

Separation and Preconcentration of Some Heavy-Metal Ions Using New Chelating Polymeric Hydrogels

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ABSTRACT: Two new chelating polymeric hydrogels, crosslinked polyacrylamide/triethylenetetraamine/CS₂Na (hydrogel I) and crosslinked polyacrylamide/diethylenetriamine/CS₂Na (hydrogel II), were prepared by the transamidation and dithiocarbamylation of crosslinked polyacrylamide. The products were characterized with elemental analysis and IR spectroscopy. In both polymeric hydrogels, the optimum pH for the removal of Cd(II), Pb(II), and Zn(II) ions ranged from 7 to 8, from 6 to 7, and from 7 to 8, respectively. The sorption isotherms of the investigated metal ions on the prepared hydrogels were developed, and the equilibrium data fitted the Langmuir and Freundlich isotherm models well. At the optimum pH for each metal ion, the maximum sorption capacities of hydrogel I toward Cd(II), Pb(II), and Zn(II) ions, estimated from the Langmuir model, were 5.3, 0.63, and

1.27 mmol/g, respectively, and those of hydrogel II were 4.1, 0.59, and 0.89 mmol/g, respectively. The experimental sorption capacities of hydrogel I toward Cd(II), Pb(II), and Zn(II) ions were 4.5, 0.6, and 1.2 mmol/g, respectively. In the case of hydrogel II, the capacities were 3.7, 0.52, and 0.88 mmol/g in the same prescribed order. The thermodynamic parameters (the free energy of sorption, enthalpy change, and entropy change) for cadmium, lead, and zinc sorption on the prepared polymers were also determined from the temperature dependence. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 1335–1344, 2009

Key words: addition polymerization; copolymerization; crosslinking; functionalization of polymers; graft copolymers

INTRODUCTION

The selective and quantitative separation of metal ions related to water pollution has become increasingly important in recent years. Chelating sorbents obtained by the immobilization of organic reagents on solid supports (adsorbed or chemically bonded) have found widespread applications in the preconcentration and separation of trace metal ions from a variety of matrices.^{1,2} The tailoring of chemically bonded chelating agents for specific needs permits the use of selective or general concentration schemes and also allows the recycling of the chelating agents.^{3,4} Additionally, interest in chelating polymers has also stemmed from the need to separate precious metals from aqueous solutions.^{5–7} Several organic reagents, such as salicylaldehyde,⁸ dithizone,⁹

N-benzoylthiourea,¹⁰ formyl salicylic acid,¹¹ 2-hydroxyacetophenone,¹² ethylenediamine and (3-amino-1,2,4-triazole-5-thiol),¹³ thiol,¹⁴ triethylenetetraamine,¹⁵ dithiocarbamate,¹⁶ and methylthiourea,¹⁶ have been immobilized on various solid supports for such purposes.

Sulfur-containing chemical groups have been used as selective ligands with high bond stability for transition-metal ions. Moreover, dithiocarbamate resins show very little affinity toward alkali and alkaline earth metal ions.¹⁷ Therefore, resins containing dithiocarbamate groups can be applied very effectively for the selective removal of several trace and heavy metals.

In this article, the synthesis, characterization, and sorption behavior of dithiocarbamate resins derived from crosslinked polyacrylamide (CPAAm) are described. The analytical characteristics of the chelating resins, such as the pH, adsorption time, and sorption capacity toward the tested metal ions [Cd(II), Pb(II), and Zn(II) ions], were established, and the optimum sorption conditions were also determined. Equilibrium isotherms were measured to determine the capacity of the new hydrogels for the tested metal ions. The most common types of models describing this type of system are the Langmuir and Freundlich models. The Langmuir adsorption model is based on the assumption that the

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maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface. The Langmuir equation can be described with the following linearized form:¹⁸

$$C_e/q_e = 1/Q_0b + C_e/Q_0 \quad (1)$$

where q_e is the amount of sorption per unit mass of the hydrogel at equilibrium (mmol/g), C_e is the equilibrium concentration (mmol/L), Q_0 is the maximum sorption capacity, and b is the energy of sorption.

The Freundlich adsorption isotherm represents the relationship between the amount of metal adsorbed per unit mass of the adsorbent (q_e) and the concentration of the metal ions in solution at equilibrium (C_e). The Freundlich adsorption isotherm¹⁸ is

$$q_e = K_F C_e^{1/n} \quad (2)$$

where K_F and n are Freundlich constants.

The equation can be linearized if we take logarithms to find parameters K_F and n :

$$\log q_e = \log K_F + (1/n) \log C_e \quad (3)$$

EXPERIMENTAL

Materials and instruments

The monomers acrylamide and *N,N*-methylene bisacrylamide (NMBA) were synthesis-grade (Merck, Darmstadt, Germany). All other chemicals used in this work were analytical-grade and were obtained from Merck or Fluka (Buch, Switzerland). Twice distilled water was used for polymerization reactions and modification reactions. Stock solutions of all the tested metal ions were prepared by the dissolution of an appreciable amount of analytical-grade nitrates or chlorides in twice distilled water and standardized with a standard ethylenediaminetetraacetic acid solution. Working standard metal-ion solutions were prepared by appreciable dilution. The pH measurements were made with a Jenway (Felsted Dunmow, England) model 3310 pH meter. The IR spectra were recorded in the wave-number range of 400–4000 cm^{-1} on a PerkinElmer (Waltham, MA) 3100 IR spectrophotometer. The elemental analysis was carried out with a PerkinElmer 2400 CHNS analyzer. The determination of the metal-ion concentration was carried out with a PerkinElmer 3100 flame atomic absorption spectro-photometer.

Preparation of the chelating polymers

CPAAm was synthesized by addition copolymerization. The initiator potassium persulfate (50 mg) and the monomer acrylamide along with NMBA in a specific molar ratio (2%) were dissolved in 100 mL of a mixture

of twice distilled water and ethanol at 50°C until the formation of the polymer. Twice distilled water (50 mL) was added, and the temperature was raised to 80°C with stirring until the powdered polymer was precipitated. The polymer was filtered, washed with water and then methanol, and allowed to dry at 80°C.¹⁹

The transamidation reaction was carried out through the reaction of CPAAm with triethylenetetraamine (TETA) or diethylenetriamine (DETA). CPAAm (10 g) was added to 100 mL of the transamidation reagent. The mixture was heated at 110°C with stirring for 9 h. The mixture was then poured into cold water. The polymer was filtered and washed with a sodium chloride solution until the filtrate was free from the transamidation reagent. The presence of the transamidation reagent could be detected with the reagent ninhydrin as it produced a deep blue color. The polymer was washed with water and methanol and then dried at 70°C.²⁰

In the dithiocarbamylation reaction, the amino-grafted copolymer was transformed into a dithiocarbamate-supporting hydrogel by the suspension of 5 g of the copolymer in a five-fold molar excess of carbon disulfide. A five-fold excess of sodium hydroxide dissolved in 50 mL of water was then added, and the mixture was stirred for 24 h at room temperature. The excess of CS_2 was removed by heating at 50°C for 4 h in a fuming hood. The resultant dithiocarbamylation beads were filtered and extensively washed with water and methanol and then dried in a vacuum oven at 60°C.

Analytical procedures

The batch equilibration technique was used for the determination of the optimum sorption conditions, such as the pH, adsorption time, and capacity of the sorbent. The chelating hydrogels were equilibrated with a judicious amount of each of the designated metal ions, and the concentration of the unchelated amount of the metal ions was determined by atomic absorption spectrophotometry (AAS). Sorption experiments were carried out in triplicate to determine the precision of the method. The percentage of metal ions chelated by the polymeric hydrogels was determined with the following equation:

$$\text{Uptake(\%)} = [(C_i - C_f)/C_i] \times 100 \quad (4)$$

where C_i and C_f are the initial and final concentrations of the metal ion (ppm), respectively.

The optimum pH value of the metal-ion uptake was determined by the batch equilibration technique. A judicious amount of the metal ions (20 mL, 30 ppm) was shaken with 20 mg of the hydrogel for 2 h. The pH of the metal-ion solution was adjusted before equilibration over a range of 3–9 with a thiel buffer solution. The hydrogel was filtered off, and

TABLE I
Elemental Analysis of the Resins

Sample name	Calculated (%)				Experimental (%)			
	C	H	N	S	C	H	N	S
Hydrogel I	29.15	3.44	11.34	38.86	28.3	4.96	11.03	38.5
Hydrogel II	30.59	3.68	11.9	36.26	27.49	6.22	10.69	35.9

the amount of metal ions remaining in the filtrate was determined with AAS.

The sorption rate of each of the tested metal ions on hydrogels I and II was determined via the shaking of several samples of the metal-ion solutions (20 mL, 30 ppm) with 20 mg of the hydrogel at different time intervals (ranging from 5 to 180 min) at room temperature in a thermostatic water bath shaker. The amount of metal ions remaining after each time interval was determined by AAS, and thus the amount of metal ions chelated to the hydrogel phase was calculated.

Sorption isotherms are the most common processes that reveal the nature of the interaction between the adsorbate and the adsorbents. The equilibrium is established between the chelated metal ions on the hydrogel and the residual metal ions in the solution during the chemisorption process. Equilibrium isotherms were measured to determine the capacity of the new hydrogels for metal ions. The most common types of models describing this type of system are the Langmuir and Freundlich models. The total sorption capacities of hydrogels I and II were determined via the shaking of 20-mL solutions with different concentrations of the metal ions with 10 mg of the hydrogel for 2 h at the optimum sorption pH at 30°C in a thermostatic water bath shaker to ensure complete equilibration. The hydrogel was filtered off, and the concentration of metal ions in the filtrate was determined with AAS.

The thermodynamic parameters of the sorption process, such as the free energy of sorption [ΔG° (kJ/mol)], the heat of sorption, and the standard enthalpy and entropy changes [ΔH° (kJ/mol) and ΔS° (kJ/mol), respectively], can be evaluated with the equations that follow.⁵⁻⁷ A metal-ion solution (20 mL, 100 ppm) was stirred with 20 mg of the resin in a mechanical shaker at different temperatures ranging from 30 to 50°C. The hydrogel was filtered off, and the concentration of metal ions in the filtrate was determined with AAS:

$$K_d = q_e/C_e \quad (5)$$

where K_d is the sorption distribution coefficient, q_e is the amount of adsorption per unit mass of the hydrogel at equilibrium (mmol/g), and C_e is the equilibrium concentration (mmol/L).

The values of K_d are used in the following equation to determine the Gibbs free energy of sorption process at different temperatures:

$$\Delta G^\circ = -RT \ln K_d \quad (6)$$

where T is the temperature (K) and R is the universal gas constant (8.314 J mol⁻¹ K⁻¹).

ΔG° can be expressed in terms of ΔH° and ΔS° as a function of T :

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (7)$$

where ΔH° is the heat of sorption (kJ/mol). The values of ΔH° and ΔS° can be obtained from the slope and intercept of a plot of ΔG° against T according to eq. (7).

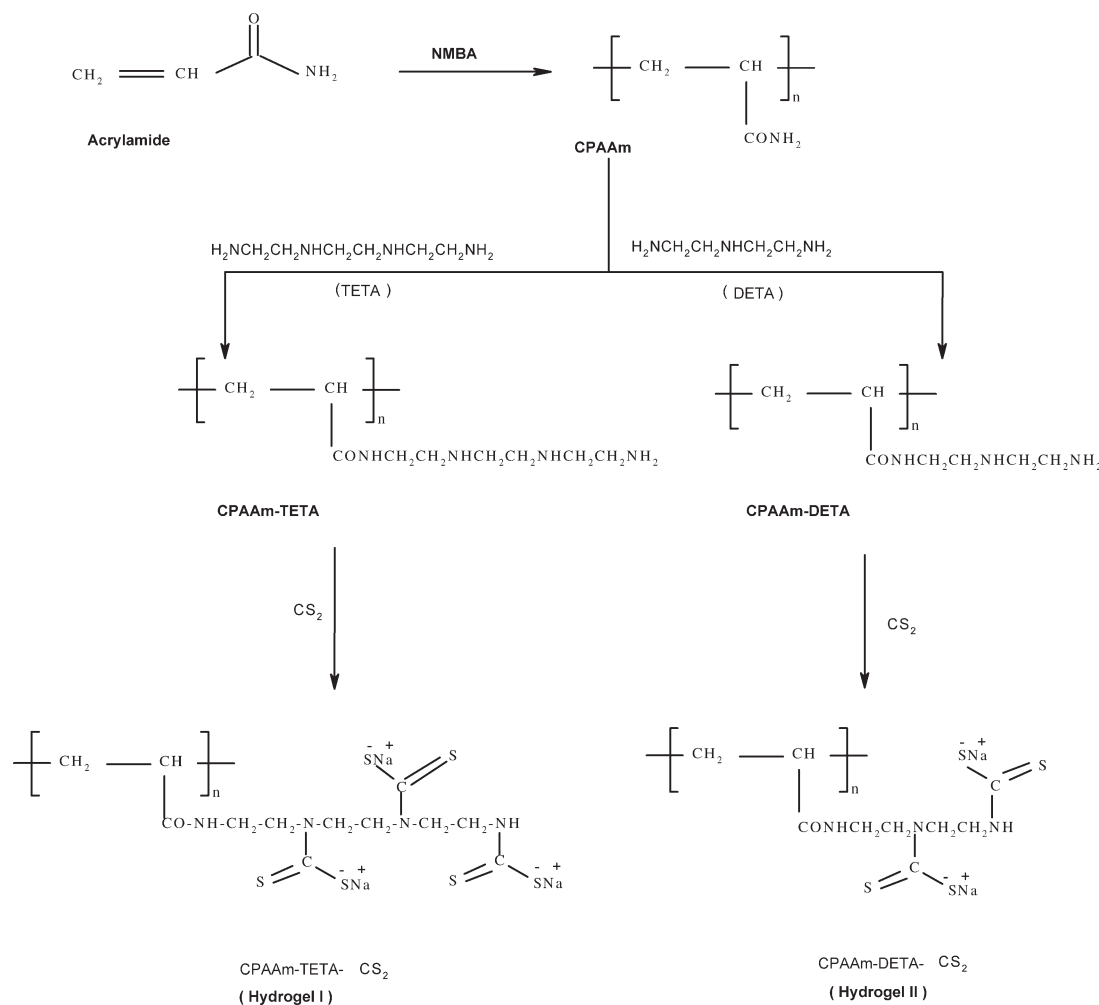
The effect of diverse ions such as Na⁺ and Ca²⁺ on the uptake of each of the tested metal ions with polymers I and II was also determined via the shaking of standard solutions (20 mL) of Cd(II), Pb(II), and Zn(II) ions (30 ppm each) containing different concentrations of the tested alkali and alkaline earth metals as interference with 20 mg of the resin in a thermostatic water bath shaker. The resin was filtered off, and the concentration of the metal ion in the filtrate was determined with AAS.

Moreover, the preconcentration and recovery of the examined metal ions with the prepared resins were carried out in a glass column (8 mm in diameter and 10 cm in length). The column was packed with 0.5 g of resin II, and then a suitable aliquot (10 mL) of a metal-ion solution (10 ppm) was passed through the column at a flow rate of 2 mL/min. The elution process of the metal ions was carried out with suitable eluting agents such as 2 mol/L HCl for Zn(II) and Cd(II) and 2 mol/L HNO₃ for Pb(II). The column separation of a mixture of Cd(II), Pb(II), and Zn(II) metal ions (10 ppm each) was also investigated.

RESULTS AND DISCUSSION

Characterization of the chelating polymeric hydrogels

The structures of the dithiocarbamate-supporting hydrogels were confirmed with IR spectra and elemental analysis data (Table I). The IR spectrum for



Scheme 1 Synthetic pathway of hydrogels I and II.

CPAAm showed two characteristic peaks: a peak at 1650 cm^{-1} for $\text{C}=\text{O}$ and a broadened peak at 3450 cm^{-1} for the amide group ($-\text{NH}_2$). After transamidation reactions, a new peak at 3700 cm^{-1} was observed in addition to the two original peaks at 1650 and 3450 cm^{-1} . This peak is related to the stretching band of the primary amino group ($-\text{NH}_2$), which emphasizes the occurrence of the transamidation reaction. Thiocarbamate-supporting resins showed the appearance of a new peak at $1400\text{--}1250\text{ cm}^{-1}$ due to $\nu_{\text{C}=\text{S}}$ stretching and the disappearance of the band related to the primary amino group ($-\text{NH}_2$), which emphasizes the occurrence of the dithiocarbamylation reaction.

The results of the elemental analysis of hydrogels I and II (reported in Table I) differ somewhat from the values expected on the basis of the formulas illustrated in Scheme 1. This could be attributed to the retention of the unreacted crosslinking and/or solvent retention that occurred in the preparation. In most cases, the insolubility of the polymer makes further purification difficult; the two prepared poly-

meric hydrogels are insoluble in water and in most of the organic solvents. The results thus obtained are in agreement with those reported in the literature.²¹ The results of the elemental analysis clearly demonstrate that the CS_2 reagent reacts not only with the primary amino group but also with the secondary ones because of its small size. This observation has been confirmed by others.¹⁴

Uptake percentage as a function of pH

The pH is the most critical parameter for metal-ion sorption as it influences both the polymer surface chemistry and the solution chemistry of soluble metal ions. The dithiocarbamate group acts as a weak acid, so its sorption behavior for metal ions is influenced by the pH value. This certainly affects the surface structure of adsorbents, the formation of metal hydroxides, and the interaction between adsorbents and metal ions. Under slightly acidic conditions, the dithiocarbamate group presents in solution both as dithiocarbamic acid and in the

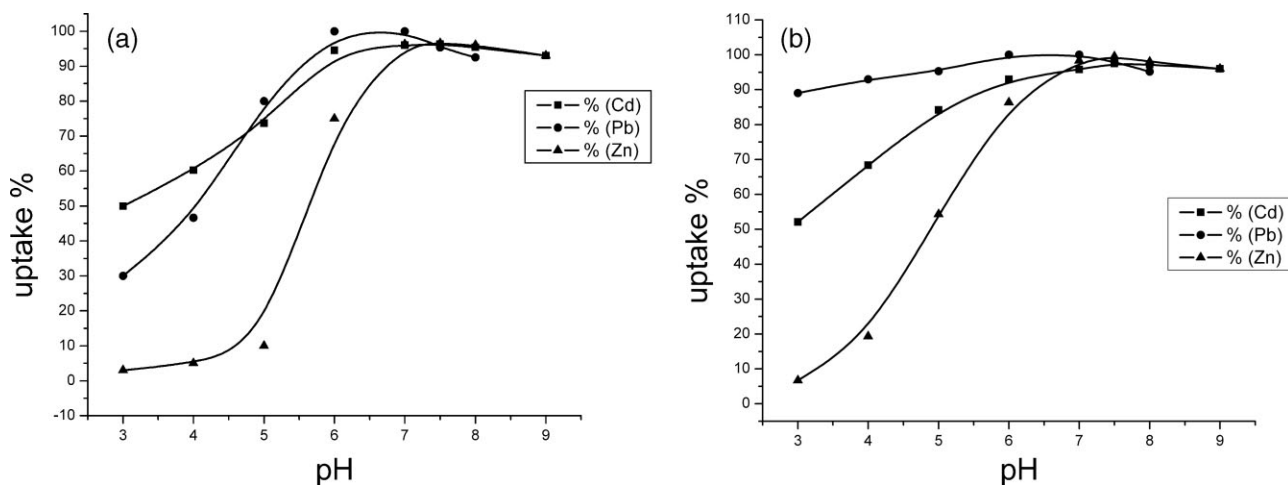


Figure 1 Effect of pH on metal-ion sorption by (a) hydrogel I and (b) hydrogel II.

delocalized anion forms. Probably only the latter species is active in the formation of Cd(II), Pb(II), and Zn(II) complexes. The influence of the pH on the uptake percentage of metal ions by a batch technique is shown in Figure 1(a,b). The results show that the sorption process is more favorable near neutral conditions, and this is also reflected in the relatively low acidity of the chelating polymers. The suitable pH values for the complex formation of Cd(II), Pb(II), and Zn(II) ions when either polymer I or polymer II was used were found to be 7–8, 6–7, and 7–8, respectively. At higher pH values, the uptake percentage slightly decreased because the expected hydrolysis of the investigated metal ions became significant and started to compete with polymer chelate formation. These results are in satisfactory agreement with those reported in the literature.^{21–24}

Sorption kinetics

The kinetics of resin–metal interactions are of considerable importance if the resin is to be used in a dynamic system such as a packed column and a flowing stream. To determine the rate of loading of Cd(II), Pb(II), and Zn(II) ions on the resin, batch experiments were carried out at the optimum pH for the respective metal ions at room temperature. The results are plotted in Figure 2(a,b). The loading half-time, defined as the time required to reach 50% of the resin's total loading capacity, was estimated from the curves, and the results are reported in Table II. The observed loading half-time of resin I and resin II toward the metal ions under investigation is shorter than that observed by other workers.^{10,21,24} The faster uptake of Cd(II), Pb(II), and Zn(II) metal ions showed better accessibility of these metals and strong bond formation with the ligand.

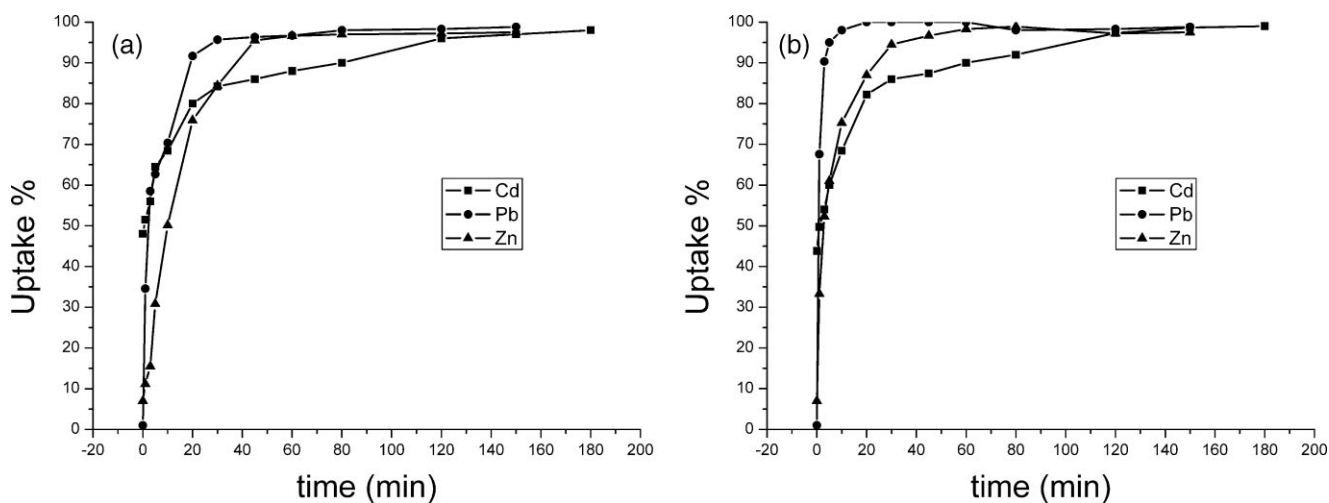


Figure 2 Sorption kinetics of (a) hydrogel I and (b) hydrogel II.

TABLE II
Loading Half-Times for the Metal Ions

Metal	Load half-time (min)	
	Hydrogel I	Hydrogel II
Cd(II)	0.5	0.5
Pb(II)	1	3
Zn(II)	3	5

TABLE III
Loading Capacities of the Resins

Metal	Capacity (mmol/g of resin)	
	Resin I	Resin II
Cd(II)	4.5	3.7
Pb(II)	0.6	0.52
Zn(II)	1.2	0.88

Sorption isotherms

The capacity of the hydrogel is an important factor in the determination of the amount of the hydrogel required to remove a specific metal ion quantitatively from a solution. The loading capacity was determined at the optimum pH, and the results, expressed as millimoles per gram of the hydrogel, are presented in Table III. The sorption extraction isotherms of hydrogels I and II are shown in Figure 3(a,b). The difference in the loading capacities for different metal ions has been attributed to variation in the stability constants of the metal chelates formed by the active sites. For the same metal ions, the differences in the loading capacities for each hydrogel may be due to the differences in the number of active sites present in each hydrogel. An increase in the number of active sites results in a remarkable increase in the loading capacities of some metal ions. The sorption capacities observed during this investigation were more or less higher than those reported for other resins based on imidazolylazobenzene and 1,4-bis(imidazolyazo)benzene,²⁴ *o*-vanillin-thiosemicarbazone,²⁵ ethylenediaminetetraacetic acid,²⁶ cysteamine,²⁷ polydiphenylamine resin,²⁸ and polyethyleneimine/acrylamide hydrogels.²⁹

The quantitative relationships describing the ratio of the quantity adsorbed to that remaining in solu-

tion at a fixed temperature at equilibrium can be illustrated by adsorption isotherms. Two types of adsorption isotherms, Freundlich and Langmuir isotherms, are generally considered. In the Langmuir isotherm model, linear plots of the specific sorption (C_e/q_e) against the equilibrium concentration [C_e ; Fig. 4(a,b)] show that the adsorption obeys the Langmuir model. Q_0 and b of hydrogels I and II toward the tested metal ions were determined from the slope and intercept of the plots and are presented in Table IV.

As for the Freundlich isotherm model, logarithmic plots of the Freundlich expression [eq. (3)] for the amount of the metal ion adsorbed per unit mass of the adsorbent (q_e) and the concentration of the metal ion at equilibrium (C_e) are shown in Figure 5(a,b). Values of K_F and n were calculated from the slope and intercept of the plots. Table IV shows the Freundlich constants and linear correlation coefficients of hydrogels I and II.

Thermodynamic parameters

Thermodynamic parameters such as ΔG° , ΔH° , and ΔS° were evaluated with eqs. (4)–(6). The Gibbs free energy serves as an indication of the degree of spontaneity of the pertinent chemisorption process. The higher negative values of ΔG° unambiguously reveal

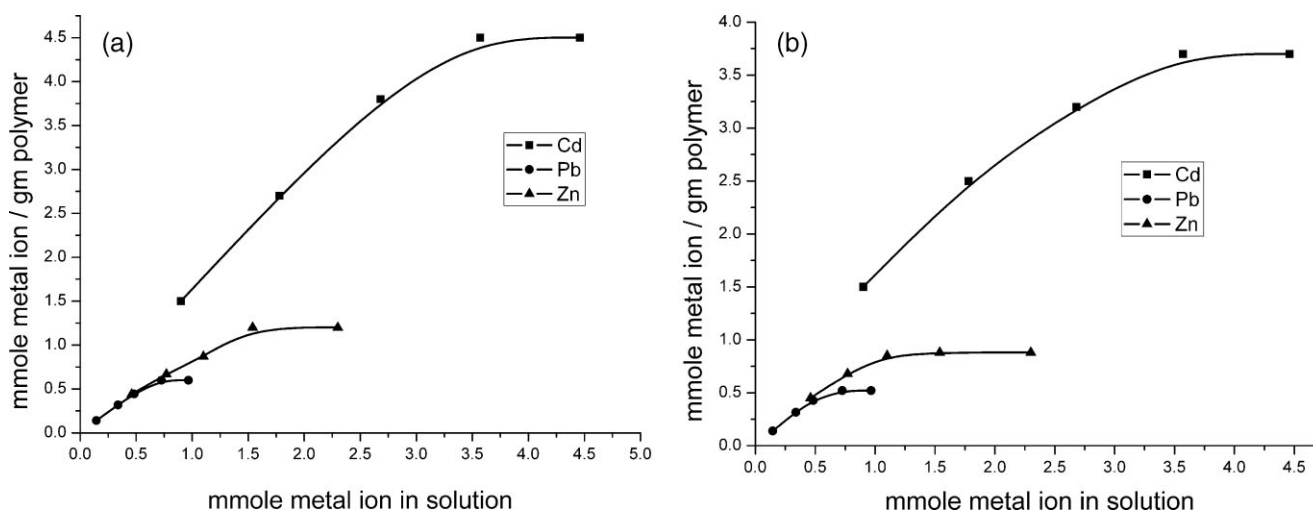


Figure 3 Extraction isotherms of (a) hydrogel I and (b) hydrogel II.

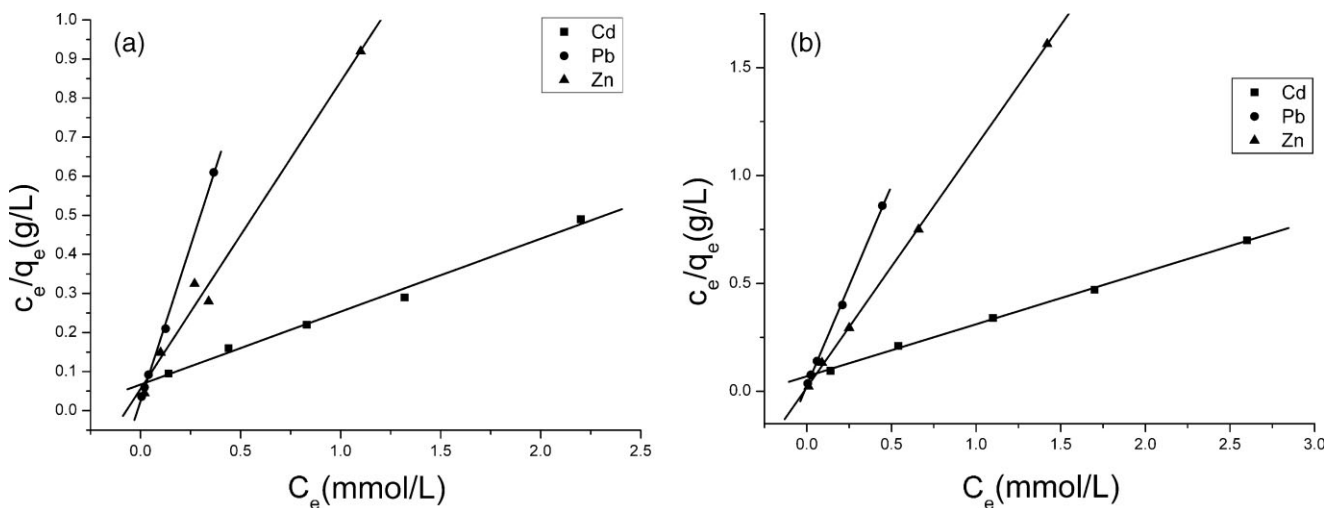


Figure 4 Langmuir plots for the adsorption of Cd(II), Pb(II), and Zn(II) ions on (a) hydrogel I and (b) hydrogel II.

TABLE IV
Comparison of the Langmuir and Freundlich Sorption Constants Obtained from the Langmuir and Freundlich Chemisorption Isotherms of Cd(II), Pb(II), and Zn(II) Ions on Hydrogels I and II at Room Temperature

Metal ion	Langmuir constants			Freundlich constants		
	Q_0 (mmol/g)	K (L/mmol)	R^2	K_F	n	R
Hydrogel I						
Cd	5.3	2.79	0.9955	3.64	2.37	0.9806
Pb	0.63	63.18	0.9995	1.076	3.02	0.9135
Zn	1.27	14.7	0.9935	1.289	3.7	0.9530
Hydrogel II						
Cd	4.1	3.49	0.9993	2.84	3.11	0.9886
Pb	0.59	54.99	0.9998	2.53	3.47	0.9845
Zn	0.89	63.97	0.9999	0.97	6.25	0.9800

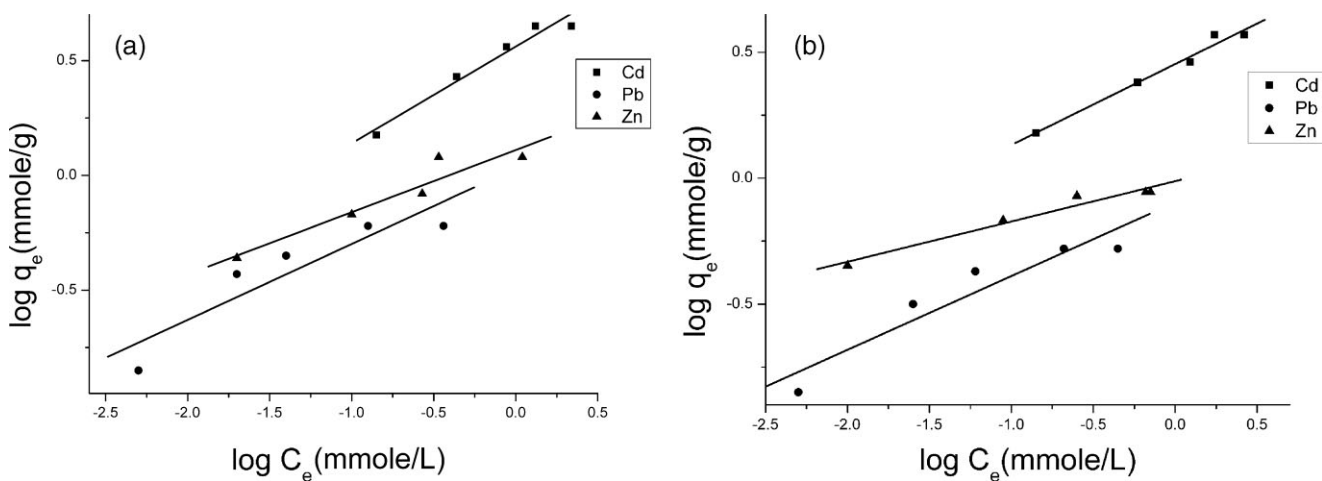


Figure 5 Freundlich plots for the sorption of Cd(II), Pb(II), and Zn(II) ions on (a) hydrogel I and (b) hydrogel II.

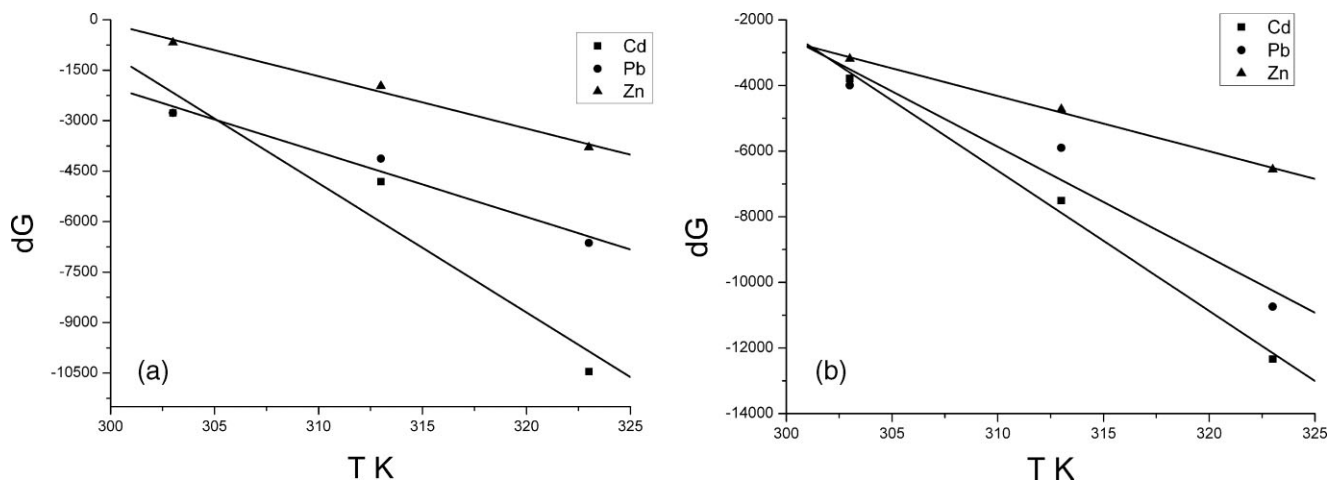


Figure 6 Plots of ΔG° against T for Cd(II), Pb(II), and Zn(II) ions on (a) hydrogel I and (b) hydrogel II.

an energetically favorable chemisorption process. ΔH° and ΔS° were obtained from the slope and intercept of a plot of ΔG° against T [Fig. 6(a,b)]. The calculated parameters are given in Table V. The negative value of ΔG° indicates the spontaneous nature of the sorption of metal ions by hydrogels I and II. The value of ΔG° becomes more negative with increasing temperature. This shows that the uptake percentage increases with an increase in the temperature. This may be attributed to the increasing diffusion of metal ions when the temperature increases as well as the increasing number of active sites available for complexation with increasing temperature. The positive values of ΔH° provide clear evidence about the endothermic nature of the sorption process, whereas the positive values of ΔS° show that the reaction is irreversible.

Effect of diverse ions

High concentrations of Na^+ and Ca^{2+} ions affected the uptake percentage of hydrogels I and II toward the investigated metal ions. The concentration of the

diverse ions was increased up to the point at which a 0% loss in the analytical signal was observed, and the data are presented in Table VI. The uptake percentage decreased with the concentration of Na^+ and Ca^{2+} ions increasing. The effect of the Ca^{2+} ion was more pronounced than that of the Na^+ ion because the former had a higher complexation affinity than the latter.

Application

The column separation of Cd(II), Pb(II), and Zn(II) ions was investigated with a glass column (10 cm long with an inner diameter of 8 mm) packed with 0.5 g of hydrogel II. The column bed was first conditioned with a thiel buffer solution of pH 7. A sample volume of 10 mL containing Cd(II), Pb(II), and Zn(II) metal ions (10 ppm each) was passed through the column at a 2 mL/min flow rate. The desorption of the metal ions was carried out with 2 mol/L HNO_3 . The chromatogram of the separation of Cd(II), Pb(II), and Zn(II) metal ions is shown in Figure 7. The order of the metal-ion separation from

TABLE V
Thermodynamic Parameters for the Adsorption of Cd(II), Pb(II), and Zn(II) Ions on Hydrogels I and II

Metal ion	ΔG° (kJ/mol)			ΔH° (kJ/mol)	ΔS° (kJ/mol)
	30°C	40°C	50°C		
Hydrogel I					
Cd	-3.8	-7.5	-12.3	46.5	0.155
Pb	-4	-5.9	-10.7	98.7	0.337
Zn	-3.2	-4.7	-6.6	47.9	0.168
Hydrogel II					
Cd	-2.8	-4.8	-10.4	114	0.384
Pb	-4.1	-2.8	-6.6	56	0.193
Zn	-0.68	-2	-3.8	46.5	0.155

the hydrogel was found to be governed by the stability constants of the complexes formed between each metal ion and the dithiocarbamate group supported on the hydrogel. Zn(II) ion, which formed the least stable complex, was separated first; then, the Pb(II) ion was separated; and finally, the Cd(II) ion, which formed the most stable complex in comparison with the other two metal ions, was separated.

Moreover, the removal of Pb(II) ions from real industrial waste was carried out with the prepared hydrogel. In this study, 50 mL of industrial waste containing lead was conditioned at pH 7, and the lead content was determined. This solution was passed through the column containing 0.5 g of hydrogel II at a flow rate of 2.0 mL/min. The removal efficiency was found to be 80%. The elution of Pb(II) ions from the resin was carried out with a 2.0 mol/L HNO₃ solution.

CONCLUSIONS

New chelating hydrogels containing dithiocarbamate groups were synthesized and employed in the removal of heavy-metal ions from wastewater. The prepared chelating hydrogels had high loading capacities for the investigated metal ions in comparison with other chelating matrices reported in the literature. Furthermore, the loading half-times of these chelating hydrogels were also short, and the kinetic studies ensured faster exchange kinetics in the process of metal-ion uptake. Sorption isotherms of the investigated metal ions on the prepared hydrogels were developed, and the equilibrium data fitted the Langmuir and Freundlich isotherm models well. The sorption process of the tested metal ions on both polymeric hydrogels was found to be spontaneous, irreversible, and endothermic in nature. The prepared hydrogels were used in the separation of a mixture of toxic metal ions and also in the removal of lead ions from industrial waste. The polymeric hydrogels could be regenerated with mineral acids

TABLE VI
Tolerance Limits for Diverse Ions

Metal ion	Tolerance limit (mol/L) ^a			
	Hydrogel I		Hydrogel II	
	NaNO ₃	Ca(NO ₃) ₂	NaNO ₃	Ca(NO ₃) ₂
Cd(II)	0.25	0.005	0.3	0.05
Pb(II)	0.2	0.01	0.25	0.2
Zn(II)	0.05	0.01	0.05	0.01

^a Up to the limit, there is a 0% loss in the analytical signal.

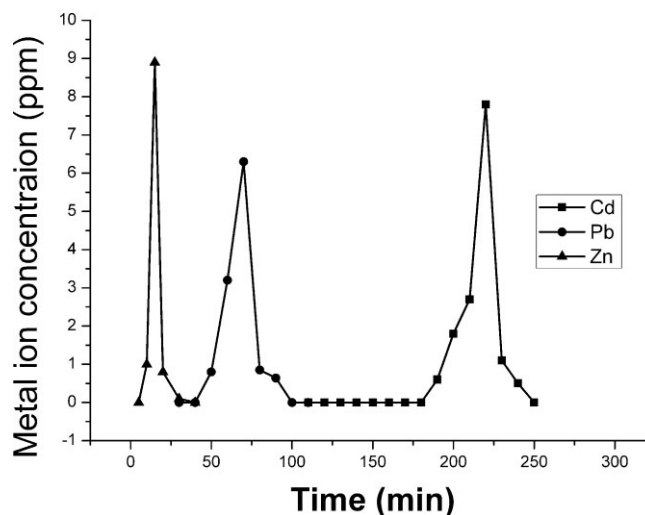


Figure 7 Chromatogram of the separation of Cd(II), Pb(II), and Zn(II) metal ions.

such as HNO₃ and HCl acids with suitable concentrations.

References

- Kantipuly, C.; Katragadda, S.; Chow, A.; Gesser, H. D. *Talanta* 1990, 37, 491.
- Rouhollahi, A.; Ganjali, M. R.; Shamsipur, M. *Talanta* 1998, 46, 1341.
- Stephanie, D. S.; Alexandratos, D. S. *Solvent Extr Ion Exch* 2000, 18, 779.
- Garg, B. S.; Sharma, R. K.; Bhojak, N.; Mittal, S. *Microchem J* 1999, 61, 94.
- Warszawsky, A. *Chelating Ion Exchangers; Critical Reports on Applied Chemistry*; Blackwell Scientific: London, 1987; p 166.
- Kabay, N.; Egawa, H. *Sep Sci Technol* 1994, 29, 135.
- Sanchez, J. M.; Hidalgo, M.; Salvado, V. *React Funct Polym* 2001, 46, 283.
- Saxena, R.; Singh, A. K.; Rathore, D. P. S. *Analyst* 1995, 120, 403.
- Ray, A.; Gupta, S. N. *J Polym Sci Part A: Polym Chem* 1997, 35, 3729.
- Rether, A.; Schuster, M. *React Funct Polym* 2003, 57, 13.
- Mahmoud, A. M.; Ezzat, M. S. *Talanta* 1997, 44, 15.
- Masud, R.; Hallensleben, M. L.; Roshan, A.; Munir, A. *Eur Polym J* 2004, 40, 2053.
- Asem, A. *Hydrometallurgy* 2005, 80, 13.
- Lezzi, A.; Cobianco, S.; Roggero, A. *J Polym Sci Part A: Polym Chem* 1994, 32, 1877.
- Mamoru, H.; Kazuyoshi, Y.; Masahiro, O.; Makoto, A.; Morio, N. *Anal Chim Acta* 2006, 561, 183.
- Lezzi, A.; Cobianco, S. *J Appl Polym Sci* 1994, 54, 889.
- Rakourskii, E. E.; Starzhitskaya, M. *Zh Anal Chim* 1974, 29, 2094.
- Rengaraj, S.; Joo, C. K.; Kim, C. K.; Yi, J. *J Hazard Mater B* 2003, 102, 257.
- George, B. K. K.; Fillet, V. N. R. *Eur Polym J* 1989, 25, 1099.
- Haridasan, V. K.; Ajayagosh, A. A.; Pillai, V. N. R. *J Org Chem* 1987, 52, 2662.
- Nuha, M. S.; Kais, A. K.; Mohammad, S. M. *React Funct Polym* 2004, 59, 63.
- Prabhakarar, D.; Subramanian, M. S. *Talanta* 2003, 59, 1227.

23. Sadhan, P.; Pulak, D.; Pabitra, C. *Talanta* 2004, 63, 485.
24. Sadhan, P.; Sanjoy, D.; Shuvendu, S.; Pabitra, C. *Anal Chim Acta* 2006, 556, 430.
25. Jain, V. K.; Sait, S. S.; Srivastav, P.; Agrawal, Y. K. *Talanta* 1997, 45, 397.
26. Sanju, F.; Lalit, V. *Rad Phys Chem* 2005, 74, 310.
27. Margot, A. L. T.; David, A. P. T.; Veronica, C. F.; Takako, N.; Toshishige, M. S. *React Funct Polym* 2002, 53, 91.
28. Mostapha, J.; Fridirique, J.; Georges, L. G. Driss Elothmani *Desalination* 2005, 180, 271.
29. Sanju, F.; Lalit, V.; Tirumalesh, K. *Rad Phys Chem* 2006, 75, 747.