

Ligating Behavior and Metal Uptake of N-Sulphonylpolyamine Chelating Resins Anchored on Polystyrene-Divinylbenzene Beads

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ABSTRACT: Amberlite XAD-2 has been functionalized by coupling through $-\text{SO}_2-$ with ethylenediamine, propylenediamine, and diethylenetriamine to give the corresponding polyamine chelating resins I–III. The solid metal-polymer complexes of the synthesized chelating resins with Cu^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} were synthesized. The polyamine derivatives and their metal complexes were characterized by elemental analysis, spectral (IR, UV/V, and ESR), and magnetic studies. The batch equilibrium method was utilized for using the chelating polyamines for the re-

moval of Cu^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} ions from aqueous solutions at different pH values and different shaking times at room temperature. The selective extraction of Cu^{2+} from a mixture of the four metal ions and the metal capacities of the chelating resins were evaluated using atomic absorption spectroscopy. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1839–1846, 2005

Key words: polyamines; metal-polymer complexes; UV-vis spectroscopy; selectivity

INTRODUCTION

Ion exchange resins are characterized by the presence of some functional groups, such as $-\text{SO}_3^-\text{H}^+$ or NR_4^+X^- , that are capable of binding and exchanging a wide range of cations and anions. This behavior is of great importance when considering some general applications, such as solvent purification from ions, hardness removal from seawater, industrial waste treatment, or metal ion preconcentration.^{1–3} The normal and commercial types of ion exchange resins are known for lack of selectivity towards metal ion extraction from mixtures containing other interfering metal ions. This may be attributed to the deficiency in the number of functional groups responsible for such selective extraction. Modified ion exchangers with chelating groups are now aimed to increase the selective properties of such resins towards metal ion extraction and separation via donor atoms, namely, oxygen, nitrogen, sulfur, or phosphorus.⁴ Several chelating resins with different donors and organic ligands were prepared, and their metal complexes and capacities as well as selective properties were reported.^{5–14} Although numerous chelating resins having amines

have been synthesized and studied, the chelating, metal capacities, and metal selectivities of the newly modified polyamine of chlorosulphonated polystyrene appeared to be less developed. Due to the critical need of being able to selectively remove and recover metal ions from relevant aqueous water solutions and our interest in synthesis, characterization, ligating behavior, and their metal capacities and selectivities, we focused on the area of environmental inorganic chemistry and discussed the synthesis and characterization of modified chelating resins of *N*-sulfonylpolyamine anchored on polystyrene-divinylbenzene beads (I–III), Scheme 1

1, as well as their coordination and removal of Cu^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} from aqueous solution. The effect of the shaking times and pHs on their metal capacities and selectivities will be discussed.

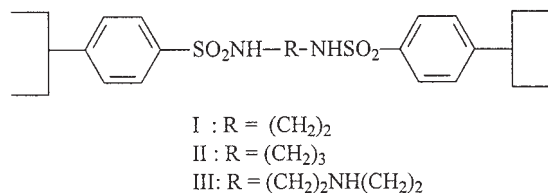
EXPERIMENTAL

Materials and solvents

Working metal ion solutions (0.1M) were prepared by diluting Merck (Germany) atomic absorption standard metal ion solutions with deionized water. pH adjustments were made with 1.0M HNO_3 and NaOH or acetate buffer solution. Amberlite XAD-2 resin was obtained from Aldrich and before being used, it was thoroughly washed with 4.0M HNO_3 and 1.0M NaOH successively, double distilled water, and dried before use. Ethylenediamine, propylenediamine, diethylenetriamine, and thionyl chloride were purchased from

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Scheme 1

Aldrich and used as received. Hydrated copper(II) chloride, zinc(II) chloride, cadmium(II) chloride, and lead(II) nitrate were purchased from Aldrich and used for complex formation without further purification.

Apparatus and elemental analysis

Atomic absorption spectrometry (AAS) were made with an atomic absorption spectrometer (AAS) model Perkin-Elmer AS -60 using an air acetylene flame with air and acetylene flow rates of 15 and 1.5 dm³ min⁻¹. FT-IR spectra were recorded as KBr discs with a Shimadzu 2000 FT-IR Spectrophotometer. Electronic spectra for the metal complexes were accomplished by Carry Varian 5 uv/vis/nir Spectrophotometer. The ESR spectra were recorded utilizing an ECS 106 spectrometer. A mechanical shaker having speed control facility was used for the batch equilibration. Microanalyses were performed on a Leco-CHNS 932 Analyzer at Analab, Kuwait University.

Synthesis of chlorosulphonated amberlite XAD-2 (PS-SO₂Cl)

This was synthesized by swelling amberlite XAD-2 (5.0 g) in CHCl₃ (50 cm³) for 2 h. A solution of ClSO₃H (50 cm³) in CHCl₃ (50 cm³) was added dropwise to the swelled amberlite. After complete addition, the reaction mixture was stirred at room temperature for 6 h, filtered off, and washed thoroughly with dry CH₂Cl₂ and dried *in vacuo* at 60°C for 24 h. This chlorosulphonated form was refluxed in 50 cm³ CHCl₃ and 20 cm³ SOCl₂ for 12 h. The resin was then filtered off, washed with dry CH₂Cl₂, and dried *in vacuo* at 60°C for 24 h. Elemental analysis for PS-SO₂Cl was found to be: % found (% calcd.): C = 46.9 (47.4), H = 3.4 (3.5), Cl = 17.3 (17.5). The data shows 99% chlorosulphonation and 1% SO₃H.

Synthesis of amberlite XAD-2 loaded with polyamines

The dry chlorosulphonated product (2.0 g) was mixed with 20–30 cm³ of the corresponding amine in 250 cm³ dry CH₂Cl₂ for 24 h at room temperature. The reaction mixture was then refluxed for a further 4–6 h, and the product in each case was filtered off, washed with

dioxan, then water, and dried in vacuum at 60°C for 24 h.

Metal capacity

Effect of pH

The batch method was used to determine the metal ion uptake from an aqueous solution containing 1.5×10^{-2} mmol in the metal ion in triplicate. 100 mg of the chelating resin I, II, or III was added to an aqueous solution (10 cm³) of the metal ion Cu⁺², Zn⁺², Cd⁺², or Pb⁺² at pH 1.0–7.0 in a stopper glass bottle. The mixture was mechanically shaken for 1 h at room temperature, filtered off, and washed with 50 cm³ deionized water. The filtrate and washings were collected in a volumetric flask (100 cm³), and the volume was completed to the mark with deionized water. An appropriate volume of each solution was analyzed for the metal ions by AAS. The metal uptake was calculated from the relation

$$a = (C_o - C_f)V/1000m \text{ (mg/g)}$$

where V is the volume of solution in contact to batch flask, C_o is the initial concentration of the metal ion (mg/L), C_f is the equilibrium concentration (mg/L), and m is the mass of the sorbent (g).

Effect of shaking time

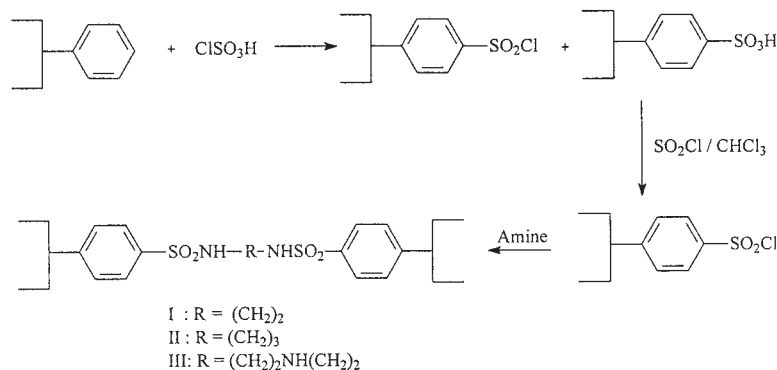
The metal capacity at shaking times (2, 5, 10, 30, 45, 60 min) was determined in triplicate by the batch equilibrium method but at the optimum pH value for each metal ion.

Separation of copper(II) from mixtures

To a solution (25 cm³) containing Cu⁺² – Zn⁺², Cu⁺² – Cd⁺², or Cu⁺² – Pb⁺² binary mixture of 0.1 mg/cm³ of each metal ion, 5 mg dry resin was added in a stopper glass bottle. The mixtures were automatically shaken for 30 min. After remaining motionless for 2 h, they were filtered off and washed with deionized water. The filtrate and washings were recovered into a 100 cm³ volumetric flask, and deionized water was added to the mark. The concentration of each ion was determined by AAS.

Synthesis of the metal complexes

The metal complexes of the chelating resins I–III were prepared by the general method, namely, a 0.01 mol aqueous of adjusted pH solution (50 cm³) of Cu⁺² (pH 6.0), Zn⁺² (pH 6.0), Cd⁺² (pH 5.5), or Pb⁺² (pH 5.5) was added to 0.01 or 0.02 mol of the corresponding chelating resin. The reaction mixture remained mo-



Scheme 2

tionless at room temperature for 24 h and then was shaken for 30 min, filtered off, washed several times with deionized water, ethanol, and diethyl ether, and dried in vacuum at 60°C for 24 h.

RESULTS AND DISCUSSION

The complex formation, metal sorption, and selectivity of chelating resins are mainly attributed to the nature of the ligand immobilized on the polymer matrix.^{15,16} However, since the ligand groups are chemically bound to the rigid polymer matrix, their free motion is greatly restricted.^{15,16} Hence, the complex formation with a chelating resin tends to be different from that observed in the homogeneous analogue.¹⁷ Therefore, we introduced $-SO_2-$ spacer between the metal binding and polymer matrix, which led to enhanced steric flexibility of the ligand.

Amberlite XAD-2 was chlorosulphonated by using $ClSO_3H$ in $CHCl_3$ at room temperature to give the

chlorosulphonated product. This product was treated with $SO_2Cl_2/CHCl_3$ at room temperature to remove any sulfonic acid on the polymer backbone. The chlorosulphonated product was then treated with ethylenediamine, propylenediamine, or diethylenetriamine (Scheme 2) to give the corresponding chelating resins I-III. The values of the amount of the ligand incorporated in mmol/g resin were calculated according to the method by Suzuki et al.,¹⁸ and the values are given in Table I.

Elemental analysis (Table I) and FT-IR showed that under the reaction conditions, the ratio between the chlorosulphonated polystyrene and the amine is 2 : 1, respectively. All chelating resins react with Cu^{+2} , Zn^{+2} , Cd^{+2} , or Pb^{+2} to give $[L_2M]X_2 \cdot nH_2O$ for $L = I$ or II and $[L_2M_3X_6] \cdot nH_2O$ for $L = III$; $n = 1-4$; $X = Cl$ or NO_3 .

The main FT-IR spectral bands of the dry chelating resins and their metal chelates with their tentative assignments after comparison with that of PS and

TABLE I
Elemental Analysis of Prepared Compounds (Found/Calcd)

| Compound | C% | H% | N% | Amount of ligand incorporated mmol/g resin |
|---|-----------|---------|---------|--|
| I: $C_{18}H_{20}N_2S_2O_4$ | 54.7/55.1 | 5.4/5.1 | 6.9/7.1 | 2.5 |
| II: $C_{19}H_{22}N_2S_2O_4$ | 55.6/56.2 | 5.6/5.4 | 6.7/6.9 | 2.46 |
| III: $C_{20}H_{25}N_3S_2O_4$ | 55.5/55.2 | 5.9/5.7 | 9.5/9.7 | 2.31 |
| Ia: $[L_2CuCl_2] \cdot 2H_2O C_{36}H_{44}N_4S_4O_{10}Cl_2Cu$ | 45.1/45.3 | 4.4/4.6 | 5.8/5.9 | |
| Ib: $[L_2ZnCl_2] \cdot 4H_2O C_{36}H_{48}N_4S_4O_{12}Cl_2Zn$ | 43.2/43.5 | 4.6/4.8 | 5.5/5.6 | |
| Ic: $[L_2CdCl_2] \cdot 3H_2O C_{36}H_{46}N_4S_4O_{11}Cl_2Cd$ | 42.0/42.3 | 4.4/4.5 | 5.6/5.5 | |
| Id: $[L_2Pb(NO_3)_2] \cdot 2H_2O C_{36}H_{44}N_6S_4O_{16}Pb$ | 37.2/37.5 | 3.7/3.8 | 7.4/7.3 | |
| IIa: $[L_2CuCl_2] \cdot 3H_2O C_{38}H_{50}N_4S_4O_{11}Cl_2Cu$ | 45.2/45.6 | 5.1/5.0 | 5.8/5.6 | |
| IIb: $[L_2ZnCl_2] \cdot 2H_2O C_{38}H_{48}N_4S_4O_{10}Cl_2Zn$ | 46.1/46.3 | 5.0/4.9 | 5.5/5.7 | |
| IIc: $[L_2CdCl_2] \cdot 2H_2O C_{38}H_{48}N_4S_4O_{10}Cl_2Cd$ | 44.0/44.2 | 4.6/4.7 | 5.5/5.4 | |
| IId: $[L_2Pb(NO_3)_2] \cdot 2H_2O C_{38}H_{48}N_6S_4O_{16}Pb$ | 38.5/38.7 | 4.0/4.1 | 7.0/7.1 | |
| IIIa: $[L_2Cu_3Cl_6] \cdot 3H_2O C_{40}H_{56}N_6S_4O_{11}Cl_6Cu_3$ | 36.1/36.2 | 4.2/4.2 | 6.4/6.3 | |
| IIIb: $[L_2Zn_3Cl_6] \cdot 2H_2O C_{40}H_{52}N_6S_4O_{10}Cl_6Zn_3$ | 36.2/36.5 | 4.0/4.1 | 6.4/6.4 | |
| IIIc: $[L_2Cd_3Cl_6] \cdot H_2O C_{40}H_{52}N_6S_4O_9Cl_6Cd_3$ | 33.1/33.4 | 3.6/3.6 | 5.6/5.8 | |
| IIId: $[L_2Pb_3(NO_3)_2] \cdot 4H_2O C_{40}H_{58}N_{12}S_4O_{30}Pb_3$ | 24.7/24.8 | 3.1/3.0 | 8.9/8.6 | |

Calculated according to reference 18.

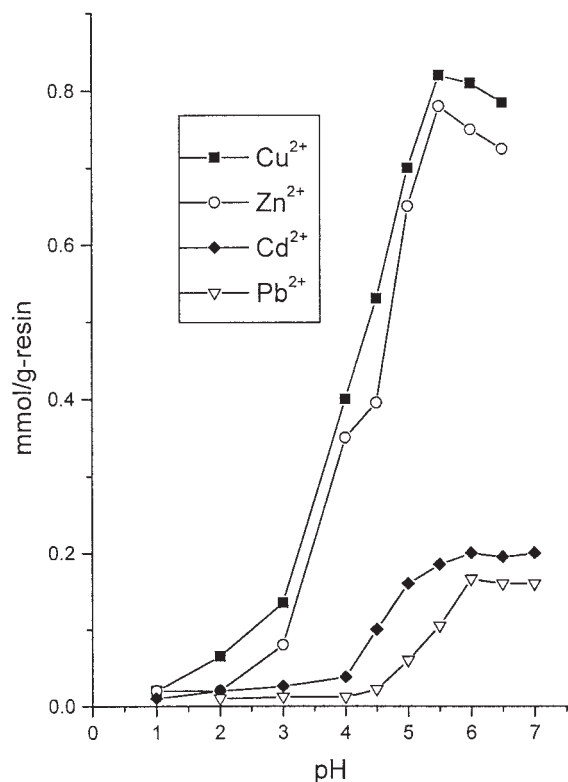


Figure 1 Effect of pH on the metal capacity of the chelating resin I after shaking time 30 min at room temperature. The solution contains 1.5×10^{-2} mmol of each metal ion and 100 mg of resin I at pH 1.0–7.0.

PS-SO₂Cl were also studied. Thus, dry chelating resins displayed a medium-strong splitted band at 3380–3320 cm⁻¹ assignable to NH group and a medium band at 3580–3430 cm⁻¹ of water molecules. The weak-medium bands at 3038–2990 and 2920–2895 cm⁻¹ are assigned to C-H aromatic and aliphatic, respectively. Furthermore, IR reveals the presence of C-N band at 1580–1570 cm⁻¹ (absent in chlorosulphonated polystyrene). The presence of -SO₂- is indicated from the appearance of a medium band at 950–860 cm⁻¹ in addition to a strong band at 1380–1325 and 1180–1140 cm⁻¹. Upon complex formation, the bands due to CH and SO₂ are not greatly affected. In all complexes the bands due to NH are blue shifted by 30–42 cm⁻¹ with a reduction of intensity and splitting, while those due to NH and C-N are red shifted. Furthermore, the spectra of all complexes display a new band at 410–388 cm⁻¹, which could be attributed to M-N. These IR data are consistent with that obtained for metal complexes with diamine or polyamine containing chelates.^{19–22} In all complexes, the spectra display a broad band at 4652–3486 cm⁻¹ due to H₂O. This band disappeared in most cases except for the complexes of resin III after heating the complexes up to 120°C for 24 h. Furthermore, the band at 316–300 cm⁻¹ in the case of resin III complexes could be attributed to

M-O.²² According to the elemental and IR spectral data, all resins are coordinated to the metal ions via the imino-nitrogen atoms.

Magnetic, electronic, and ESR spectral studies

The room temperature magnetic moment values for copper complexes are found to be 1.79, 1.83, and 1.22 B.M. for resins I, II, and III, respectively. The former two values indicate magnetically diluted complexes with $s = \frac{1}{2}$, while the third value indicates a magnetically concentrated species. Furthermore, this reduced value indicates a magnetic exchange interaction that may be via direct copper-copper interaction or via bridging ligands.

The nujol mull electronic spectra of all complexes display intense bands at 35,700–27,600 cm⁻¹ and a shoulder at 24,000–22,700 cm⁻¹. The lower energy band could be assigned to $\pi-\pi^*$ and $n-\pi^*$ while the shoulder is due to the charge transfer between the metal ion and the ligand (LMCT).²³ The relatively broad band at 37,000 cm⁻¹ is assigned to $\sigma(N)-M^{2+}$ CT.²⁴ The spectra of the copper(II) complexes [L₂Cu]Cl₂·nH₂O, L = I or II, exhibit two broad low intense bands at 16,600–16,900 and 15,000–15,400 cm⁻¹. These bands are assigned to ${}^2B_{1g} \rightarrow {}^2E_g$ and ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transitions, respectively, for Cu(NN)₂ chro-

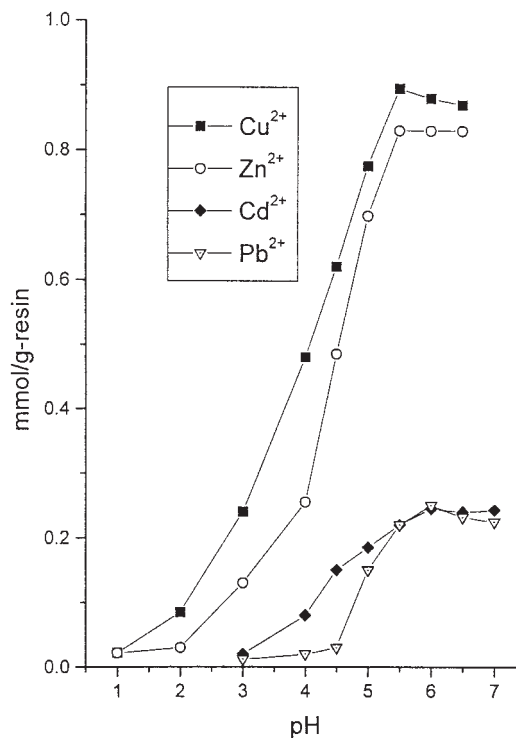


Figure 2 Effect of pH on the metal capacity of the chelating resin II after shaking time of 30 min at room temperature. The solution contains 1.5×10^{-2} mmol of each metal ion and 100 mg of resin II at pH 1.0–7.0.

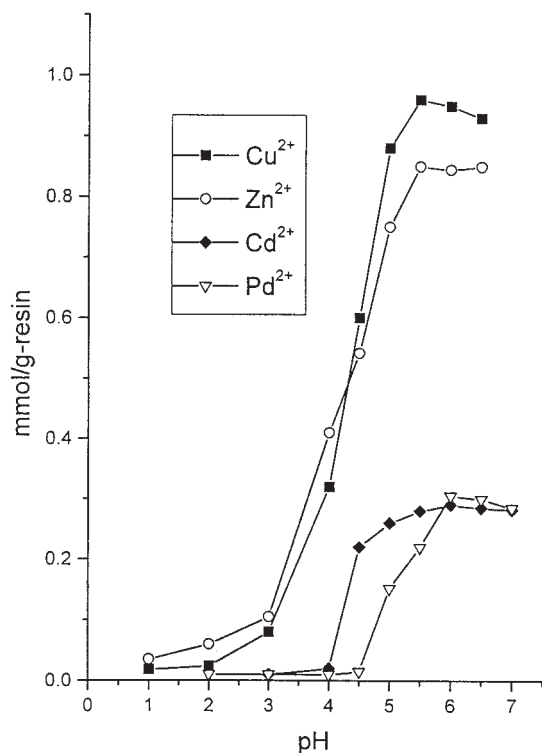


Figure 3 Effect of pH on the metal capacity of the chelating resin III after shaking time of 30 min at room temperature. The solution contains 1.5×10^{-2} mmol of each metal ion and 100 mg of resin III at pH 1.0–7.0.

mophores in a square planar ligand field.²⁵ The band due to the ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transition could not be traced due to the asymmetric nature of the lower energy band.

The spectrum of $L_2Cu_3Cl_6 \cdot (H_2O)_3$, $L = III$ displays a broad splitted band at $16,400 \text{ cm}^{-1}$ with a shoulder at $11,000 \text{ cm}^{-1}$, which is consistent with polymeric square pyramidal copper(II) complexes²¹ and rather consistent with the spectral data for copper complexes with similar coordinating groups.^{25,26} Assuming C_{4v} symmetry for this complex, the higher energy band can be considered to consist of two bands due to ${}^2B_1 \rightarrow {}^2E$ and ${}^2B_1 \rightarrow {}^2B_2$ transitions and the shoulder due to the ${}^2B_1 \rightarrow {}^2A_1$ transition.

The room temperature X-band ESR spectra of the polycrystalline $[L_2Cu]Cl_2 \cdot nH_2O$, $L = I$ or II display only one broad signal with $\Delta_{\text{peak-peak}} = 120$ and 126 G, with $g_{\parallel} = 2.136$ and 2.128 for $L = I$ and II , respectively. The spectra at 77 K display axial patterns with $g_{\parallel} = 2.252, 2.250$ and $g_{\perp} = 2.082$ and 2.079 for $L = I$ and II , respectively. It was shown that $g_{\parallel} > g_{\perp} > g_e$, indicating the unpaired electron in the $d_{x^2-y^2}$ orbital. The average g -values calculated from $g = 1/3[g_{\parallel} + 2g_{\perp}]$ are found to be 2.139 and 2.136, respectively. The G values defined as $G = g_{\parallel} - 2/g_{\perp} - 2$ equal 3.07 and 3.160, respectively, suggesting the presence of a magnetic exchange interaction

between the copper centers in the solid state. The spectrum of $[L_2Cu_3Cl_6] \cdot 3H_2O$ at room temperature shows a very broad unresolved signal but that at 77 K appeared to be of rhombic shape with $g_z = 2.140$, $g_y = 2.099$, and $g_x = 2.041$. The average $g = 1/3[g_3 + g_2 + g_1] = 2.099$. The parameter $R = g_2 - g_1 / g_3 - g_2 = 0.53$ indicates a $d_{x^2-y^2}$ ground state and further, is consistent with a square pyramidal ligand field around the copper(II). The low average g value suggests a geometry involving grossly misaligned tetragonal axes. The spectrum also displayed two pairs of ill defined seven hyperfine lines resulting from the zero field splitting at 2000–3200 G region with an average spacing $A_{\parallel} = 83$ G, and two weak lines at 4080 and 4820 G characteristic of polymeric copper(II) complexes and assigned to the transition within triplet state.^{27–30} The spectrum also exhibited a weak unresolved signal in the midfield region with $g = 3.98$ due to the $\Delta M_s = \pm 2$ transition characteristic of polymeric copper complexes. Furthermore, these data are comparable to those reported for copper(II) complexes in similar environments.^{25–29}

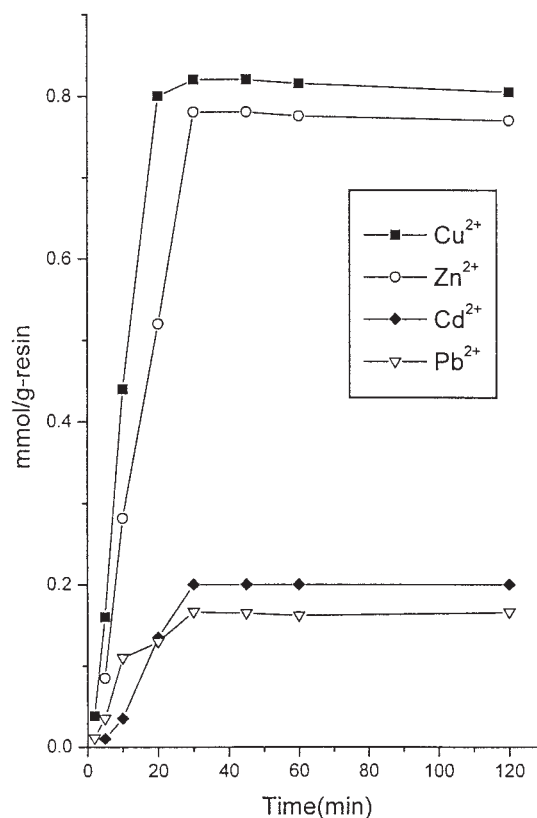


Figure 4 Effect of shaking time (2, 5, 10, 30, 45, and 60 min) on the metal capacity of the chelating resin I. pH values 6.0 for Cu^{2+} and Zn^{2+} and 5.5 for Cd^{2+} and Pb^{2+} at room temperature. The solution contains 1.5×10^{-2} mmol of each metal ion and 100 mg of resin I.

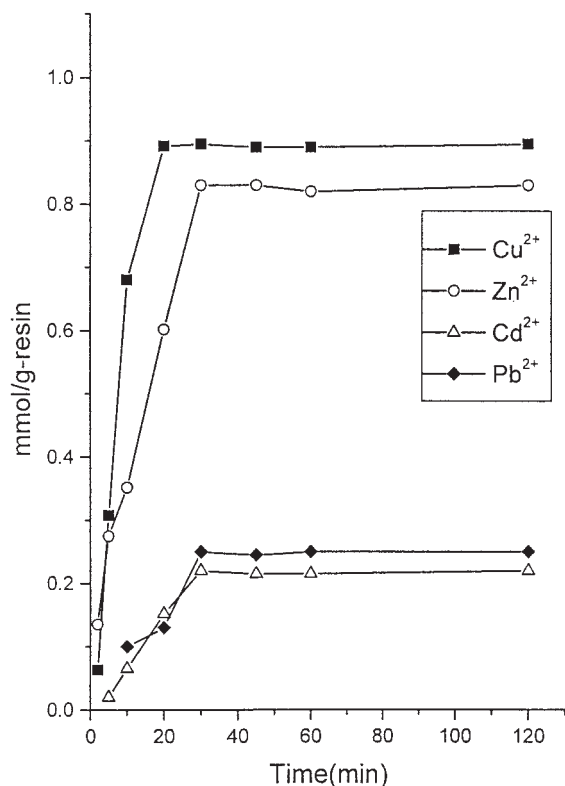


Figure 5 Effect of shaking time (2, 5, 10, 30, 45, and 60 min) on the metal capacity of the chelating resin II. pH values 6.0 for Cu²⁺ and Zn²⁺ and 5.5 for Cd²⁺ and Pb²⁺ at room temperature. The solution contains 1.5×10^{-2} mmol of each metal ion and 100 mg of the resin.

Metal capacity of the chelating resin as a function of pH

The metal capacities of the chelating resins (I–III) as a function of pH are shown in Figures 1–3. The observed extraction of metal ions is attributed to the complex formation with the introduced polyamines, since the polystyrene itself did not retain these metal ions. Almost quantitative adsorption of Cu²⁺ and Zn²⁺ was attained at pH 5.5, of Pb²⁺ and Cd²⁺ at pH 6.0. As shown from the data, the metal capacities of the resins for all metal ions in a mixture are in the sequence, III > II > I. The higher metal capacity of the chelating resin III compared with II and I can be attributed to the presence of three nitrogen atoms in the repeating unit and also to the molecular association, while II and I each contain two nitrogen atoms and gave only one metal ion per repeating unit as was observed from the elemental analysis of the solid complexes. Since the absorption of the metal ions took place via complex formation, therefore the higher metal capacity of II compared to I can be attributed to the effect of the size of the chelate-ring. In the case of II, a six-membered ring is formed, which is energetically more favorable than the five-membered ring formed in I. It is also observed that the metal capacity of the three resins

towards the four metal ions is in the order: Cu²⁺ (0.86–0.96) > Zn²⁺ (0.78–0.85) > Cd²⁺ (0.20–0.29) > Pb²⁺ (0.166–0.275). This means that these types of N-donors bonded readily to the metal ions in the same order and is further consistent with our previous observations.⁶ Furthermore, the extraction of both Pb²⁺ and Cd²⁺ appeared to be less favorable compared to Cu²⁺ and Zn²⁺. This could be attributed to the softer nature of both Pb²⁺ and Cd²⁺ than Cu²⁺ and Zn²⁺ and the smaller sizes of Cu²⁺ and Zn²⁺ compared to the others.

Metal capacity of the chelating resins as a function of the shaking time

The variation of the metal uptake by the three chelating resins I–III is shown in Figures 4–6. Complete saturation was reached after 30 min of contact at the optimum pH for each metal ion at room temperature. The high absorption rates were observed during the first 10 min for Cu²⁺ and Zn²⁺ and 15 min for Cd²⁺ and Pb²⁺. Furthermore, the chelating resin III exhibited the best absorption characterization with respect to all metal ions.

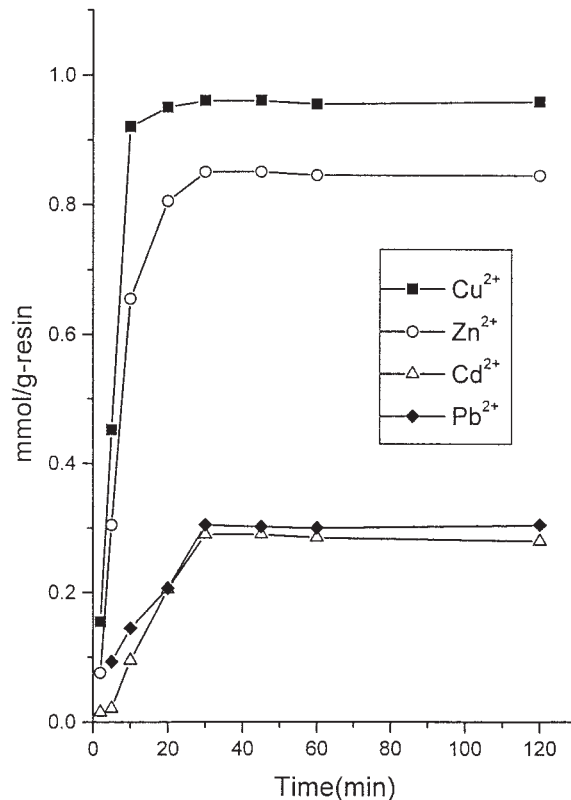


Figure 6 Effect of shaking time (2, 5, 10, 30, 45, and 60 min) on the metal capacity of the chelating resin III. pH values 6.0 for Cu²⁺ and Zn²⁺ and 5.5 for Cd²⁺ and Pb²⁺ at room temperature. The solution contains 1.5×10^{-2} mmol of each metal ion and 100 mg of the resin.

TABLE II
Absorbing Selectivity of the Chelating Resins*

| Resin | mg/mL of M ²⁺ | | Cu ²⁺ – Zn ²⁺ | | Cu ²⁺ – Cd ²⁺ | | Cu ²⁺ – Pb ²⁺ | |
|-------|--------------------------|-----------------|-------------------------------------|-------|-------------------------------------|-------|-------------------------------------|-------|
| I | C _{A1} | C _{B1} | 0.550 | 0.420 | 0.550 | 0.420 | 0.551 | 0.420 |
| | C _{A2} | C _{B2} | 0.400 | 0.395 | 0.370 | 0.405 | 0.373 | 0.405 |
| | K | | 5.93 | | 13.14 | | 12.81 | |
| II | C _{A1} | C _{B1} | 0.550 | 0.420 | 0.550 | 0.420 | 0.550 | 0.420 |
| | C _{A2} | C _{B2} | 0.275 | 0.385 | 0.250 | 0.395 | 0.246 | 0.405 |
| | K | | 11.00 | | 18.96 | | 22.36 | |
| III | C _{A1} | C _{B1} | 0.550 | 0.420 | 0.550 | 0.420 | 0.550 | 0.420 |
| | C _{A2} | C _{B2} | 0.185 | 0.370 | 0.155 | 0.388 | 0.146 | 0.392 |
| | K | | 14.60 | | 30.89 | | 38.74 | |

* Separation of Cu²⁺ from binary mixtures of 0.1mg/mL of each metal ion and 5 mg of the dry chelating resin.

According to the data obtained from the effects of pH and shaking time on the metal capacity of the chelating resins I–III, we could conclude that the absorption of the metal ions Cu²⁺, Zn²⁺, Cd²⁺, and Pb²⁺ is governed by the nature of the metal ion (soft or hard), the number of the coordinating centers per repeating unit, and the stability of the formed complex at constant temperature. The higher preference of copper(II) can be attributed to the higher stability constant for the complex formed in each case compared to the other ions.

Sorption selectivity

The chelating resins I–III are used to study the possibilities of their potential uses for the selective separation of Cu²⁺ present in binary mixtures with other metal ions. The batch method was employed for the separation of Cu²⁺ from the binary mixtures containing Cu²⁺ – Zn²⁺, Cu²⁺ – Cd²⁺, and Cu²⁺ – Pb²⁺ at pH 5.5, shaking time of 30 min, at room temperature. The separating factor K was calculated from the formula

$$K = (C_{A1} - C_{A2})C_{B2} + (C_{B1} - C_{B2})C_{A1}$$

where C_{A1} and C_{A2} stand for the concentration of metal ion A (in this case, Cu²⁺) before and after separation, and C_{B1} and C_{B2} are the concentration of the second metal ion (Zn²⁺, Cd²⁺, or Pb²⁺) before and after separation. The data in Table II show that for the same resin, the absorption of Cu²⁺ in the presence of Zn²⁺ < Cd²⁺ ≤ Pb²⁺, that is, Zn²⁺ ions most negatively affected the sorption of Cu²⁺ relative to both Pb²⁺ or Cd²⁺. This could be attributed to the higher complexing ability of Zn²⁺ than Cd²⁺ or Pb²⁺, but all are still lower than the ability of Cu²⁺. For the same mixture, the values of K are in the order resin I < resin II < resin III, in accordance with the ligating capacity of the resin. Therefore, the chelating resin III is the best resin for separation of Cu²⁺ from these binary mixtures. From the values given in Table II, it appeared

that the separation of Cu²⁺ – Pb²⁺ binary mixture is the easiest.

CONCLUSION

In this study, new modified N-sulfonylpolyamine chelating resins anchored on polystyrene-divinylbenzene beads have been prepared and characterized. These chelating resins were found to have a higher ability to form metal chelates with Cu²⁺ and Zn²⁺ than with Cd²⁺ and Pb²⁺. The synthesized chelating resins were applied to remove Cu²⁺, Zn²⁺, Cd²⁺, and Pb²⁺ from aqueous solution, and their metal capacities were found to be shaking time and pH dependent. Furthermore, the optimum conditions for separation of Cu²⁺ from other metal ions were found to be at pH 5.5 and shaking time of 30 min at room temperature. Therefore, these chelating resins can be used for removal of these heavy elements from aqueous solutions and for selective isolation of Cu²⁺ in mixtures.

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