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Synthesis and characterization of a new iminodiacetate chelating resin for removal of toxic heavy metal ions from aqueous solution by batch and fixed bed column methods

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Abstract–New porous chelating resin beads CPN-IDA were prepared by the reaction of poly (acrylonitrile-co-N,N′-methylenebisacrylamide) with etheylenediamine and sodium chloroacetate, respectively. The composition and morphology of the chelating resin was characterized by Fourier transform infrared spectroscopy (FTIR), thermal analysis (TGA and DrTGA), scanning electron microscopy (SEM), surface area measurements by N_2 adsorption (S_{BET}) and water regain (w%). Batch adsorption experiments were employed to study the impact of some factors that control the adsorption of metal ions including solution pH, concentration of metal ions, contact time and the temperature of the solution. Batch sorption results showed that the chelating resin had high affinity towards Cu(II), Cd(II) and Pb(II). The saturated adsorption capacity at 25 °C was 2.43, 1.93 and 1.45 $\mathrm{mmolg^{-1}}$ resin for Cu(II), Cd(II) and Pb(II), respectively. Among the empirical isotherm models, the equilibrium adsorption results were obviously fitted with Langmuir model. The kinetics was analyzed using pseudo-first-order, pseudo-second-order, and intra-particle diffusion equations. The adsorption kinetic data were well elucidated with pseudo-second-order kinetic model. Thermodynamic parameters were calculated for the uptake of the metal ions under study and it was found to be a spontaneous process. Moreover, the adsorption of metal ions has been studied using column technique. The regeneration of CPN-IDA was experimentally performed by using nitric acid. The chelating resin was used repeatedly for five times with a little decrease in sorption of metal ions.

Keywords: Iminodiacetate, Polyacrylonitrile, Adsorption, Heavy Metals, Isotherms, Kinetics

INTRODUCTION

One of the most serious environmental problems today is the pollution caused by heavy metals due to its toxic effect on human health and on the natural environment [1,2]. Copper, lead, zinc and cadmium are the most harmful metal ions in wastewater that can cause serious diseases such as cancer [3]. The recommended maximum acceptable concentrations given by the World Health Organization (WHO) in drinking water are 1.5 mg L^{-1}, 0.05 mg L^{-1} and 0.003 mg L^{-1} for Cu(II), Pb(II) and Cd(II), respectively [4]. Many separation methods have been used for removal of metal ions from aqueous solution such as precipitation, membrane filtration, biological treatment and chelating resin [1-3]. Adsorption of metal ions using chelating resins is preferred because of their high adsorption capacity, availability of different resins, selectivity, ease of handling and durability [5-9]. Chelating resins consist of polymer matrix of three-dimensional mesh construction with chelating functional group(s) that catches metal ions from aqueous solution. These resins are mainly effective in recovery of metal ions when the concentration of metal ions in aqueous solution is small. The efficiency of adsorption of metal ions depends on some factors, such as charge and type of metal ion, pH of the solution, concentration of metal ion, equilibrium time, salinity, temperature, the presence of organic matter. It depends also on the properties of the chelating resin, such as swelling, cross-linking type, cross-linking degree and chelating groups. Chelating resins with different chelating group such as amino, oxime, carbamate, thiols, aminophosphoric and carboxylate have been prepared and illustrated in the literature [5-13]. Chelating resins with iminodiacetate group are commercially available, such as Purolite S390, Chelex 100, Amberlite IRC-748 and Lewatit TP 207. Iminodiacetate chelating resin was used to treat wastewater containing metal ions, such as copper, cadmium, nickel, lead, manganese and zinc due to their high selectivity [12-18]. In our previous study, iminodiacetate chelating resin based on crosslinked polyacrylamide was synthesized for efficient removal of lead, cadmium, manganese and zinc [12]. Dinu et al. synthesized chelating resin containing iminodiacetate group derived from acrylonitrile-divenylbencene copolymers for the removal of lead, cadmium and zinc [19].

In the present study, iminodiacetate chelating resin (CPN-IDA) derived from acrylonitrile-N,N′-methylenebisacrylamide copolymer was prepared and used for the removal of copper, cadmium and lead from aqueous media by batch and column techniques. The effects of different parameters that influence the metal ions removal were examined and different kinetics and thermodynamic parameters of the adsorption process were also studied. Furthermore, column technique was also used for removal of copper, cadmium and lead from aqueous media by new synthesized CPN-IDA.

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MATERIALS AND METHODS

1. Materials

Acrylonitriles (AN), N,N′-methylenebisacrylamide (MBA), were used as pure grade products of Merck Co.-(W. Germany). 2,2-Azobis(isobutyronitrile) (AIBN), ethylenediamine, chloroacetic acid, sodium carbonate, nitric acid were purchased from Sigma-Aldrich, USA. Metal salts $CuSO_4 \cdot 5H_2O$, $CdBr_2 \cdot 4H_2O$ and $Pb(NO_3)_2$ were used as sources for Cu(II), Cd(II) and Pb(II), respectively. All the chemicals were used as received without further purification.

2. Synthesis of Iminodiacetae Chelating Resin (CPN-IDA)

2-1. Synthesis of Cross-linked Polyacrylonitrile (CPN)

Crosslinked polyacrylonitrile was synthesized according to the method reported in our earlier work [11]. In brief, CPN beads were synthesized by suspension polymerization in the presence of toluene as solvent (50 ml) and AIBN (0.2 g) as initiator. Polymerization of AN (9.5 g) and MBA (0.5 g) in presence of initiator in toluene was carried out at 80-90 °C for 3 h. The nitrogen gas was purged into the solution to remove oxygen for 10 min. The mixture was cooled to room temperature and the resin was filtered off, washed carefully (with distilled water and methanol), and then dried in air. The resin was sieved and the 150-250 μm fraction was used for further synthesis with a yield of 73%.

2-2. Synthesis of Polyacrylonitrile Containing Amino Groups (ACPN)

Polyacrylonitrile bearing amino group (ACPN) resin was prepared according to our previously reported method [11]. CPN (5.0 g) was mixed with 80% (v/v in water) ethylenediamine solution (100 ml) and the mixture was stirred during heating at 115-120 °C for 10 h. The resin was filtered off and washed with NaCl solution (0.2 M) until the filtrate was free from ethylenediamine. The resin was washed with water and then with methanol and consequently dried at 50 °C. The amine content of the resin was determined using the volumetric method [20]. A total amine value of ACPN resin was estimated as 4.6 mmol/g.

2-3. Synthesis of Iminodiacetate Chelating Resin (CPN-IDA)

Iminodiacetate chelating resin (CPN-IDA) was prepared by heating and stirring a mixture of ACPN (5 g) and sodium monochloroacetate (40 g) in 200 ml of water at 75 °C for 72 h. The resin was filtered off, repeatedly washed with distilled water and acetone and finally air dried.

3. Characterization of the Resins

Fourier transform infrared spectra (FTIR) were recorded on a Shimadzu 8201 PC spectrophotometer in the range of 400 to 4,000 cm^{-1} in KBr phase.

Water regain (W%) is defined as amount of water absorbed by one g of dry chelating resin. Water regain was determined according to the previously reported procedure [19]. 1.0 g of the swollen chelating resin was packed in a column with suitable size and centrifuged for 5 min at 3,000 rpm to remove excess water and then weighed. The resin was then dried at 75 °C until complete dryness, then weighed again. To calculate water regain Eq. (1) was used [19].

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

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

The surface morphology of chelating resin (CPN-IDA) and its complexes chelated with metal ions were examined by using FEI QUANTA 250 FEG scanning electron microscope (SEM) after gold coating at 20 KV and 5000 magnifications.

The thermal degradation of the chelating resin was investigated using SDT Q600 TA instrument, USA. The experiment was performed under nitrogen atmosphere and the sample was heated from room temperature to 700 °C with heating rate of 10 °C min^{-1}.

4. Adsorption Experiments

4-1. Uptake of Metal Ions Using Batch Method

Batch adsorption studies were examined by contact of 0.1 g of chelating resin (CPN-IDA) with 100 mL aqueous solution containing single-metal ion in 250 ml conical flask. The mixture was agitated at 250 rpm for 2 h at 25 °C unless otherwise stated. The desired pH was adjusted using HNO_3 or NaOH solution. After adsorption, the remaining concentration of metal ions in the solution was analyzed by Hitachi atomic absorption Z-6100 polarized Zeeman. Adsorption experiments were replicated three times for the sake of accuracy. The amount of adsorbed metal ions by the chelating resin was calculated according to Eq. (2).

$$q = \frac{(C_0 - C_e)V}{W} \qquad (2)$$

where q is the adsorption capacity ($mmolg^{-1}$), C_o and C_e are initial and the equilibrium ion concentrations (mmol L^{-1}), respectively, V is the volume of the aqueous phase (L), and W is the mass of dry CPN-IDA (g).

To determine the optimum pH value for adsorption of metal ions by CPN-IDA, adsorption experiments were conducted at different pH values by mixing 0.1 g of CPN-IDA with 100 ml (5 mmol L^{-1}) metal ion solution. The contents were shaken for 2 h at controlled pH values. Adsorption experiments were avoided above neutral pH due to the precipitation of metal hydroxides in alkaline medium.

Adsorption isotherms were conducted by mixing 0.1 g resin with 100 ml of solution containing metal ions at definite concentrations in the range of (1-20 mmol L^{-1}) and at optimum pH values. After being shaken for 2 h, the solution was filtered and the residual concentration metal ion in solution was determined.

In kinetic studies, 0.1 g of CPN-IDA and 100 ml of metal ion solution were mechanically stirred at the optimum pH and at maximum initial concentration of metal ions. The samples of the aqueous solution were withdrawn at pre-settled time interval (5 min, 10 min, 15 min, etc.) to determine the residual concentration of the metal ions.

Thermodynamic studies were carried out for other sets of samples containing 0.1 g of the resin in 100 ml of metal ion solution with initial concentration of 1 mmol L^{-1}. The samples were stirred at 25 °C, 35 °C, and 45 °C under the optimum shaking time and pH value. After adsorption, the remaining concentration of metal ion was measured as previously mentioned.

4-2. Uptake of Metal Ions Using Column Method

Packed bed column experiments were performed in a glass column with 1.0 cm of internal diameter and 10 cm height. The column was packed with one gram of CPN-IDA. Solutions containing metal ions Cu(II), Cd(II) and Pb(II) with initial concentration of 5 mmol L^{-1} at optimum pH value and 25 °C were pumped in an upward direction through the column at a flow rate of 1 ml min^{-1}. Several samples were collected at the column outlet and the metal ions concentration was analyzed at different time intervals as described above. The column experiments were stopped when the outlet concentration of metal ions was equal to the initial concentration of metal ions.

The used chelating resin was eluted using 0.2 M HNO_3. Then the resin was carefully washed with distilled water and finally it was washed with 0.2 M NaOH solution. After regeneration, the resin was again carefully washed with distilled water to become ready for reuse. The sorption/desorption process of metal ions was carried out for five times to evaluate the adsorption capacity.

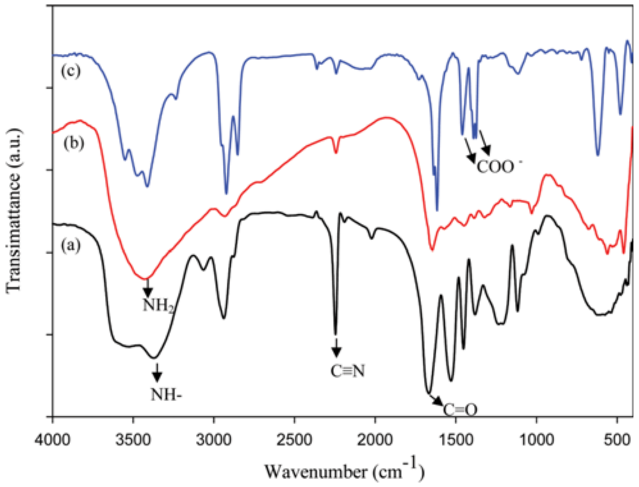
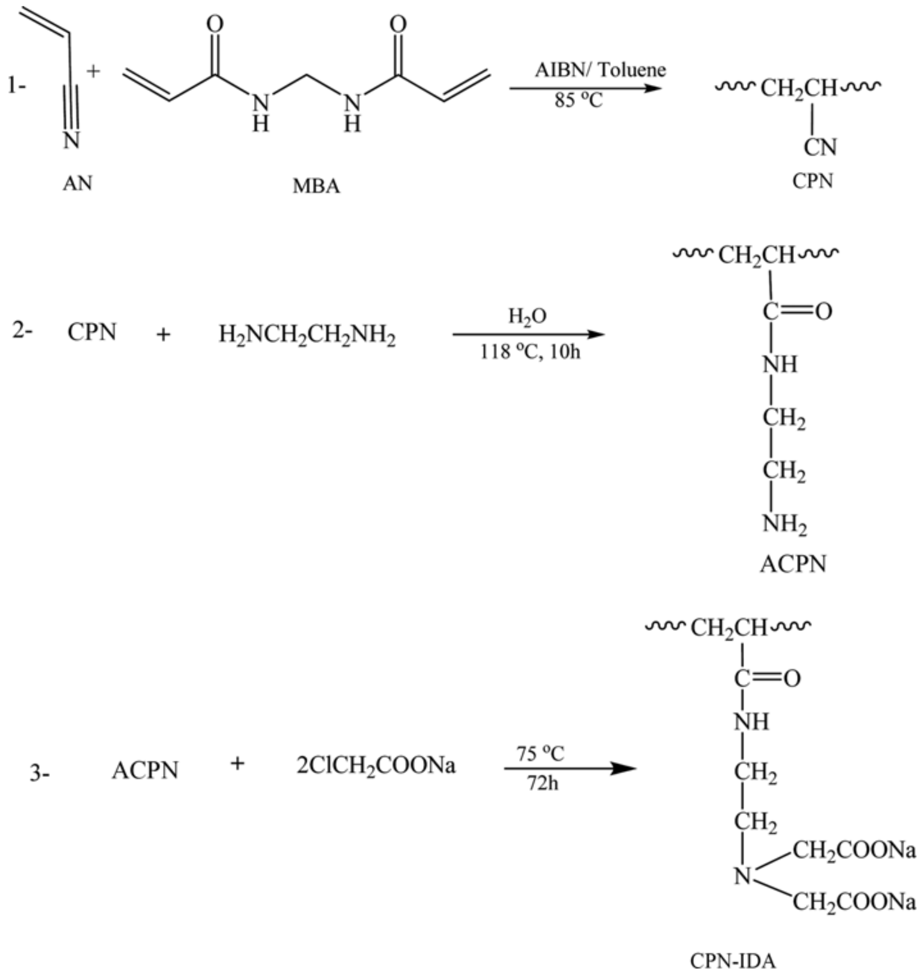


Fig. 1. IR spectra of (a) CPN, (b) ACPN and (c) CPN-IDA.

RESULTS AND DISCUSSION

1. Characterization of the Synthesized Resins

The structure of the prepared resins was confirmed by FTIR spectroscopy and the spectra are shown in Fig. 1. The IR spectrum of CPN (Fig. 1(a)) exhibited bands at 3,371, 2,245, and 1,666 cm^{-1} which are characteristic of N-H, C≡N, and C=O, respectively [11]. The IR spectrum of ACPN (Fig. 1(b)) showed a decrease in the intensity of C≡N peak (2,245 cm^{-1}) (Fig. 1(b)), which confirms the conversion of C≡N to amine (3,431 cm^{-1}). With respect to CPN-IDA, the carboxylate groups showed strong peak near 1,676 cm^{-1} (Fig. 1(c)). Also, the new bands at 1,455 and 1,397 cm^{-1}, assigned to carboxylic groups, were observed in the FTIR spectra of the imi-



Scheme 1. Schematic illustration of the preparation process of CPN-IDA chelating resin.

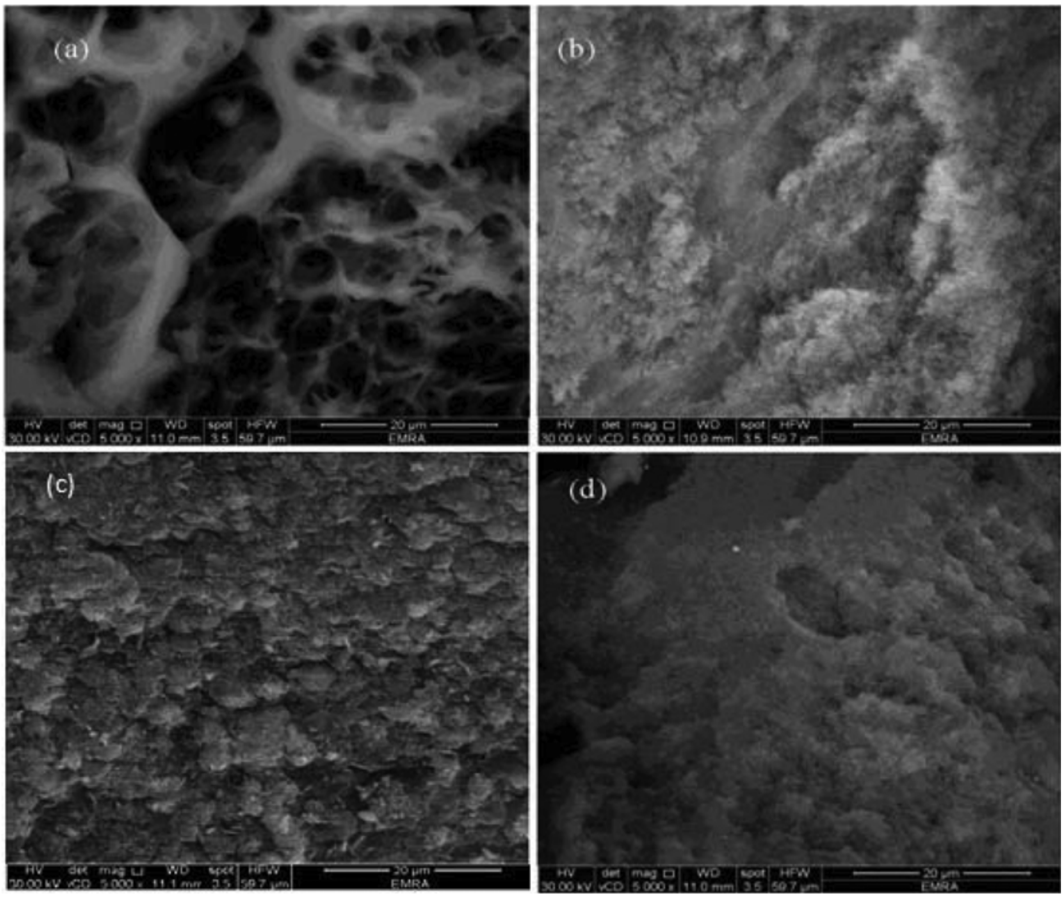


Fig. 2. SEM micrographs of CPN-IDA resin (a), CPN-IDA-Cu (b), CPN-IDA-Cd (c), and CPN-IDA-Pb (d) with magnification of 5000×.

nodiacetic acid resin [12,22].

The water regain (W%) value for iminodiacetate resin (CPN-IDA) was found to be 29.3 mmol/g (W%=52.7). This high value is explained by the hydrophilic surface of the chelating resin which enhances the adsorption of metal ions.

The SEM images of CPN-IDA and its metal complexes in 5000x magnifications are indicated in Fig. 2. Surface morphology of CPN-IDA resin before sorption of metal ions (Fig. 2(a)) indicates many pores with wide distribution of diameters on the surface of the chelating resin, which may be important for uptake of metal ions. After sorption of metal ions, the resin surface became completely packed and the pores disappeared. This is related to sorption of metal ions onto the surface of the resin.

The surface texture measurements of CPN-IDA chelating resin were measured using an N_2 sorptometer. The BET surface area of the chelating resin was found to be 52 m^2/g with total pore volume of 0.01 cm^3/g. The average pore diameter was found to be 12.2 nm and is considered as mesoporous structure [23]. It improves the transfer of metal ions to the internal sorption sites.

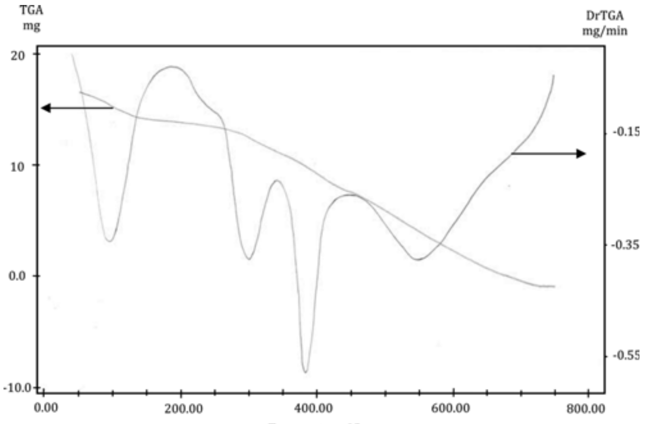


Fig. 3. TGA/DrTGA Thermal analysis of CPN-IDA chelating resin.

The thermal behavior of CPN-IDA chelating resin was measured by TGA/DrTGA and the obtained results are illustrated in Fig. 3. Several changes were observed with elevation of the sample temperature. An early weight loss of 15% was observed below 150 °C. This initial step corresponds to the endothermic peak in the DrTGA curve at 94 °C, which may be attributed to the loss of adsorbed water molecules in the external surface and internal pores or cavities of the chelating resin. The high water content confirms the hydrophilicity of iminodiacetate chelating resin. A weight loss of 30-33 wt% between 220 and 350 °C was observed. It shows endothermic beak at 300 °C in DrTGA curve. It is attributed to the collapse of organic functional groups anchored on the chain. A major weight loss above 350 °C which has endothermic peak at 387 and 544 °C and is attributed to the decomposition of the resid-

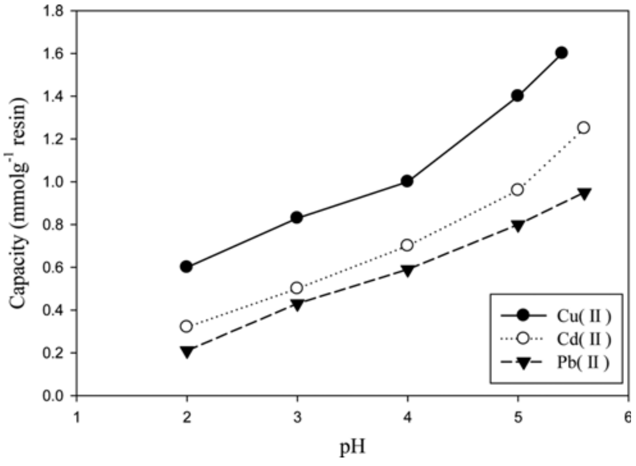


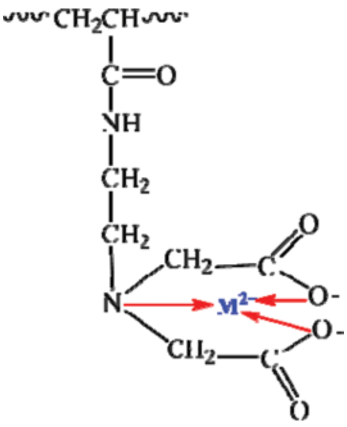
Fig. 4. Effect of pH on the uptake of Cu(II), Cd(II) and Pb(II) ions 100 ml (5 mmolL^{-1}); 0.1 g CPN-IDA resin; contact time 2 h; shaking rate 250 rpm, 25 °C.

ual polyacrylonitrile chains.

2. Uptake of Metal Ions by Batch Technique

2-1. Optimum pH of Metal Ions Adsorption

Batch technique was used to determine the effect of pH on the adsorption of metal ions at 25 °C and the results are illustrated in Fig. 4. In this study the adsorption property of the chelating resin was investigated in the pH range of 1.0-5.6 (experiment showed that further increase of pH resulted in the hydrolysis and precipitation of metal ions). These results are in good agreement with those described by earlier work [8,10-12,14]. At low pH value, hydrogen ion (H^+) reacts with carboxylate ions (COO^-) and tertiary amine (R_3N) and thus, the chelating resin has low sorption capacity. Note that no uptake of metal ion was obtained at pH=1.0 since, at this pH value, the concentration of hydrogen ion was greater than concentration of metal ion; accordingly, the adsorbed amount of metal ions being zero should be acceptable. These results are in agreement with previous studies [12,14,24]. With rising of pH, the uptake of metal ions increases until reaching the maximum value (optimum) at the natural pH of the metal ion solution (Cu(II) 5.4, Cd(II) 5.6, Pb(II) 5.6). Therefore, in this study all the following experiments were done at these optimum pH values. Above the natural pH, metal (II) hydroxide precipitate is formed and adsorption cannot be measured accurately. The possible chelation model of iminodiacetate resin with metal ions is indicated in Scheme 2.



Scheme 2. Possible model of iminodiacetate chelation with metal ions.

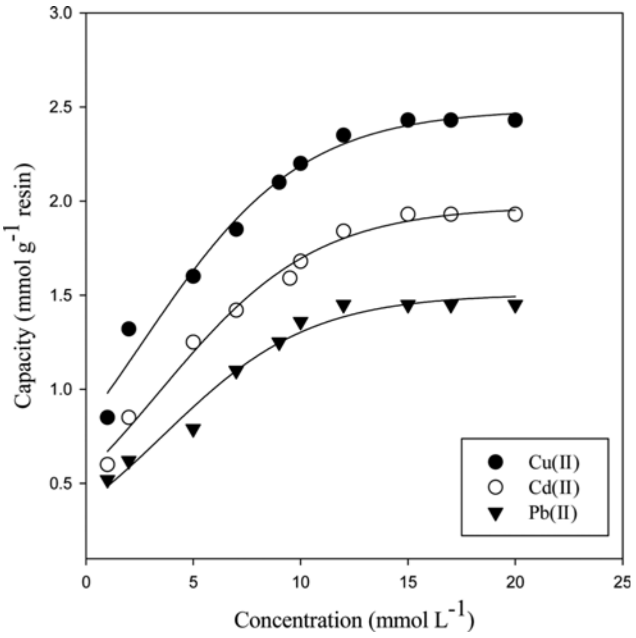


Fig. 5. Adsorption isotherms of Cu(II), Cd(II) and Pb(II) ions using CPN-IDA chelating resin (initial concentration 1.0-20 mmolL^{-1}, 0.1 g CPN-IDA, optimum pH values, shaking rate 250 rpm, contact time 2 h at 25 °C).

2-2. Effect of Initial Concentration and Equilibrium Isotherm Models

The effect of initial metal ion concentrations in the range of 1-20 mmolL^{-1} on adsorption was investigated and the results are shown in Fig. 5. It is seen that the amount of metal ion adsorbed on CPN-IDA increased with the increase in initial metal ion concentration before reaching a plateau. The adsorption capacity (mmolg^{-1}) was calculated at the optimum pH and 25 °C, Table 1. The results indicated that the maximum adsorption capacity of Cu(II), Cd(II) and Pb(II) reached 2.43, 1.93 and 1.45 (mmolg^{-1}) at maximum initial concentration of 15, 15 and 12 (mmolL^{-1}), respectively. These differences in metal ions uptake are possibly related to the difference in ionic radius of these ions. The ionic radius of these metal ions is in the order of Cu(II) (0.70 Å)<Cd(II) (0.92 Å)<Pb(II) (1.12 Å) [25]. This means that the smaller the ionic radius, the higher the amount of metal ions adsorbed. Cu(II) was the most adsorbed by iminodiacetate chelating resin (Fig. 5) because of its smaller ionic radius since it is easily taking place in the pores of chelating resin.

A comparison between the present (CPN-IDA) chelating resins with those of different types of sorbents in lately published articles is listed in Table 1. With careful inspection of the results listed in Table 1, it can be concluded that the prepared resin-Cu has higher capacity than previously reported data [8,13,17,18]. Moreover, resin-Cd is much higher than previously prepared Cd-containing resin [12,17-19] and comparable with other sorbents [5,11]. Whereas, resin-Pb was more or less than previously reported Pb-containing

Table 1. Comparison of maximum adsorption capacity of CPN-IDA chelating resin with those of some other chelating resins reported in literature for the adsorption of Cu(II), Cd(II) and Pb(II)

Adsorbents	Metal ions	Sorption capacity (mmol g^{-1})	Conditions	Ref.
Magnetic hydroxamic acid modified polyacrylamide adsorbent (M-PAM-HA)	Cd(II) and Pb(II)	1.92 and 0.88	pH 4.5, 25 °C	[5]
Amidoxime chelating resin (AO AN/MA)	Cu(II) and Pb(II)	2.01 and 0.06	pH 3.0, 25 °C	[8]
Dithiocarbamate chelating resin (DTMAN)	Cd(II) and Pb(II)	1.94 and 1.14	pH 6.0 and 5.6, 25 °C	[11]
AAM/MBA iminodiacetate	Cd(II) and Pb(II)	1.77 and 1.7	pH 6.0 and 5.6, 25 °C	[12]
Poly (MVE-alt-MA-1)	Cu(II) and Cd(II)	1.28 and 1.39	pH 5.0, 25 °C	[13]
GMA/DVB magnetic resin containing Iminodiacetate group	Cd(II) and Pb(II)	2.0 and 2.3	pH 6.6 and 6.0, 25 °C	[16]
Iminodiacetate chelating resin NJC-702	Cu(II), Cd(II) and Pb(II)	2.27, 0.65 and 1.27	pH 5.0, 30 °C	[17]
Iminodiacetate chelating resin IRC748	Cu(II), Cd(II) and Pb(II)	1.81, 0.8 and 1.18	pH 5.0, 30 °C	[18]
Iminodiacetate chelating resin NDC702	Cu(II), Cd(II) and Pb(II)	2.04, 0.82 and 1.28	pH 5.0 and 3.0, 25 °C	[18]
Iminodiacetate chelating resin (CR-10)	Cd(II) and Pb(II)	0.81 and 0.69	pH 5.5, 20 °C	[19]
Iminodiacetate chelating resin (CR-15)	Cd(II) and Pb(II)	0.99 and 0.51	pH 5.5, 20 °C	[19]
CPN-IDA chelating resin	Cu(II), Cd(II) and Pb(II)	2.43, 1.93 and 1.45	pH 5.4, 5.6 and 5.6, 25 °C	This work

Table 2. Parameters of Langmuir, Freundlich and Temkin isotherms for ion exchange of metal ions 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
Cu(II)	2.59	0.828	0.990	0.224	1.33	0.976	61.72	0.347	0.937
Cd(II)	2.19	0.950	0.993	0.374	1.36	0.973	6.19	0.421	0.984
Pb(II)	1.89	0.279	0.991	0.561	0.352	0.947	7.04	0.419	0.958

sorbents. Generally, these previously reported data proved that the synthesized (CPN-IDA) chelating resin in this work has a good advantage for removing heavy metal ions from aqueous media.

Adsorption isotherms are used to describe the distribution of the metal ions between aqueous solution and chelating resin at equilibrium state. Adsorption data are usually evaluated by adsorption isotherms, such as Langmuir, Freundlich and Temkin isotherms.

The Langmuir isotherm model is developed to illustrate the monolayer uniform adsorption of solute molecules onto a homogenous and flat surface of sorbents. Langmuir adsorption model equation is given in Eq. (3) as follows [26]:

$$\frac{C_e}{q}=\frac{C_e}{Q_{max}}+\frac{1}{KQ_{max}} \tag{3}$$

where C_e is the concentration after equilibrium (mmolL^{-1}), q is the amount of metal ions adsorbed at equilibrium (mmolg^{-1}), K (Lmmol^{-1}) is the Langmuir affinity constant and Q_{max} (mmolg^{-1}) is the maximum amount of metal ions adsorbed assuming monolayer of metal ions uptaken by the chelating resin. The parameters of Langmuir equation are summarized in Table 2. Langmuir isotherm model also can be expressed in terms of the dimensionless constant (separation factor, R_L) [27] which is indicated as follows:

$$R_L=\frac{1}{1+KC_o} \tag{4}$$

where K is the Langmuir constant (related to energy of adsorption) and C_0 is the initial metal ion concentration (mmolL^{-1}). R_L values indicates the adsorption nature to be unfavorable (R_L>1), linear (R_L=1), favorable (0<R_L<1) and irreversible (R_L=0) [28,29]. Plotting R_L against C_0 is illustrated in Fig. 6. The calculated values of R_L are greater than zero but less than one for all metal ions, indicating that Langmuir isotherm is favorable. As demonstrated in Fig. 6, the R_L values decreased with the increase in the initial

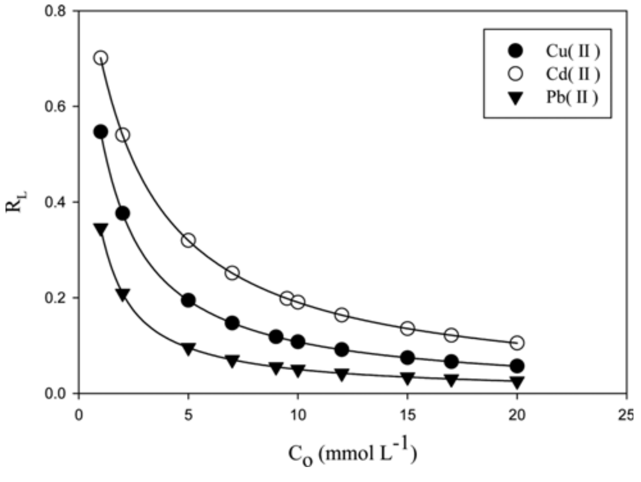


Fig. 6. Variation of adsorption intensity (R_L) with initial metal ion concentration (C_o).

concentration of metal ions, which reveals that thee equilibrium sorption is favorable at higher initial concentration.

Freundlich isotherm model is commonly used to describe the adsorption process occurring on the adsorbent with heterogeneous adsorption system. The linearized form of Freundlich isotherm model is mathematically written as Eq. (5) [30]:

$$\log q = N \log C_e + \log K_F \tag{5}$$

where q and C_e are defined as above, K_F and N are the Freundlich constants related to the adsorption capacity (mmolL^{-1}) and sorption intensity, respectively. The values of K_F and N were calculated from the slopes and intercepts of the straight lines and are reported in Table 2. Similar to R_L values of Langmuir model the parameter N values in the Freundlich model show that the isotherm is considered to be favorable because ($0<N<1$). It is also noticed that the correlation coefficient is much lower than in the case of the Langmuir equation.

The Temkin isotherm was also used for modeling adsorption isotherm and can be described by Eq. (6)[31]:

$$q = B \ln K_T + B \ln C_e \tag{6}$$

where B and K_T are constants related to surface heterogeneity of the adsorbent and the equilibrium binding constant corresponding to the maximum binding energy, respectively, and they are listed in Table 2.

The correlation coefficients (R^2) and the isotherm constants were calculated and reported in Table 2. After comparing the correlation coefficients of the three models, it is clear that Langmuir model closely fits to the experimental data very well with high correlation coefficients of ($0.990 \le R^2 \le 0.993$) as compared to the ones given by Freundlich model ($0.947 \le R^2 \le 0.976$) and Temkin model ($0.937 \le R^2 \le 0.984$).

2-3. Adsorption Kinetics

Adsorption kinetic studies of metal ions were done at 25 °C, optimum pH and maximum concentration of metal ions. Fig. 7 shows the effect of shaking time (contact time) on sorption of metal ions. As indicated in Fig. 7, the sorption process attains equilibrium within 70, 70 and 60 min for Cu(II), Cd(II) and Pb(II), respectively. Half-load time ($t_{1/2}$) was less than 10 min for Cu(II) and less than 20 min for Cd(II) and Pb(II). The high initial sorption capacities reveal that the adsorption of metal ions occurs mainly on the surface of chelating resin beads [32].

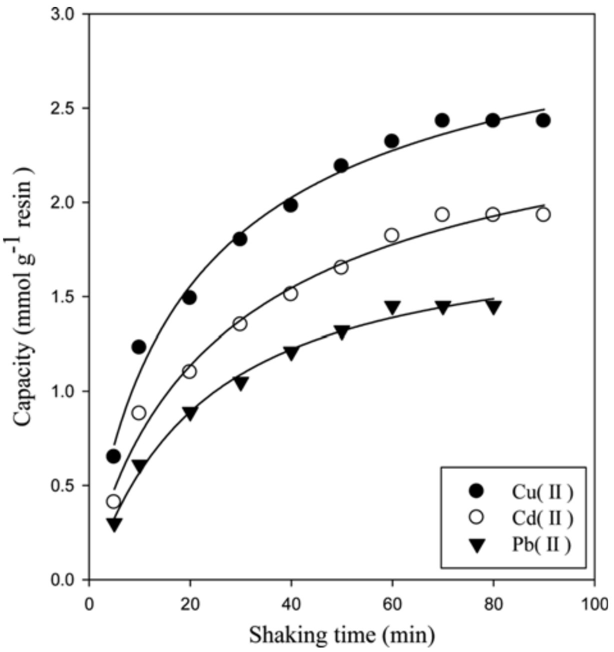


Fig. 7. Effect of shaking time on the uptake of Cu(II), Cd(II) and Pb(II) using CPN-IDA (initial concentration of metal ions 15, 15 and 12 (mmolL^{-1}), respectively). 0.1 g CPN-IDA, optimum pH values, shaking rate 250 rpm at 25 °C).

The adsorption kinetic studies were used to investigate the reaction pathway and mechanism which controls the sorption process. The most commonly kinetic models used to describe the adsorption kinetics and rate limiting step during sorption process are Lagergren's pseudo-first order, pseudo-second order and intra particle diffusion. It was revealed that the pseudo-first-order kinetic model [33] (Eq. (7)) is the most suitable equation in case of low concentration of metal ions.

$$\log(q - q_t) = \log q - \left(\frac{K_{ads}}{2.303}\right)t \tag{7}$$

where K_{ads} is the Lagergren rate constant (min^{-1}) of the adsorption, q and q_t are the adsorption capacity (mmolg^{-1}) at equilibrium and at time t (min), respectively. The Lagergren constants were estimated and tabulated in Table 3.

The adsorption data were also treated by pseudo-second order

Table 3. First-order, second-order and intra particle diffusion rate constants

Equations	Parameters	Cu(II)	Cd(II)	Pb(II)
Pseudo-First order kinetic equation	q (mmolg^{-1})	2.37	1.86	1.48
	K_{ads} (min^{-1})	0.046	0.023	0.032
	R^2	0.973	0.980	0.984
Pseudo-Second-order kinetics	q (mmolg^{-1})	3.13	2.61	1.93
	K_2 (g mmol^{-1} min^{-1})	0.046	0.036	0.0414
	h (mmol g^{-1} min^{-1})	0.45	0.25	0.15
	R^2	0.994	0.995	0.993
Intraparticle diffusion equation	K_{id} (mmolg^{-1} min$^{-1/2}$)	0.257	0.219	0.172
	R^2	0.962	0.974	0.955

kinetic model which was presented by Ho [34] as follows:

$$\frac{t}{q_t}=\frac{1}{K_2q^2}+\left(\frac{1}{q}\right)t \tag{8}$$

$$h=K_2q^2 \tag{9}$$

where K_2 (g mmol^{-1} min^{-1}) is the rate constant of pseudo second order reaction adsorption and h (mmol g^{-1} min^{-1}) is the initial adsorption rate constant. The obtained kinetic parameters for such model are presented in Table 3. The results clearly show that R^2 values of the second order kinetic model are closer to 1 than the results obtained from the first-order kinetic model. Consequently, the second-order kinetics fits with the adsorption of Cu(II), Cd(II) and Pb(II) onto CPN-IDA chelating resin. Therefore, the calculated initial rate constants (h) followed the order of Cu(II)>Cd(II)>Pb(II), indicating higher affinity of CPN-IDA towards Cu(II) more than that of Cd(II) or Pb(II). Additionally, the values of adsorption constants (K_2) may be related to the attraction between metal ions and the electron rich sites in chelating resin CPN-IDA. Therefore, there may be a direct relation between K_2 values [Cu(0.046)>Pb(0.0414)>Cd(0.036)] and electron affinity of the studied metal ions (Kj mol^{-1}) [Cu(118)>Pb(35)>Cd(0)] [25] since both of them have the same order.

To examine how diffusion influenced the rate of the sorption of metal ions, a model of intraparticle diffusion was used [35] according to the following Eq. (10):

$$q_t=K_{id}t^{0.5} \tag{10}$$

where K_{id} (mmolg^{-1} min$^{-0.5}$) is the intraparticle diffusion rate constant. K_{id} can be obtained from the plots of q_t (adsorption capacity at any time, mmol g^{-1}) against the square root of the time. The parameters of these plots are reported in Table 3. With respect to Eq. (9), if this plot gives a straight line, then intraparticle diffusion can be accepted as the only rate-controlling step for the adsorption process. Fig. 8 shows the plots with multi-linearity for all metal ions, which indicates that the adsorption process includes more than one kinetic stage. For instance, the CPN-IDA exhibited three stages, which can be related to each linear portion of the figure. The first linear step was related to the diffusional process of metal ions from solution to CPN-IDA surface [36], hence, was the fastest adsorption stage. The second portion, attributed to intraparticle diffusion, gradual sorption step. The third stage may be regarded as the final equilibrium stage, diffusion of metal ions through smaller pores, which is followed by the establishment of equilibrium [36].

2-4. Adsorption Thermodynamics

Thermodynamics of the adsorption process was investigated by mixing 100 ml of 1.0 mmol L^{-1} metal ions with 0.1 g of chelating resin under continuous stirring until equilibrium at optimum pH value and at different temperatures (25 °C, 35 °C and 45 °C). The equilibrium distribution coefficient for metal ion uptake, K_d, was estimated by Eq. (11) [37].

$$K_d=\frac{C_o-C_e}{C_e}\times\frac{V}{W} \tag{11}$$

where C_o and C_e are the initial and equilibrium metal ions concentration (mmolL^{-1}), V is the total volume of the solution in (L) and W is the weight of CPN-IDA used in grams. Thermodynamic parameters including free energy change (ΔG^o_{ads}), enthalpy change (ΔH^o_{ads}) and entropy (ΔS^o_{ads}) of sorption process can be respectively calculated by the following equations [38,39].

$$\Delta G^o_{ads}=-RT\ \ln K_d \tag{12}$$

$$\ln K_d=\frac{\Delta S^o_{ads}}{R}-\frac{\Delta H^o_{ads}}{RT} \tag{13}$$

where T is the absolute temperature (K); R is the universal gas constant (8.314 Jmol$^{-1}\cdot$K^{-1}). From a linear plot between ln K_d versus 1/T the values of ΔH^o_{ads} and ΔS^o_{ads} were obtained from the slope

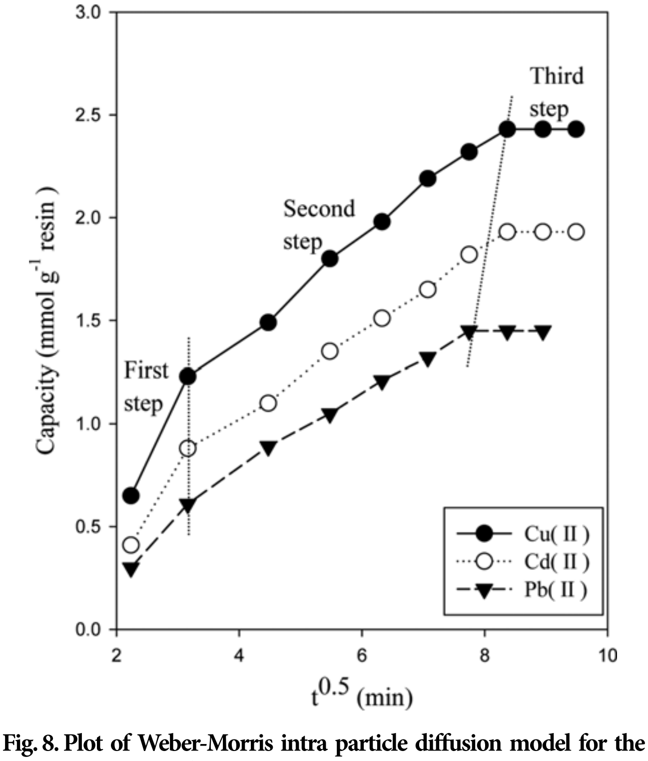


Fig. 8. Plot of Weber-Morris intra particle diffusion model for the adsorption of metal ions on chelating resin.

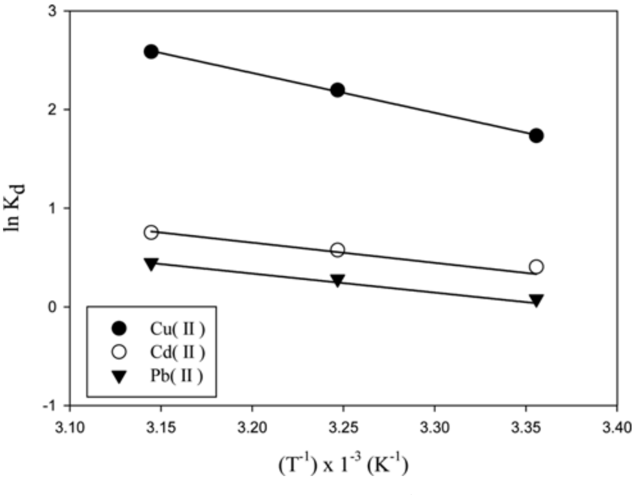


Fig. 9. Arrhenius plot of ln K_d against (T^{-1}) for the adsorption of metal ions on chelating resin.

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

Metal ion	$-\Delta G^{o}_{ads}$ (kJ/mol)			ΔH^{o}_{ads} (kJ/mol)	ΔS^{o}_{ads} (J/mol)	R^2
	25 °C	35 °C	45 °C			
Cu(II)	4.29	5.62	6.83	33.58	127.12	0.999
Cd(II)	0.799	1.47	1.99	17.00	59.77	0.994
Pb(II)	0.297	0.721	1.18	12.87	59.63	0.999

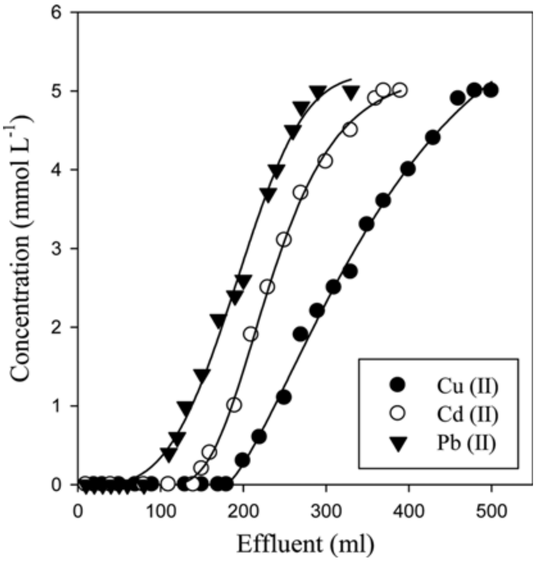


Fig. 10. Break-through curves for Cu(II), Cd(II) and Pb(II); initial concentration is 5.0 mmolL^{-1}, flow rate is 1.0 mL min^{-1} at optimum pH and at 25 °C.

and the intercept (Fig. 9), respectively. Thermodynamic parameters including ΔG^{o}_{ads}, ΔH^{o}_{ads} and ΔS^{o}_{ads} for adsorption of metal ions using CPN-IDA are reported in Table 4. The positive values of ΔH^{o}_{ads} confirm endothermic nature of the adsorption process. It was also found that the adsorption capacity increases with the temperature. This may be due to its effect on the ionization degree of the carboxylate groups associated to iminodiacetate chelating resin [40]. Additionally, the positive values of ΔS^{o}_{ads} mean that the randomness increased at the solid-solution interface during the fixation of metal ions onto CPN-IDA surface, which suggests that the uptake of metal ions is an entropy-driven process [41]. As well, the positive values of ΔS^{o}_{ads} may be due to the exchange of the metal ions with more mobile ions ($RNa_2+M^{2+}\rightarrow RM+2Na^{+}$) present on the exchanger, which would cause increase in the entropy, during the adsorption process [42]. Finally, the negative values of ΔG^{o}_{ads} confirm the spontaneous nature of the uptake process. A more negative of ΔG^{o}_{ads} with increasing temperature implies a greater driving force of sorption at higher temperature, which in return leads to the higher uptake of metal ions. This possibly is attributed to the dehydration of metal ions, which facilitates their interaction with the chelating active groups [43].

3. Adsorption of Metal Ions Using Column Technique

Iminodiacetate chelating resin (CPN-IDA) was also tested in a packed bed column for the removal of Cu(II), Cd(II) and Pb(II). The break-through curves of metal ions adsorption are shown in Fig. 10. The solution containing single metal ion (1.0 mmol L^{-1}) was allowed to flow gradually through the glass column at 25 °C with a flow rate of 1.0 mLmin^{-1}. The obtained breakthrough curves showed that using 1.0 mLmin^{-1} flow rate of metal ions, solutions start to break-through at 180, 150, and 110 mL of effluent for Cu(II), Cd(II) and Pb(II), respectively. Adsorption capacities of the metal ions were estimated and listed in Table 5.

4. Elution and Regeneration Cycles

The iminodiacetate chelating resin (CPN-IDA) saturated with metal ions were eluted with 0.2 M HNO_3 solution at 25 °C. It was formerly mentioned that the uptake of the metal ions was equal and almost zero at pH less than or equal to 1. This illustrates that 0.1 M H^+ could prevent the uptake of metal ions. Accordingly, to enhance the elution efficiency 0.2 M H^+ was applied. To check the reusability of (CPN-IDA) chelating resin, five consecutive adsorption-desorption cycles were performed. From the uptake-elution process, it is clear that the adsorption capacities were barely affected after the repeated five regeneration cycles. The sorption capacity decreased from 100% in all metal ions to 91, 86 and 90% for Cu(II), Cd(II), and Pb(II), respectively, after five adsorption-desorption cycles. These results suggest that CPN-IDA is a durable adsorbent in removal of metal ions from waste solution. After breakthrough, HNO_3 solution was passed through the column to remove metal ions from resin-metal ion complexes. Hydrogen ions could replace the metal ions adsorbed by (-COONa) groups within CPN-IDA to form carboxylic acids (-COOH) and quaternary ammonium salts, respectively. If CPN-IDA was used to uptake metal ions in the earlier sorption conditions, no more than 40% of initial uptake value would be recorded. However, when CPN-IDA was neutralized with NaOH solution to form carboxylate salt (-COONa) and tertiary amine, the sorption capacities could reach 86-91% of the first

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

Metal ion	Capacity (mmol of M(II) g^{-1} resin) %					
	Recycle 0	Recycle 1	Recycle 2	Recycle 3	Recycle 4	Recycle 5
Cu(II)	100[a]	99	96	94	92	91
Cd(II)	100[b]	96	93	92	89	86
Pb(II)	100[c]	98	97	95	92	90

[a] Cu(II); Sorption capacity of the original chelating resin was 1.48 mmolg^{-1} resin

[b] Cd(II); Sorption capacity of the original chelating resin was 1.13 mmolg^{-1} resin

[c] Pb(II); Sorption capacity of the original chelating resin was 0.89 mmolg^{-1} resin

sorption step (Table 5). Similar results were obtained by other researchers [12,14]. By regeneration of iminodiacetate chelating resin, the initial adsorption capacities did not exceed 40%. However, after neutralization of the resin with NaOH, the resorption capacities exceeded 80% of its initial value.

CONCLUSIONS

A new iminodiacetate chelating resin CPN-IDA was successfully prepared for removal of Cu(II), Cd(II) and Pb(II) from aqueous solutions. The sorption of metal ions using CPN-IDA is depend on several factors such as pH, concentration of metal ions, shaking contact time and solution temperature. In batch equilibrium adsorption method, the optimum sorption pH for all metal ions was found in the range of 5.4 to 5.6 depending on the metal ion used. The maximum sorption capacity of CPN-IDA followed the order Cu(II)>Cd(II)>Pb(II). Half- load time ($t_{1/2}$) was less than 10 min for Cu(II) and less than 20 min for Cd(II) and Pb(II). The minimum shaking time for reaching the equilibrium was about 70, 70 and 60 min for Cu(II), Cd(II) and Pb(II), respectively. The Langmuir isotherm model provided the best fit of the equilibrium sorption data and illustrate that the monolayer adsorption is dominant. The kinetic experiments showed that adsorption data were best fitted by the pseudo-second-order kinetic model. Thermodynamic parameters suggest that sorption process of metal ions on CPN-IDA is spontaneous and endothermic in nature for all metal ions. The prepared iminodiacetate chelating resin was well efficient for removal of Cu(II), Cd(II) and Pb(II) by batch method in addition to column method. The resin could be regenerated using 0.2 M HNO_3 followed by 0.2 M NaOH and CPN-IDA was used repeatedly for five times with more than 86% of initial adsorption capacities. Finally it can be concluded that CPN-IDA is a good resin for adsorption of metal ions from aqueous media, due to its efficiency and durability.

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