

[30] E.S. Dragan, E. Avram, M.V. Dinu, Organic ion exchangers as beads. Synthesis, characterization and applications, Polym. Adv. Technol. 17 (2006) 571–578.

[31] C.Y. Chen, M.S. Lin, K.R. Hsu, Recovery of Cu(II) and Cd(II) by a chelating resin containing aspartate groups, J. Hazard. Mater. 152 (2008) 986–993.

[32] A. Atia, A.M. Donia, K.Z. ELwakeel, Adsorption behavior of non-transition metal ions on a synthetic chelating resin bearing iminoacetate functions, Sep. Purif. Technol. 43 (2005) 43–48.

[33] F. Liu, L. Li, P. Ling, X. Jing, C. Li, A. Li, X. You, Interaction mechanism of aqueous heavy metals onto a newly synthesized IDA-chelating resin: Isotherms, thermodynamics and kinetics, Chem. Eng. J. 173 (2011) 106–114.

[34] P. Ling, F. Liu, L. Li, X. Jing, B. Yin, K. Chen, A. Li, Adsorption of divalent heavy metal ions onto IDA-chelating resins: Simulation of physicochemical structures and elucidation of interaction mechanisms, Talanta 81 (2010) 424–432.

[35] L. Li, F. Liu, X. Jing, P. Ling, A. Li, Displacement mechanism of binary competitive adsorption for aqueous divalent metal ions onto a novel IDA-chelating resin: Isotherm and kinetic modeling, Water Res. 45 (2011) 1177–1188.

[36] F. An, B. Gao, X. Dai, Efficient removal of heavy metal ions from aqueous solution using salicylic acid type chelate adsorbent, J. Hazard. Mater. 192 (2011) 956–962.

[37] F. Ge, M.M. Li, H. Ye, B.X. Zhao, Effective removal of heavy metal ions Cd(II), Zn(II), Pb(II), Cu(II) from aqueous solution by polymer-modified magnetic nanoparticles, J. Hazard. Mater. 211–212 (2012) 366–372.

[38] M. Monier, D.A. Abdel-Latif, Preparation of cross-linked magnetic chitosan-phenylthiourea resin for adsorption of Hg(II), Cd(II) and Zn(II) ions from aqueous solutions, J. Hazard. Mater. 209–210 (2012) 240–249.

[39] C. Ji, R. Qu, C. Wang, H. Chen, C. Sun, Q. Xu, Y. Sun, C. Wei, A chelating resin with bis[2-(2-benzothiazolylthioethyl)sulfoxide]: Synthesis, characterization and properties for the removal of trace heavy metal ion in water samples, Talanta 73 (2007) 195–201.

[40] Z. Wang, P. Yin, R. Qu, Q. Xu, Heterogeneous synthesis of chelating resin organophosphonic acid-functionalized silica gel and its adsorption property of heavy metal ions from fuel ethanol solutions, J. Appl. Polym. Sci. 126 (2012) 544–551.

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

[42] T.W. Weber, R.K. Chakravot, Pore and solid diffusion models for fixed bed adsorbents, AiChE Journal. 20 (1974) 228–238.

[43] 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.

[44] X.S. Wang, J. Huang, H.Q. Hua, 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.

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

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

[47] H. Kasgoz, S. Ozgumus, M. Orbay, Modified polyacrylamide hydrogels and their application in removal of heavy metal ions, Polymer 44 (2003) 1785–1793.

[48] S. Lagergren, B.K. Svenska, Zur theorie der sogenannten adsorption geloester stoffe, Veternskapsakad Handlingar 24 (1898) 1–39.

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

[50] C. Sarici-Ozdemir, Y. Onal, Equilibrium, kinetic and thermodynamic adsorptions of the environmental pollutant tannic acid onto activated carbon, Desalination 251 (2010) 146–152.

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

[52] V.C. Srivastava, M.M. Swamy, I.D. Mall, B. Prasad, I.M. Mishra, Adsorptive removal of phenol by bagasse fly ash and activated carbon: Equilibrium, kinetics and thermodynamics, Colloids Surf. A: Physicochem. Eng. Aspects 272 (2006) 89–104.

[53] 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.

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

[55] 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.