

Chelation Properties of Poly(β -diketone) Polymer and Its Oxime Toward Heavy Metal Ions

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ABSTRACT: The chelation behavior of poly(β -diketone), polymer I, and poly(β -diketone) oxime, polymer II, toward the divalent metal ions, Cu^{2+} , Zn^{2+} , Ni^{2+} , and Cd^{2+} , and the trivalent lanthanide metal ions, La^{3+} , Nd^{3+} , Sm^{3+} , Gd^{3+} , and Tb^{3+} was investigated by a batch equilibration technique as a function of contact time, pH, and counter ion. Polymer II exhibited improved chelation characteristics toward lanthanide metal ions in comparison with polymer I and the metal-ion uptake follows the order

$\text{Tb}^{3+} \approx \text{Gd}^{3+} \approx \text{Sm}^{3+} > \text{Nd}^{3+} \approx \text{La}^{3+}$. On the other hand, polymer I showed relatively higher capacity than polymer II, toward the investigated divalent metal ions, where the metal-ion uptake follows the order $\text{Cu}^{2+} > \text{Cd}^{2+} \approx \text{Zn}^{2+} > \text{Ni}^{2+}$. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2415–2420, 2008

Key words: poly(β -diketone); oxime; lanthanide metal ions; chelation behavior; counter ion

INTRODUCTION

Chelate-forming polymers are produced by incorporating chelating groups into a polymeric matrix;^{1,2} such chelating groups may be covalently bound to a polymer matrix as pendent groups or incorporated into the repeating units of the polymer backbone by polymerization of a suitable monomer containing the required chelating group. The chelation characteristics of these materials is largely dependent on the nature of the active chelating groups incorporated into the polymeric matrix and the type of intervening spacer groups connecting the active chelating ligands.³

The role played by toxic heavy metals in the aquatic environment has stimulated considerable activity and interest in the development of metal chelating polymers that found widespread use in the separation and monitoring of trace heavy metal ions, including lanthanides, from aqueous solutions.^{4–26} Moreover, the use of chelating polymers in radioactive nuclear waste treatment is attracting a great deal of interest.

Oximes, $>\text{C}=\text{N}-\text{OH}$, an important class of chelating agents,¹⁸ have found numerous applications as highly selective reagents for the separation and determination of a number of metal ions.^{18–20} Hence, the incorporation of the oxime group in polymers is an attractive route to the preparation of selective chelating polymers. Several oxime-containing polymers, along with methods to incorporate the oxime

group in chelate-forming polymers, have been described in the literature.^{16,27–35}

In connection with our recent work on the synthesis and sorption properties of chelate-forming polymers,^{7–15} the present article deals with the synthesis and characterization of poly(β -diketone) and poly(β -diketone) oxime. The chelation properties of these polymers toward some transition metal ions (Cu^{2+} , Zn^{2+} , Ni^{2+} , and Cd^{2+}), and toward some trivalent lanthanide ions (Tb^{3+} , Gd^{3+} , Sm^{3+} , Nd^{3+} , and La^{3+}) in aqueous solutions under different experimental conditions of contact time and pH are investigated.

EXPERIMENTAL

Chemicals

Unless otherwise indicated, all chemicals were obtained from commercial sources and were used as received. Poly(vinyl alcohol) (99%), chromium oxide, and sulfuric acid were obtained from Fluka (Buchs, Switzerland). Hydroxylamine hydrochloride was received from Aldrich (Milwaukee, WI). The following salts were also used as received without further purification: $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ from Aldrich, $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ from K and K Laboratories (Jamaica, NY), CuCl_2 from BDH Chemical (Poole, England), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ from Panreac (Barcelona, Spain), $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ from Fluka, and $\text{Zn}(\text{NO}_3)_2$ from Scharlau (Port Adelaide, Australia).

Instrumentation

Infrared spectra of the polymers were recorded, as KBr discs, on a Nicolet Impact 400 FTIR-Spectropho-

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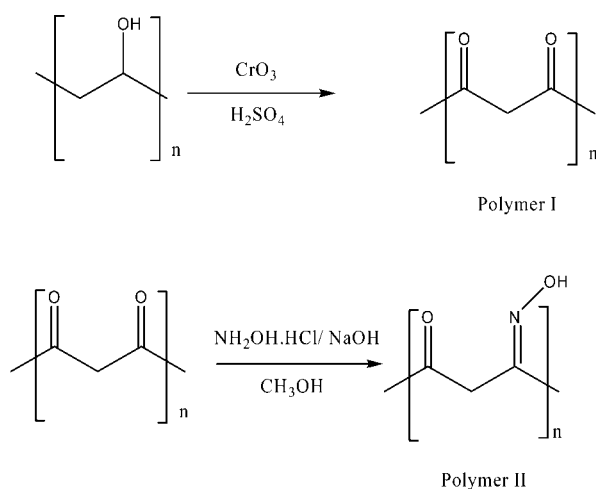
tometer from 400 to 4000 cm^{-1} . Atomic absorption measurements were carried out with the aid of a Varian Atomic Absorption Spectrophotometer (AAS). Polymer metal-ion batch equilibration samples were shaken using a GFL-1083 shaker thermostated water bath maintained at 25°C. Complexometric titrations were performed with a Metrohm 655 Dosimat Titrator.

Preparation of poly(β -diketone): polymer I

This polymer was synthesized according to the following general procedure³⁶ (Scheme 1): A solution made from 28.50 g of chromium oxide (0.285 mol), 500 mL of H_2O , and 175 mL of concentrated sulfuric acid was slowly added to a stirred suspension of 25 g of poly(vinyl alcohol) (99% hydrolyzed) in 375 mL of H_2O . The oxidizing agent was added at such a rate that the temperature did not exceed 60°C. The stirred mixture was then heated to 90°C, where it was maintained for 24 h. The dark brown solid product was filtered and washed thoroughly with water. The solid polymer was dried in vacuum at 40°C for 24 h, crushed, and sieved through mesh size 35–60 (0.25–0.50 mm). Satisfactory elemental analyses were obtained. Found %C 50.90, %H 4.06, calculated for $[\text{C}_3\text{H}_2\text{O}_2]_n$: %C 51.44, %H 2.88

Water content or water regain (α)

Samples of the dry polymers I and II were suspended in water and were left for different periods of 2 and 24 h. The polymers were centrifuged, water decanted, weighed, and then dried at 80°C and reweighed. Water regain (α) was calculated using the following equation.



Scheme 1

$$\alpha = \frac{\text{mass of polymer bound water (g)}}{\text{mass of dry polymer (g)}}$$

The results of water regain ratio for the chelating polymers (I–II) in g g^{-1} are 1.353 after 2 h and 1.497 after 24 h for polymer I and are 1.523 after 2 h and 1.556 after 24 h for polymer II.

Preparation of poly (β -diketone oxime): polymer II

A solution of 20.9 g of hydroxylamine hydrochloride (0.30 mol) in 300 mL of methanol was poured into a 1-L flask fitted with a condenser. Then 15.2 g of sodium hydroxide (0.28 mol) was added to the solution followed by 10.0 g of polymer I; poly (β -diketone). The suspended mixture was refluxed for 24 h with slow stirring. The brown solid polymer was filtered and washed with methanol, 1M hydrochloric acid solution, methanol, deionized water, and methanol in order. Further purification of the resin was achieved by soxhlet extraction with methanol for 24 h. The resin was then dried in a vacuum oven at 40°C and sieved through mesh size 35–60 (0.25–0.50 mm). Satisfactory elemental analyses were obtained. Found: %C 43.13, %H 3.72, %N 14.95, calculated for $[\text{C}_3\text{H}_3\text{NO}_2]_n$: %C 42.36, %H 3.55, %N 16.47 and calculated for $[\text{C}_3\text{H}_4\text{O}_2\text{N}_2]_n$: %C 36.03, %H 4.03, %N 27.99.

Sorption of metal ions on the polymers

The metal chelation characteristics of the resins for each metal ion were studied by the batch equilibrium method; duplicate experiments involving 0.10 g of dry, 35–60 mesh size, resin samples were suspended with 15.0 mL of sodium acetate-acetic acid buffer (pH = 7.0) for 2 h to equilibrate. Then, 10.0 mL of metal ion solution containing a total of 15.0 mg of metal ion was added, with a total ionic strength of 0.10 M (with sodium perchlorate). After being shaken for a given period of time (0.08–24 h) at 25°C, the mixture was filtered and the amount of metal ion remaining was determined by complexometric titration in the case of lanthanide metal ions using standard (0.011 M) EDTA solution and xylenol orange solution as an indicator and by atomic absorption spectrometry (AAS) using standard solutions for calibration in the case of the divalent metal ions.

The extent of metal-ion uptake was studied under similar experimental conditions, where the contact time varied from 0.08 to 24 h at 25°C after it was equilibrated with distilled water. Similar experiments were also carried out in buffered solutions, in

which the pH was varied between 4.0 and 7.0 for a fixed contact time of 6 h.

RESULTS AND DISCUSSION

Characterization of the of the polymers

The IR spectra of the polymers and their chelates were consistent with the structures assigned to them. Typical structures of these polymers are depicted in Scheme 1 and Scheme 2. The IR spectrum of poly(β -diketone); polymer I, shows characteristic stretching bands. The broad bands in the $3000\text{--}3500\text{ cm}^{-1}$ region are assigned to the intramolecular hydrogen bonded O—H stretching vibration; this is due to unoxidized secondary alcohol groups and/or to enol (Scheme 2). The strong absorption bands at about 1710 cm^{-1} (absent in the starting material, poly(vinyl alcohol)) and at about 1620 cm^{-1} were assigned to the C=O, and to the C=C stretching, respectively; this behavior has been observed by other workers.³⁶ Meanwhile, the strong band at about 1640 cm^{-1} in the spectrum of the poly oxime is attributed to the C=N stretching vibration, while the broad absorption bands in the $3000\text{--}3500\text{ cm}^{-1}$ region were attributed to the O—H stretching of the oxime and enol groups.³⁷ IR data for polymer I suggest that form 2 of the diketone is the dominant one, as indicated by the strong and broad absorption bands in the $3000\text{--}3500\text{ cm}^{-1}$ region. In addition, the IR spectrum of polymer II indicates that form 4 of the oxime is more significant than form 3.

Additionally, elemental analysis of polymer II indicates that hydroxylation of the carbonyl groups of polymer I has taken place, to a large extent, on one of the carbonyl groups (Scheme 1).

Polymers I and II are insoluble in water and in organic solvents such as DMF, DMSO, acetone, chloroform, dichloromethane, benzene, pyridine, acetonitrile, acetic acid, and methanol. The polymers are

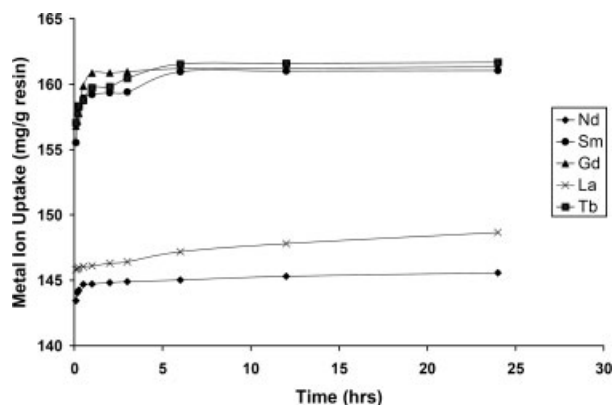
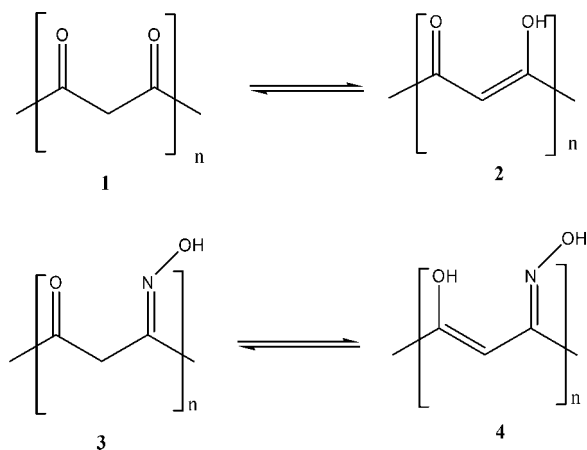


Figure 1 Rate of Ln(III) uptake by resin I as a function of contact time.

also insoluble in concentrated acids such as HCl, or bases such as NaOH; this makes it difficult to use certain spectroscopic techniques, such as NMR, for characterization.

The water regain parameter, α , provides an indirect measurement of the hydrophilic character of the resins.²⁷ A high α may indicate the presence of microporous hydrophilic sites, which provide the water-transport channels required for the effective sorption of metal ions from aqueous solutions. The experimental values of α in g g^{-1} were 1.50 and 1.56 for polymers I and II, respectively.

Rate of lanthanide metal-ion uptake as a function of contact time

The rate of lanthanide metal-ion uptake by the polymers as a function of contact time was investigated by a batch equilibrium technique. Figures 1 and 2 show the dependence of lanthanide metal-ion uptake on contact time for polymers I and II, respectively. The metal-ion uptake increases with time until it reaches a steady state after about 3–4 h. In addition, the results indicate fast rates of equilibration; about

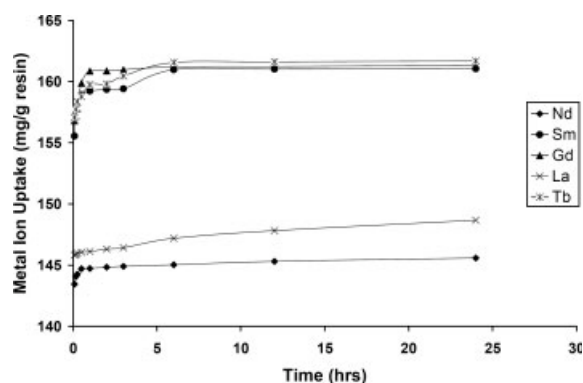


Figure 2 Rate of Ln(III) uptake by resin II as a function of contact time.

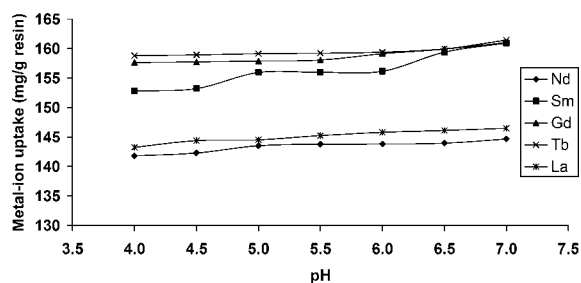


Figure 3 Ln(III) uptake by resin I as a function of pH.

80% metal-ion uptake was achieved after 2–3 h. The metal-ion uptake capacities of the polymers toward the investigated metal ions (Ln^{3+}), in general, increased with decreasing ionic radii of the lanthanide ions and follow the order $\text{Tb}^{3+} > \text{Gd}^{3+} \approx \text{Sm}^{3+} > \text{La}^{3+} > \text{Nd}^{3+}$ and may also be due to the stability constants of the complexes the ions may form with the polymers; this was consistent with earlier investigations.^{10,12–14} The results also show that both resins have comparable metal-ion uptake capacities toward the investigated lanthanide metal ions. This may suggest that the chelation between the lanthanide metal ions and the polymers takes place through the oxygen atoms of the diketone (in polymer I) and the oxygen atoms of the oxime (in polymer II) since lanthanides favor oxygen over nitrogen for chelation.

pH dependence of the metal-ion uptake

The binding capacities of polymers I and II toward the Ln^{3+} was studied in the pH range 4–7 under continuous shaking for a fixed contact time of 6 h at 25°C and at an ionic strength of 0.10M. At higher pH values, hydrolysis of the metal ions investigated becomes significant and may compete with polymer chelate formation. Typical pH-binding capacity profiles are illustrated in Figures 3 and 4, for polymers I and II, respectively. The results reveal that metal-ion uptake slightly increased with the pH of the medium and approached a steady state at about pH 7.0. These findings are in agreement with the

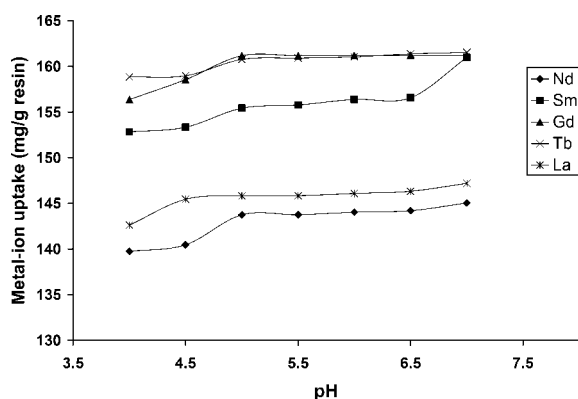


Figure 4 Ln(III) uptake by resin II as a function of pH.

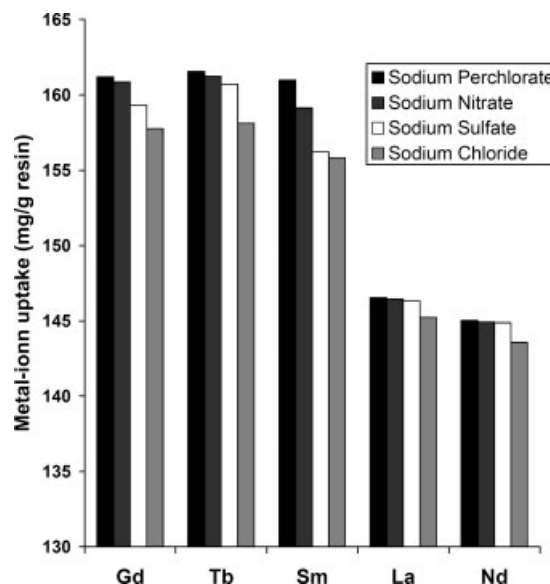


Figure 5 Ln(III) uptake by resin I as a function of counter ion.

pH profiles of most chelating polymers with N,O binding sites.^{7–17}

Effect of counter ions on the sorption of lanthanide metal ions

The effect of counter ion on the chelation properties of the polymers was investigated by the determination of the metal-ion uptake as a function of the counter ion at 25°C, and in an acetate-acetic acid buffer at pH 7.0 for a fixed contact time of 6.0 h. Ionic strength was maintained at 0.10 M with different types of electrolytes including NaClO_4 , NaCl , NaNO_3 , and Na_2SO_4 . The average of two duplicate runs was used, and typical results are displayed in Figure 5 for polymer I for La^{3+} , Nd^{3+} , Sm^{3+} , Gd^{3+} , and Tb^{3+} . The observed metal-ion uptake with chloride, nitrate, perchlorate, and sulfate as counter ions followed the order $\text{Tb}^{3+} > \text{Gd}^{3+} > \text{Sm}^{3+} > \text{Nd}^{3+} > \text{La}^{3+}$. This trend was observed in earlier investigations^{10,14} and followed the increase in the hydrated ionic radius in going from Tb^{3+} to La^{3+} . The results of these experiments for the two polymers also show that the rate of metal-ion uptake increased in the order $\text{ClO}_4^- > \text{NO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$. This order may have been related to the free energy of hydration of the anion^{8,10} and could also be explained in terms of the stability constants of complexes of Ln^{3+} with the anions. These findings are in agreement with our previous investigations.¹⁵

Sorption of transition metal ions on the polymers

The sorption of various divalent metal ions (Cu^{2+} , Zn^{2+} , Cd^{2+} , and Ni^{2+}) on polymers I and II was

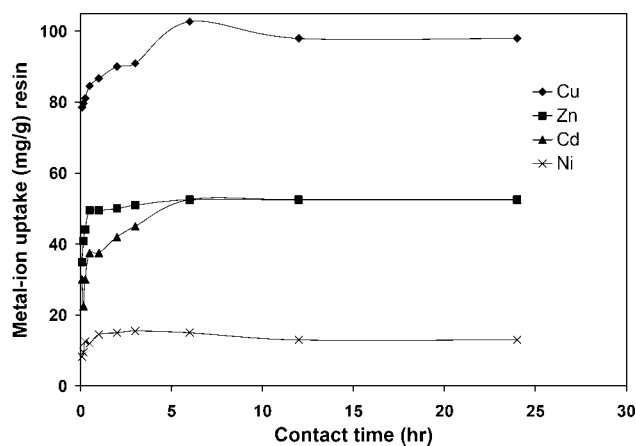


Figure 6 M(II) uptake by resin I as a function of contact time.

studied by a batch equilibration technique as a function of contact time at a fixed pH of 7.0. The results for the dependence of metal-ion uptake on contact time for polymers I and II are presented in Figures 6 and 7, respectively. These results indicate fast rates of equilibration; the rate of metal-ion uptake increases in the first 3 h and reaches a steady state after about 6 h. Over 70–80% of the metal ions are taken by the polymers in the first hour. Results also revealed that the metal-ion uptake of the various divalent metal ions follow the order $\text{Cu}^{2+} > \text{Zn}^{2+} \approx \text{Cd}^{2+} > \text{Ni}^{2+}$ for both resins.

The pH dependence of metal-ion uptake by polymers I and II was investigated in the pH range 4.0–7.0 under continuous shaking for a fixed contact time of 6 h. At higher pH values, hydrolysis of the metal ions investigated become significant and may compete with polymer chelate formation. The pH-uptake profiles are displayed in Figures 8 and 9 for polymer I and II, respectively.

In general, the binding capacities of the polymers under investigation towards the various divalent

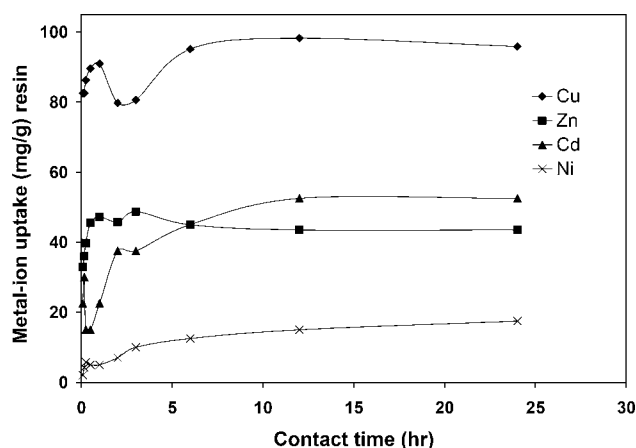


Figure 7 M(II) uptake by resin II as a function of contact time.

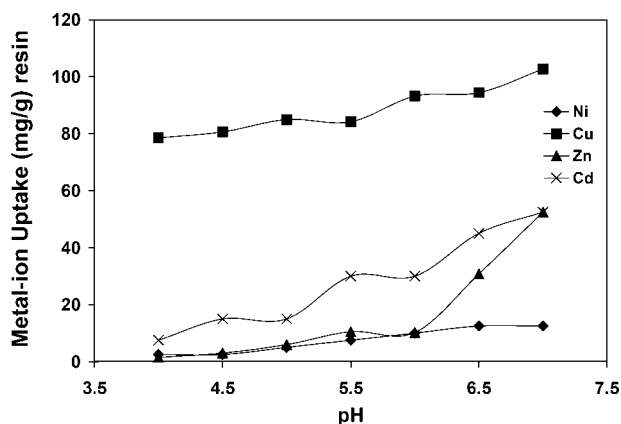


Figure 8 M(II) uptake by resin I as a function of pH.

metal ions increase as the pH increased which is in agreement with earlier investigations conducted in our laboratory.^{8,15}

Selectivity of polymers I and II was studied by equilibrating 0.10 g of the polymer with 10 mg of each of Cu(II), Zn(II), Cd(II), and Ni(II) at 25°C, pH 7, and at a fixed contact time of 6 h. Results revealed that for the two resins, the selectivity towards the investigated divalent metal ions followed the order $\text{Cu}^{2+} > \text{Zn}^{2+} \approx \text{Cd}^{2+} > \text{Ni}^{2+}$. This is in agreement with our earlier investigations which may attribute these differences to a combination of factors including metal-ligand stability constants, metal ionic radii, and stereochemical configuration of active chelating sites among others.³

CONCLUSIONS

In this investigation, the sorption properties of the chemically synthesized poly(β -diketone) and poly

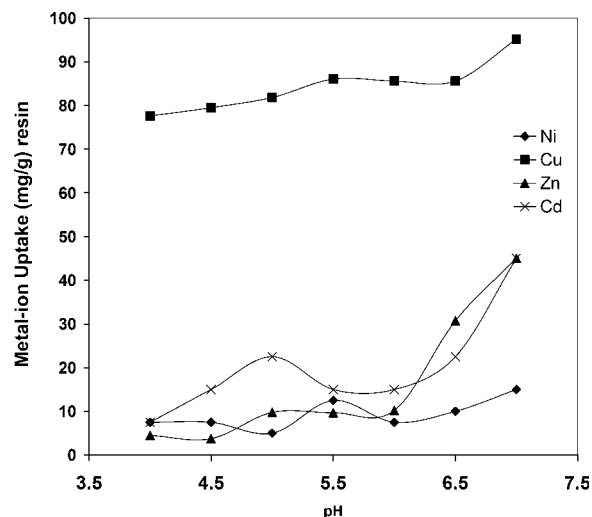


Figure 9 M(II) uptake by resin II as a function of pH.

(β -diketone) oxime resins toward some divalent metal ions and trivalent lanthanide metal ions in aqueous solutions were investigated. The effect of exposure time on the metal-ion uptake was studied by a batch equilibrium technique and showed that a time of 6–10 h was enough to achieve maximum metal-ion sorption and that the extent of metal-ion uptake followed the order $\text{Cu}^{2+} > \text{Zn}^{2+} \approx \text{Cd}^{2+} > \text{Ni}^{2+}$ for both resins for the investigated divalent metal ions and followed the order $\text{Tb}^{3+} > \text{Gd}^{3+} \approx \text{Sm}^{3+} > \text{La}^{3+} > \text{Nd}^{3+}$ for the studied trivalent lanthanide metal ions. The pH binding capacity profiles showed that the metal-ion uptake of the resins slightly increased with increasing pH and reached a maximum at pH 7.0. The effect of counter ion on the extent of metal-ion uptake of the resins was also investigated.

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