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Kais A. K. Ebraheem[a][b]; Mohammad S. Mubarak[a]; Samer I. Al-Gharabli[a]
[a] Department of Chemistry, University of Jordan, Amman, Jordan [b] Department of Chemistry, University of Petra, Amman, Jordan

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SYNTHESIS AND CHELATION PROPERTIES OF SOME NEW MANNICH CONDENSATION POLYMERS CONTAINING A SALICYLALDOXIME GROUP

Kais A. K. Ebraheem,*,† Mohammad S. Mubarak,*
and Samer I. Al-Gharabli

Department of Chemistry, Faculty of Science,
University of Jordan, Amman 11942, Jordan

ABSTRACT

A new oxime containing polymer, Poly(salicylaldoxime-3,5-diyl (N,N′-dimethylethylenediamine N,N′-bismethylene)), polymer 1, was prepared through a Mannich-type condensation of salicylaldoxime with formaldehyde and N,N′-dimethylethylenediamine. Polymer 2, a crosslinked chelating ion exchange resin, was obtained by a similar Mannich condensation in presence of resorcinol as the crosslinker. The sorption properties of these polymers towards the divalent ions, Mg^{2+}, Ca^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, and Cu^{2+} were studied by a batch equilibration technique as a function of contact time and pH. Crosslinking is found to have profound effects on the surface morphology and the chelation properties of these polymers. The crosslinked Polymer 2 exhibited improved chelation characteristics in comparison with Polymer 1 and displayed faster rates of metal ion uptake and relatively higher capacities and selectivities. These findings are in keeping with the observed increase in hydrophilic character upon crosslinking.

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*Corresponding authors.

†Current address: Department of Chemistry, University of Petra, Amman, Jordan.

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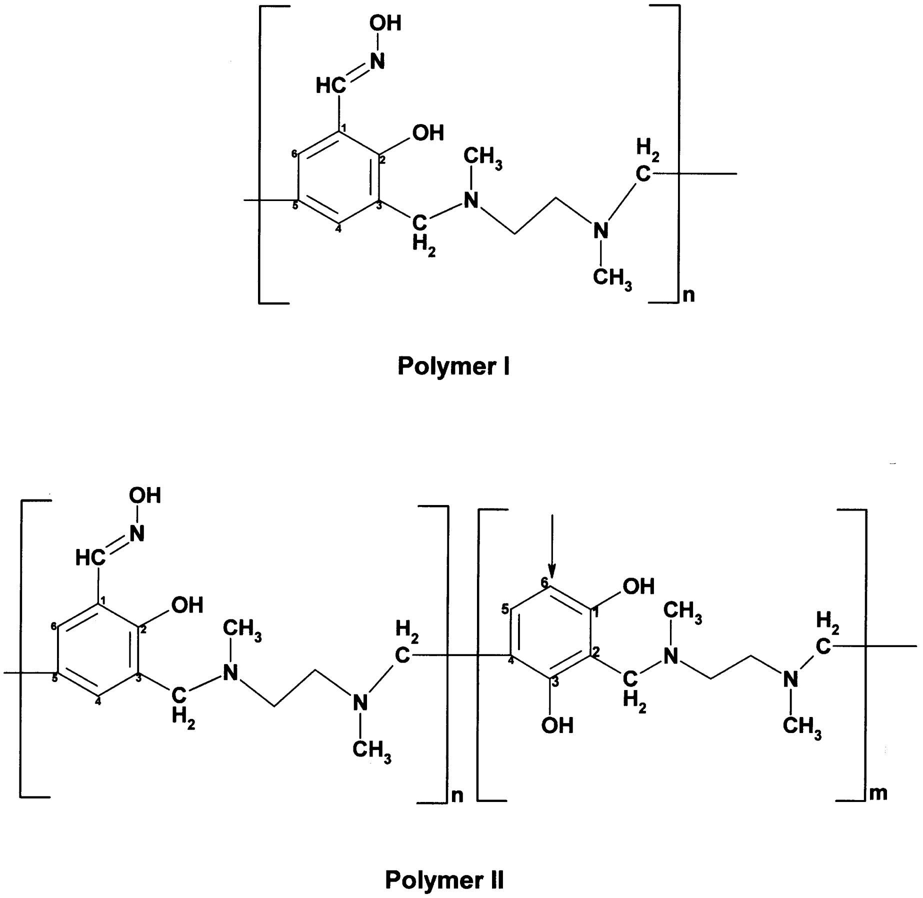
INTRODUCTION

The use of chelating polymers is widespread in the separation technology [1–5] and has met with considerable success in the separation and monitoring of trace heavy metal ions from aqueous solutions [4–14]. Chelating polymers are normally produced by incorporating active chelating groups into a polymeric matrix [1–3]; such chelating groups may be covalently bound to a polymer matrix as pendant groups or incorporated into the repeating units of the polymer backbone by polymerization of a suitable monomer containing the required chelating group. Oximes, $>C=N-OH$, an important class of chelating agents [15], have found numerous applications as highly selective reagents for the separation and determination of a number of metal ions [15–17]. 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 groups in chelate forming polymers, have been described in the literature [8, 18–28]. Recently [8], we have demonstrated that a phenol-formaldehyde chelating polymer derived from salicylaldoxime and formaldehyde exhibited high capacity and selectivity towards Cu^{2+} ions.

It has been amply demonstrated [1–3] that the nature of the intervening groups connecting the active chelating ligands in chelating polymers plays a paramount role in the chelation process. In phenol-formaldehyde polymers, the chelate-forming phenol moieties are linked by methylene groups ($-CH_2-$); to change these linkages, one may use the more versatile Mannich-type condensation reaction [29–35] in which a compound with an active hydrogen is condensed with formaldehyde and a primary or secondary amine. Mannich reaction [29, 30], has become an important tool in the synthesis of a diversity of specialty chemicals such as polymers [31–35], pro-drugs and pharmaceuticals [36–38], antibiotics and antibacterial agents [39–41], anti-tumor agents [42], azacrown ethers and cryptands [43] among others. Mannich bases are also important in the synthesis or chemical modification of polymeric molecules suitable for many different applications including the production of polymeric antioxidants for plastics and the synthesis of anionic/cationic exchange resins.

In this paper, we report the synthesis and characterization of new oxime-containing polymers, by Mannich-type condensation of salicylaldoxime, formaldehyde and N,N′-dimethylethylene diamine. Crosslinking is achieved by incorporating resorcinol which acts as a trifunctional crosslinker through Mannich-type condensations at positions 2, 4 and 6 of the resorcinol moiety. Typical structures of polymers 1 and 2 are depicted in Scheme 1. The chelation properties of these polymers towards a number of divalent metal ions in aqueous solutions are investigated.



Scheme 1. Typical structures of polymers 1 and 2.

EXPERIMENTAL

Reagents

Unless otherwise indicated, all chemicals used were of analytical grade and were used as received; salicylaldoxime and N,N′-dimethylethylenediamine were obtained from Fluka (Switzerland); formaldehyde solution (37–41%) was purchased from Riedel-deHaen (Germany); dimethylformamide was received from Acros (USA); and resorcinol was obtained from Greenland Chemical Company (UK). The following metal ion salts were also used without further purification: Cupric chloride from BDH Chemical Ltd. (England); zinc nitrate from RBL (Belgium); nickel chloride 6-hydrated from Montplet Estepan SA (Spain).

Instrumentation

Infrared spectra of the polymers were recorded as KBr discs using a Nicolet Impact 400 FTIR-Spectrophotometer from 4000 to 400 cm^{-1}. Elemental analyses (C,H,N) were carried out at M.H.W. Laboratories (USA). Atomic absorption data were obtained using a Varian Atomic Absorption Spectrophotometer. Scanning electron microscope (SEM) photographs were recorded with a DSM 950 electron microscope which allowed a wide range of magnification up to × 1200. Samples were shaken using a GFL-1083 shaker thermostated water bath maintained at 25°C.

Polymer Preparation

Polymer 1 was prepared by dissolving 13.7 g (0.1 mol) of salicylaldoxime and 10.8 mL (0.1 mol) of N,N′-dimethylethylenediamine in 180 mL of DMF. To this solution, 19 mL (0.25 mol) of 37% aqueous formaldehyde was slowly added with stirring at room temperature. After 4 hours, the mixture was heated, gradually in an oil bath, to 90°C and heating was then continued for 4 more hours. An additional 10 mL of 37% formaldehyde was slowly added to the reaction mixture in three portions. After 12 hours. of continuous heating, the reaction mixture was cooled and the precipitate was collected and washed with methanol. After soxhlet extraction with methanol for 24 hours, the polymer was dried in vacuum, crushed, and sieved through mesh size 35–60 (0.25–0.50 mm). Satisfactory elemental analyses were obtained. Found: %C 61.78, %H 6.38, %N 13.34: Calcd. for $[C_{13}H_{19}N_3O_2]_n$ %C 62.63, %H 7.68, %N 16.85.

Polymer 2 was synthesized by dissolving 13.7 g (0.1 mol) of salicylaldoxime and 10.8 mL (0.1 mol) of N,N′-dimethylethylenediamine in 180 mL of DMF. To this solution, 19 mL (0.25 mol) of 37% aqueous formaldehyde was slowly added with stirring at room temperature. After 4 hours, the mixture was heated gradually in an oil bath to 90°C and heating was then continued for 4 more hours. Then, 0.11 g (1% with respect to the oxime) of resorcinol dissolved in 5 mL of DMF was slowly added to the polymer. To this mixture, a total of 6 mL of formaldehyde was added in three portions over a 6-hour period. After 12 hours. of continuous heating and stirring, the reaction mixture was cooled and the precipitate was collected, purified and sieved as described for Polymer 1.

Sorption of Metal Ions on the Polymer

The metal chelation characteristics of the polymer for each metal ion were studied by the batch equilibrium technique; duplicate experiments involving dry 0.25 g, 35–60 mesh size, resin samples were suspended in 75 mL of sodium acetate-acetic acid buffer solutions for 4 hours and were left to equilibrate. Then, 25 mL of metal ion solution containing a total of 25 mg metal ion was added. After being shaken for a definite period of time at 25°C, the mixture was filtered and the amount of metal ions remaining in the filtrate was determined by atomic absorption spectrometry. The rate of metal ion uptake was studied under similar experimental conditions where the contact time was varied from 1 hour to 24 hours at 25°C after being equilibrated with distilled water. Similar experiments were carried out, in buffer solutions, in which the pH was varied between 2 and 8 at a fixed contact time of 6 hours.

RESULTS AND DISCUSSION

Characterization of the Polymer

The polymers are insoluble in all organic solvents. They are also insoluble in strong acid and strong base solutions; this makes it difficult to use certain spectroscopic techniques for characterization. The hydrophilic character of the resins, reflected by water regain are 1.29 g water/g resin after 2 hours and 4.51 g water/g resin after 24 hours for Polymer 1 and 1.56 g water/g resin after 2 hours. and 6.67 g water/g resin for Polymer 2; these values are relatively higher than that of poly(N-butylsalicylaldimine 3,5-diylmethylene) [9] and of poly(salicylaldoxime-3,5-diylmethylene) [8]. IR spectra of the polymers and their polymeric chelates resemble those of the monomers and are consistent with the structures assigned to the polymers depicted in Scheme 1. The broad bands in the 3200–3550 cm^{-1} region are assigned to the intramolecularly hydrogen bonded O–H stretching vibration [44–46]. These bands are also observed in the spectra of the metal chelates, since only a fraction of the ligands moieties on the polymers are involved in chelate formation. The absorption bands observed at about 2950 cm^{-1} and 2860 cm^{-1} have been attributed to the C–H stretching of the methylene groups connecting the aromatic rings with the amine. The C–N stretching vibrations of the oxime groups were observed at 1610 and 1620 cm^{-1} for polymers 1 and 2, respectively. Scanning electron microscope photographs were employed to show the surface morphology of the resin and the changes that result from the interaction of the resin with metal ions. Plates 1 and 2 show the surface morphology of polymers 1 and 2, respectively. Plate 1 displays spheroidal shape indicating a crystalline structure while a grape shape morphology with a huge number of voids has been observed in plate 2. Upon complexation with metal ions, the surface morphology of Polymer 1 undergoes slight changes probably, due to the spheroidal surface morphology of Polymer 1 and to the relatively low capacity towards metal ions. A more noticeable difference, however, was observed when copper was chelated with Polymer 2 resulting in a substantial coverage of surface voids. Less noticeable changes in the surface morphology of Polymer 2 were found for other metal polymer chelates.

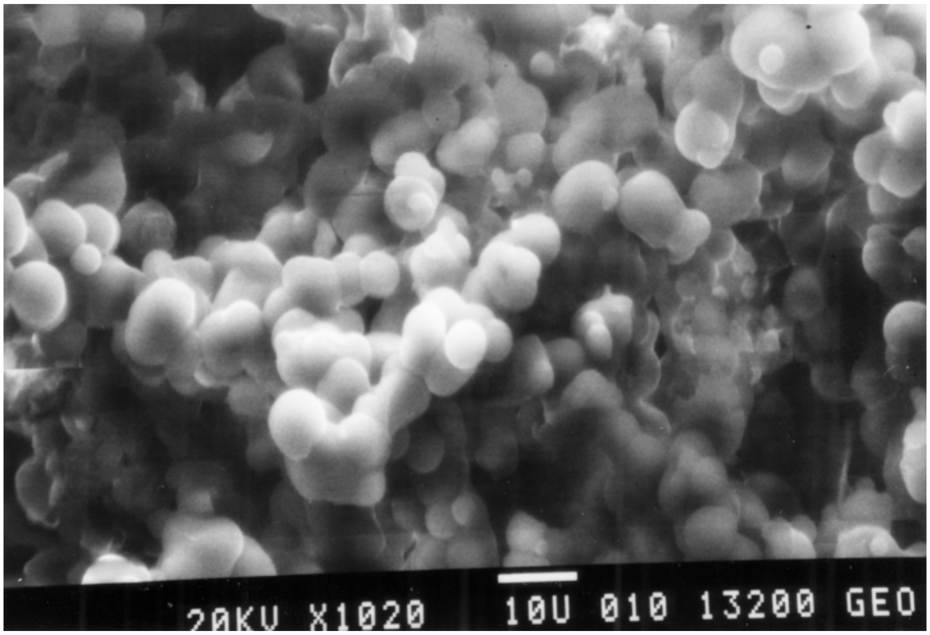


Plate 1. Scanning electron microscope photograph for polymer 1.

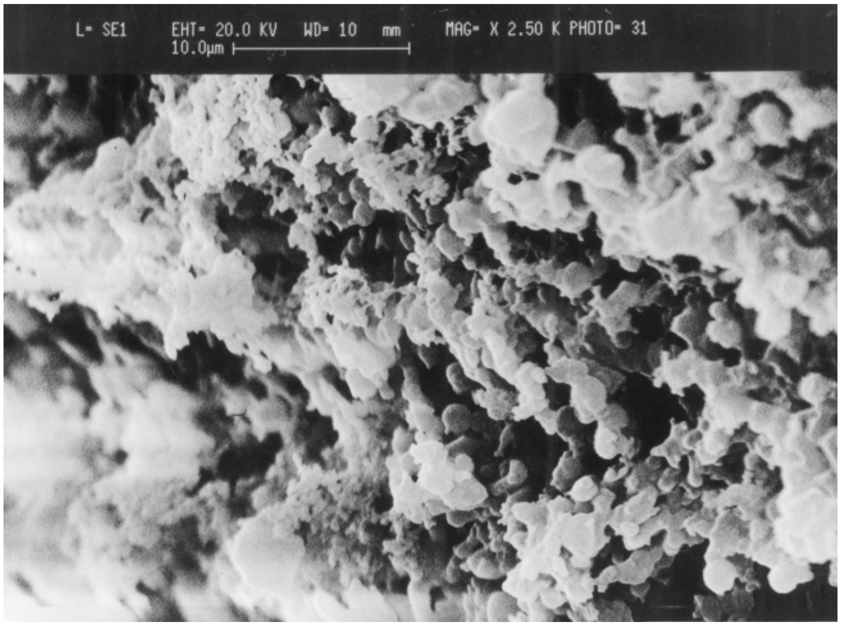


Plate 2. Scanning electron microscope photograph for polymer 2.

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Sorption of Metal Ions on the Resin

The sorption of various divalent metal ions (Mg^{2+}, Ca^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, and Cu^{2+}) on polymers 1 and 2 was investigated by a batch equilibrium technique as a function of contact time. The results for the dependence of the metal ion uptake on contact time for polymers 1 and 2 are presented in Table 1 and Figs. 1 and 2. These results indicate fast rates of equilibration; the rates of metal ion uptake increases in the first 1–3 hours and reaches a steady state after 5 to 6 hours. The chelation characteristics of chelating

Table 1. The Rate of Metal Ion Uptake by Polymers 1 and 2 at 25.0°C and pH 7.0

M^{2+}	1 hrs	2 hrs	3 hrs	4 hrs	5 hrs	6 hrs	10 hrs	24 hrs[b]
i) Metal ion uptake in mg per 1.0 g of Polymer 1[a]								
Cu^{2+}	44.17	45.17	45.92	46.92	48.17	48.42	48.92	48.92 (382.8)
Cd^{2+}	8.76	9.61	9.61	9.61	9.61	9.61	9.61	9.61 (42.91)
Ni^{2+}	5.85	8.98	9.60	10.23	10.23	10.23	10.23	10.23 (45.76)
Zn^{2+}	19.80	20.20	20.60	20.60	20.60	20.60	20.60	20.60 (104.30)
Mg^{2+}	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22 (0.87)
Ca^{2+}	0.29	2.29	2.29	2.81	2.81	2.81	2.81	2.81 (11.96)
ii) Metal ion uptake in mg per 1.0 g of Polymer 2[a]								
Cu^{2+}	53.58	54.08	55.33	56.58	57.08	59.83	61.83	67.82 (766.9)
Cd^{2+}	4.39	7.04	9.64	10.54	10.54	10.54	11.39	11.39 (51.9)
Ni^{2+}	4.60	7.34	7.34	7.34	7.34	7.34	7.34	8.24 (36.2)
Zn^{2+}	17.85	18.70	19.15	19.60	20.25	20.90	21.55	21.55 (111.0)
Mg^{2+}	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30 (1.25)
Ca^{2+}	0.075	3.28	3.28	3.75	3.75	3.75	3.75	3.75 (16.7)

[a] Volume of solution = 100 mL. Initial metal ion content in solution = 25.0 mg. Mass of polymer sample used = 0.25 g.

[b] Values between brackets are for distribution coefficients K_d, defined as $K_d = [M]_{resin}/[M]_{solution}$ where $[M]_{resin}$ is the amount (in mg) of metal ions taken up by 1 g of resin and $[M]_{solution}$ is the amount (in mg) of metal ions remaining in 1 mL of solution.

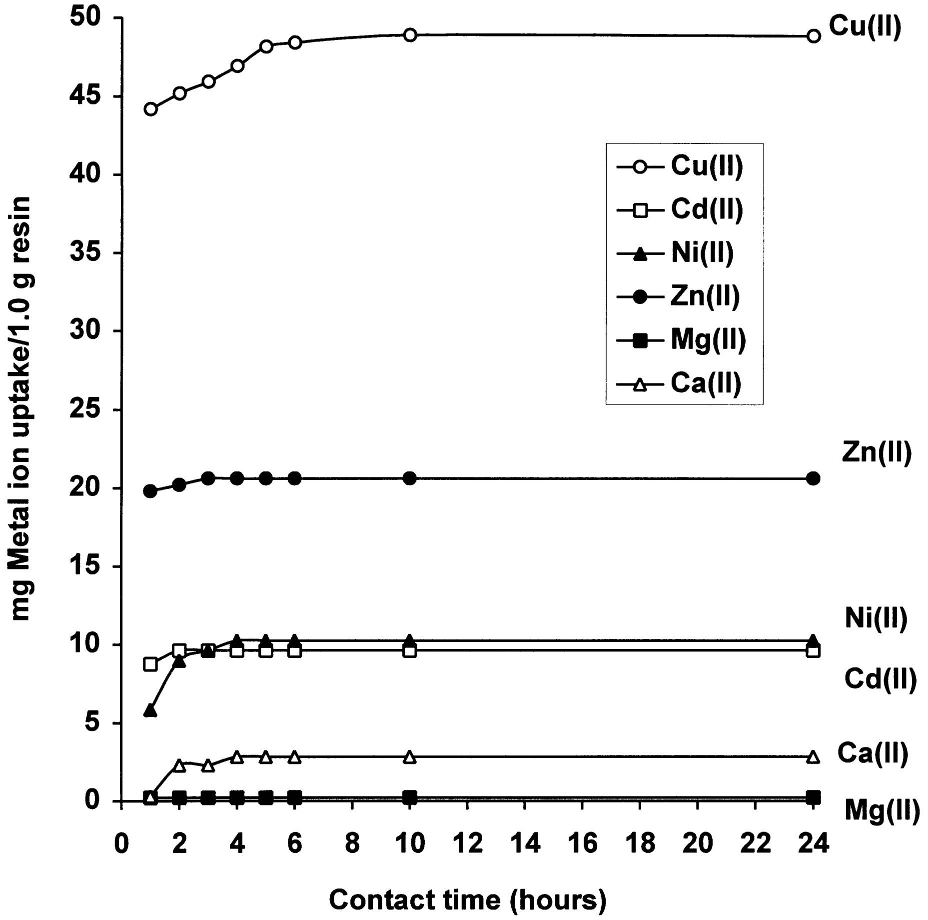

Figure 1. Metal ion uptake by polymer 1 as a function of contact time.

polymers are more conveniently compared in terms of the distribution coefficients, K_d, [8] defined as:

$$K_d = \frac{[M]_{\text{resin}}}{[M]_{\text{solution}}}$$

where $[M]_{\text{resin}}$ is the amount (in mg) of metal ions taken up by 1 g of resin and $[M]_{\text{solution}}$ is the concentration (in mg/mL) of metal ions remaining in solution.

The calculated values of K_d at a contact time of 24 hours are also reported in Table 1. These results clearly indicate pronounced effects of crosslinking on the sorption capacity towards various metal ions to different degrees. The 1% crosslinking was found sufficient to enhance the hydrophilic character of the resin with minimal steric effects. The most pronounce

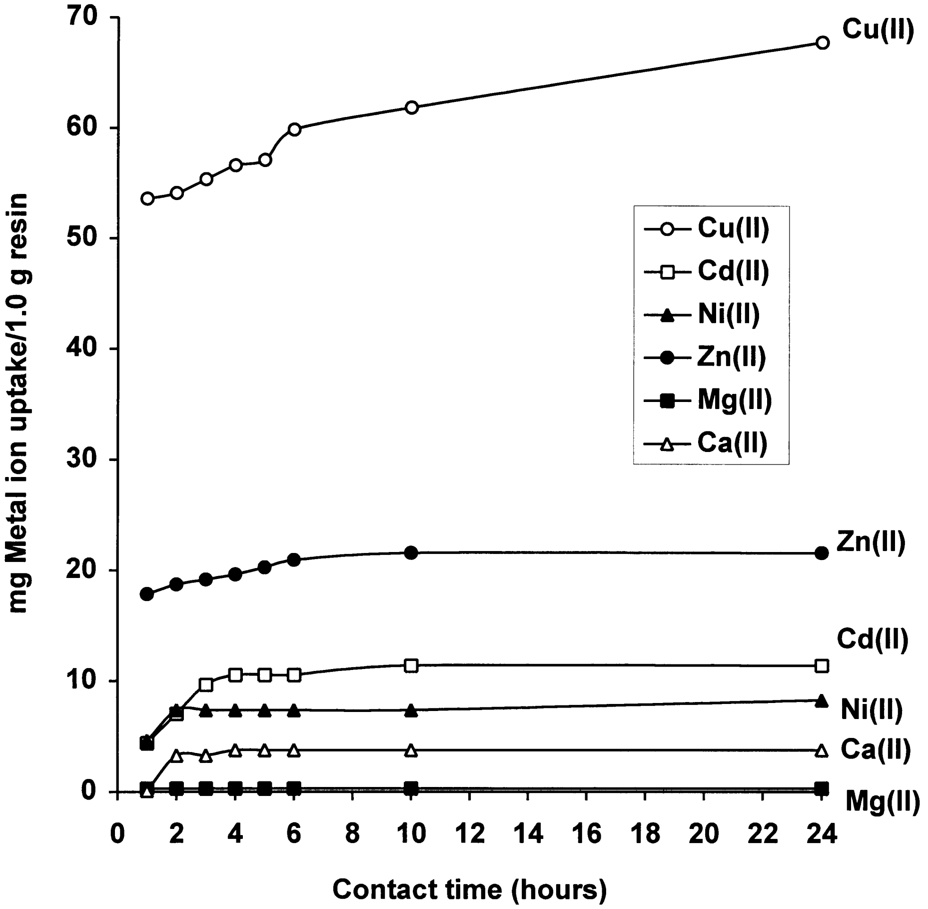

Figure 2. Metal ion uptake by polymer 2 as a function of contact time.

enhancement in chelation capacity is observed in Cu^{2+} ions. As a result, the two polymers exhibited slightly different selectivity patterns towards various metal ions as:

Polymer 1: $Cu^{2+} > Zn^{2+} > Ni^{2+} > Cd^{2+} > Ca^{2+} > Mg$

Polymer 2: $Cu^{2+} > Zn^{2+} > Cd^{2+} > Ni^{2+} > Ca^{2+} > Mg^{2+}$

This pattern is consistent with the reported chelation characteristics of the closely related polymer, poly(salicylaldoxime 3,5-diylmethylene) [8]. The extremely low binding capacity of polymers I and II towards Ca(II) and Mg(II) is a desired feature of a chelating resin designed for the removal and recovery of heavy metal ions from environmental and industrial waters.

The results presented in Table 1 and Figs. 1 and 2 clearly show that Polymer 2 is a more efficient chelating agent than Polymer 1 and shows

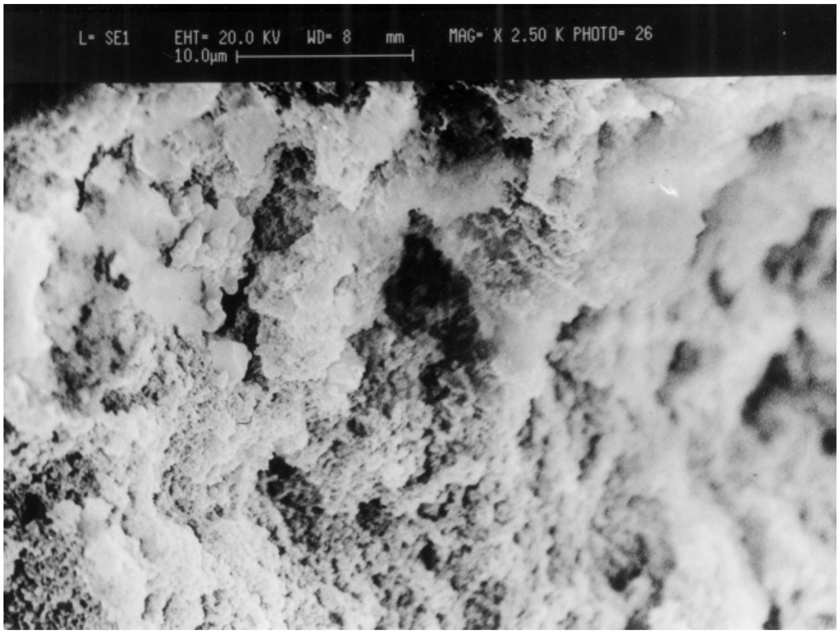

Plate 3. Scanning electron microscope photograph for polymer 2-Cu chelate.

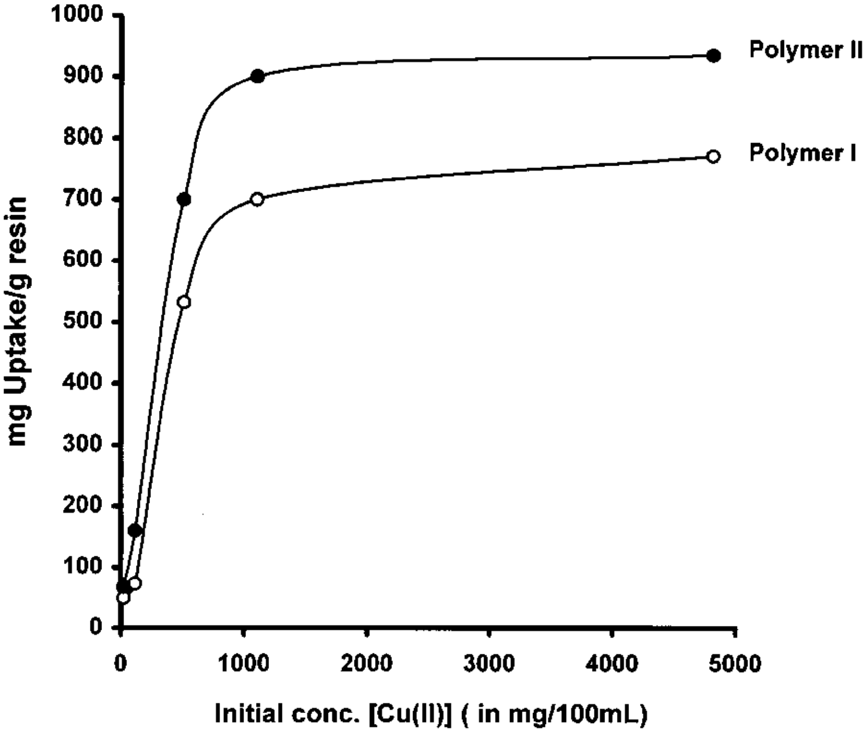

Figure 3. Copper ion uptake capacity of polymers 1 and 2.

enhanced selectivity for Cu^{2+} ions. These results are in accord with our recent findings [7] on the effect of crosslinking on the chelation properties of poly(8-hydroxyquinoline 5,7-diylmethylene). The binding capacity of polymers 1 and 2 towards Cu(II) ions was determined by equilibrating a given amount of the polymer with Cu(II) solutions of different concentrations ranging from 25 to 4800 mg/100 mL for a contact time of 48 hours. The results are given in Fig. 3. Binding capacity values of 770 and 930 mg Cu(II) per g resin were found for polymers 1 and 2, respectively.

The pH dependence of metal ion uptake by polymers 1 and 2 was studied in the pH range 2–8 for a fixed contact time of 6 hours. At higher pH values, hydrolysis of the metal ions investigated becomes significant and may compete with polymer chelate formation. In general, as the pH increases the metal ion uptake increases with Polymer 2 exhibiting higher capacity and selectivity towards Cu^{2+} ions than Polymer 1. For Polymer 1, the metal ion uptake is maximum at $pH > 4$ for copper ions and more than 85% of Cu^{2+} ions were chelated at this range. For other metal ions, the maximum uptake was at $pH > 6$ except for Zn^{2+} which was at pH 4. For Polymer 2, the results demonstrate that as the pH increases the metal ion uptake increases; this could be attributed to the more availability of lone pairs of electrons on nitrogen and oxygen atoms at higher pH values. These findings are in agreement with the pH-profiles of most chelating polymers with N,O binding sites [6–9, 44].

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