Removal of Transition Metal Cations and Their Counteranions by Crosslinked Epoxy–Amine Polymer

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ABSTRACT: Reaction of epichlorohydrin with ethylenediamine is very exothermic, and severe explosions occur, even when a few milliliters of the reagents are interacted without solvent. A controlled reaction has been achieved safely by suspension polycondensation of epichlorohydrin with ethylenediamine. 1,2-Diaminoethane units in the resulting crosslinked polymer provide high chelating ability for transition metal ions, such as Cu(II), Ni(II), Co(II), Cd(II), Fe(III), and Cr(III). Having all-amine ligating groups, the polymer represents unique properties and can sorb not only metal cations but also their counteranions, such as chloride, sulphate, nitrate, and acetate. The crosslinked polymer is stable hydrolytically and regenerable by acid without losing its activity. It can be recycled and offers a means of simultaneous removal of cations and anions from aqueous solutions. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 103–109, 1998

Key words: epoxy–amine resin; sorbtion of cation and anions; condensation polymer; epichlorohydrin–ethylenediamine water purification; cationic hydrogel

INTRODUCTION

Crosslinked polymers bearing various ligating groups are promising materials for hydrometallurgical applications, water purification, etc. There have been recent attempts in the incorporation of many different chelating groups into polymeric networks.[1,2] Although many chelating polymers with high metal-uptake ability have been reported, most suffer from their hydrolytic instabilities. In view of this, polymers having hydrolyzable or oxidable groups are not suitable for large-scale applications, even though they have good metal-sorption abilities.

During our research, we realized that all-amine ligating polymers offer advantages of nonhydrolyzability, better ability of metal sorption and anion-binding ability. In these polymers, chelata-

tion is expected to occur by formation of cationic metal complexes. The counteranion of metal salts must also be bound ionically either to the cationic complex being formed or to other free amine groups of the polymer. Coordination chemistry of low-molecular-weight amines, such as ethylenediamine,[3] and diethylenetriamine[4] have been extensively studied in the literature. With these ligands, the counteranion of the metal complexes formed is the hydroxide or anion of the metal salt involved. At present, only a few nonhydrolyzable polyamines are known in the literature. These are polyvinylpyridines, polyethyleneimine, and polyvinylamine. Among them, only polyvinylpyridines and its monomers are commercially available. Polyethyleneimine is obtained either by cationic ring opening of ethyleneimine monomer[4] or by hydrolysis of oxazoline polymers.[5] Vinylamine monomer does not exist, and its polymer is prepared by hydrolysis of poly(*N*-vinylamides)[6,7] or poly(*N*-vinyl *t*-butyl carbamate).[8] Recently, we have demonstrated that it can also be prepared

by Hofmann's *N*-bromamide method, from poly-acrylamide in ethylene glycol.[9] There are many articles dealing with metal complexes of poly-vinylpyridines,[10] polyvinylamine,[11] and polyethyleneimine.[12]

In our previous article, we have demonstrated that a resinous polymer, obtained by condensation of *p*-dichloromethylbenzene with ethylenediamine, is capable of binding transition metal ions together with their counteranions.[13] However, after regeneration with concentrated HCl solutions, the polymer loses its original activity due to acid-catalyzed side reactions, probably a Sommelet rearrangement, through phenyl rings.[14]

In order to overcome this drawback, in the present study, we have prepared a crosslinked aliphatic polyamine by condensing epichlorohydrin with ethylenediamine. Its preparation and metal complexes have been described in some patent literature,[15] but its anion-binding character has not been dealt with so far. In the present work, preparation and metal uptake from aqueous solutions and anion-binding ability (with chloride, sulphate, acetate, and nitrate anions) of the resulting polymer have been investigated.

EXPERIMENTAL

All the chemicals were analytical grade chemical products: ethylenediamine (E. Merck, Germany), epichlorohydrin (Fluka, Switzerland), and metal salts (E. Merck, Germany) were used without any further purification.

Preparation of the Crosslinked Polymer

Fifty milliliters of liquid parafin was placed in a 250 mL volume two-necked flask equipped with a reflux condenser and a dropping funnel. The whole system was immersed in an ice bath. Ten milliliters ($0.15M$) of ethylenediamine and 15 mL of L-methyl−2-pyrrolidone were added to the flask. While stirring with a magnetic stirring bar ($350−400$ rpm), 12.9 mL ($0.165M$) of epichlorohydrin was added cautiously to the mixture through a dropping funnel. A white flocculant occurred after stirring for 45 min. Stirring was continued for another 18 h at room temperature, then the mixture was heated to 70°C for 3 h. The solid precipitated was filtered and washed with 30 mL toluene. The product was dispersed in 30 mL of toluene and refluxed for 30 min to remove paraffin residues, and filtered then washed with ethanol

and water. The product was transferred into the 50-mL 5% NaOH solution and stirred for 2 h to obtain HCl-free resin. After filtration, the white-yellow product was washed, with excess water and 20 mL of ethanol, then dried at 80°C for 24 h *in vacuo*. Yield was 15.7 g (86.0%).

Determination of Accessible Amine Content

The accessible amine content was determined according to the procedure described elsewhere.[13] For this purpose, 0.5 g of the resin sample was soaked in 20 mL of $1M$ HCl solution and left in contact overnight while stirring in a closed bottle. The excess of unreacted acid was titrated with $0.1M$ NaOH solution in the presence of phenolphthalein as an indicator. The accessible amine content was calculated as 11.4 mmol NH_2/g resin.

Swelling of the Resin Sample

Disc-shaped samples with a diameter of 1 cm and a thickness of 3.3 mm were prepared from 0.25 g of dry polymer by an infrared (IR) pellet sampler under 10 tons/cm^2 of pressure. Each disc was placed in a 100-mL volume, sintered glass funnel in a closed bottle containing 150 mL of buffer solution (sodium citrate−HCl for a pH of 2.0 and acetic acid−sodium acetate for a pH of 5.5). The level of buffer solution was adjusted so that the upper level was 5 cm higher than that of the sample. The bottle was sealed to prevent any CO_2 uptake, which might cause shifts in pH.

The samples were allowed to stand in contact with the buffer solutions for 6 weeks at room temperature. From time to time, the glass funnels were taken out, filtered by suction, and weighed. The swelling ratios (w/w_o) found were recorded as a function of time (Fig. 1).

Determination of Metal Loading Capacities

To estimate maximum metal-sorption capacities, 0.5-g samples of the polymer were contacted separately with 50 mL of buffer solution (acetic acid−sodium acetate, pH = 4.3) containing 10.0 mmol of the metal salts ($CuCl_2 \cdot 2H_2O$, $CoCl_2 \cdot 6H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $NiCl_2 \cdot 6H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$, and $FeCl_3 \cdot 6H_2O$), which is a 2.50-fold excess of the theoretical capacity. The mixtures were stirred for 30 min, filtered, and washed with distilled water. The filtrates and washings were combined and made up to the level of 250 mL in volumetric flasks. Metal ion contents of these
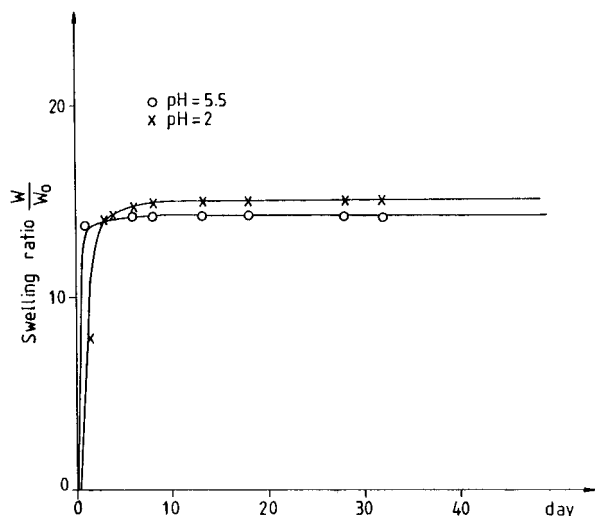
Figure 1 Variation of the swelling ratio of the crosslinked polymer in different pHs.

solutions were assayed by atomic absorption spectrometry (AAS). The difference of the metal contents between starting and interacted solutions and the amounts of sorbed metal ions were calculated and are tabulated as shown in Table I.

Determination of the Anion-Binding Capacities

Anion-binding capacities of the crosslinked polymer were determined by direct interaction of the metal salts. In these experiments, buffer solutions deliberately were not used to avoid any possible interferences coming from the components of the buffer. $Cd(NO_3)_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $NiSO_4 \cdot 6H_2O$, and $Cd(CH_3COO)_2 \cdot 4H_2O$ were used as nitrate, chloride, sulphate, and acetate anion sources. Nonsorbed anion concentrations of the interacted solutions were determined by classical

analytical procedures, and sorbed amounts were calculated in a similar fashion. Chloride ion was determined gravimetrically as AgCl by addition of $0.1M$ $AgNO_3$ solution in the presence of 0.5-mL conc. HNO_3. Sulphate ion was determined gravimetrically by precipitation as $BaSO_4$. For determination of nitrate and acetate, Cd(II) was first precipitated as cadmium sulphide by bubbling H_2S through the dilute solutions. The filtered solutions were refluxed to remove traces of H_2S, then the resulting HNO_3 and CH_3COOH were determined by conductometric titrations with $0.1M$ NaOH solution.

Metal-Uptake Kinetics

Simple batch kinetic experiments for metal sorptions were performed as follows: A 0.5-g sample of the crosslinked polymer was soaked in 50 mL of a solution of one of the metal salts, which were prepared previously by mixing 25 mL of buffer solution (acetic acid–sodium acetate, pH = 4.3) with 25 mL of metal ion solutions in $0.024M$ concentrations. Aliquots (1.0 mL) of the stirred solutions were taken at appropriate time intervals and transferred in volumetric flasks through filter papers. The filtrates and washings were combined and made up to 50 mL. Metal contents were assayed by AAS. The relevant data for different metal ions are shown in Figure 2.

pH Dependence of Metal Sorbtions

pH-dependent metal sorptions were performed by interacting 0.5-g polymer samples with the metal ion solutions (2.0 mmol metal ion in 50 mL of each buffer solution). The mixtures were stirred for 30 min at room temperature. The pHs of the buffer

Table I Metal Sorption Characteristics of Crosslinked Polymer

Metal Ions	AAC[a] (mmol/g Resin)	Max Loading (mmol/g Resin) (pH, 4.3)	Amine–Metal[b] (mol/mol)	Stripped Metal[c] Ion (mmol/g Resin)
Cu(II)	11.4	2.3	4.84	1.4
Ni(II)	11.4	2.8	3.97	2.6
Co(II)	11.4	3.7	3.02	1.8
Cd(II)	11.4	2.0	5.57	1.8
Cr(III)	11.4	4.7	2.37	1.2
Fe(II)	11.4	4.5	2.47	1.6

[a] AAC is the abbreviation for accessible amine content.
[b] Based on the accessible amine content.
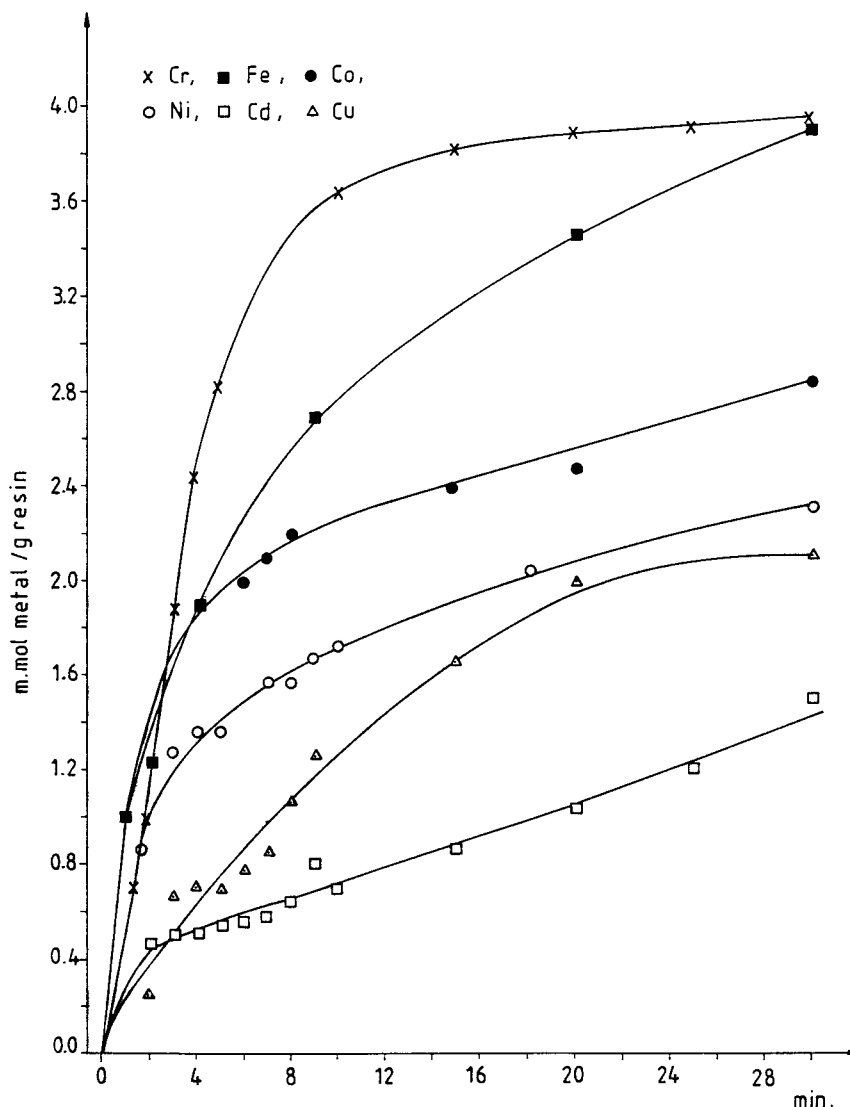[c] By treating with $1M$ HCl solution for 30 min.

Figure 2   Metal-uptake kinetics of the resin at pH 4.3.

solutions (sodium citrate–HCl) were 1.00, 1.70, 2.40, 3.60, and 4.30.

The pH values were chosen to be below 5.0 so that none of the metal hydroxide precipitates. Small fluctuations were observed in pH values during the experiments. For this reason, the referenced pH values were taken at the end of each experiment.

Unreacted metal ion contents of the used solutions were found by determination of the metal ion concentrations of the diluted solutions of 1.0 mL aliquots. The sorbed amounts were calculated similarly. The sorbed amounts per gram resin were plotted as a function of pH, as shown in Figure 3.

Recovery of the Metal Ions from the Loaded Samples

Metal ions were recovered by decomplexation of the metal ions from the loaded samples by treating with 50-mL $1M$ HCl for 30 min. After filtering, concentrations of the stripped metal ions were determined by AAS. For comparison, the stripped and sorbed metal contents of the same samples are listed in Table I.

Regeneration of the Crosslinked Polymer

After a first treatment with HCl solutions, metal sorbed polymer samples remained colored, which
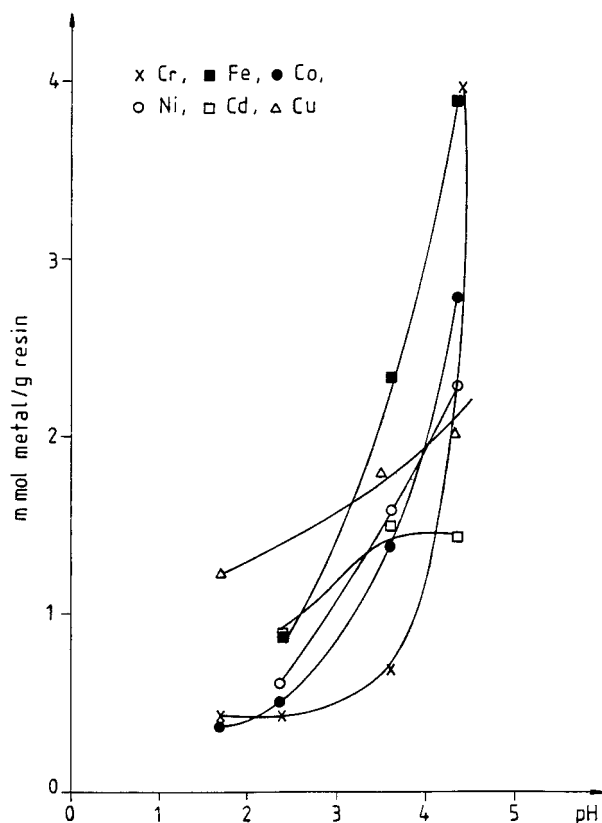
Figure 3 pH dependence of the metal sorptions of the resin.

means decomplexation has not been completed. For this reason, the acid treatment processes were repeated at least three times. Then, to obtain the polymer samples in free-amine form, they were treated with 50 mL of $2M$ NaOH solutions. The filtered samples were washed with excess of distilled water and 20 mL of ethanol. The resulting regenerated polymer is in the free-amine form and ready for use in the next cycle.

RESULTS AND DISCUSSION

Violent explosions occur when contacting small amounts of epichlorohydrin with ethylenediamine, especially when used without solvent. The reaction is believed to proceed in the following two steps: (1) ring opening of the epoxide group, and (2) condensation of amine with the halogen group. Obviously, the first step is fast and responsible for the explosions.

The present study reveals that this drawback can be overcome by using liquid paraffin and toluene as the dispersing phase. The ring opening step

can be performed safely by careful addition of epichlorohydrin to the mixture of ethylenediamine, N-methyl–2-pyrrolidone and liquid paraffin at 0°C. At the end of the heating step, a crosslinked resinous polymer is obtained as particles. However, the particles are not spherical.

The structure of the polymer is shown in Scheme 1.[16] In the IR spectra (with KBr disc) of the polymer, N—H stretching vibrations, which are expected to appear in the $3200-3400$ cm^{-1} range, are not distinguished clearly due to superposition of the broad O—H stretching bands at the same frequencies. The band observed at 1580 cm^{-1} can be attributed to N—H plane bending vibrations.

Swelling characteristics of the polymer have similarities with those of polyelectrolyte gels. Being a cationic hydrogel, in acid conditions, polymer segments tend to expand due to increasing ionization. This factor is important in affecting the rate of regeneration, because, during the regeneration by acid treatment, expansion of the polymer segments may provide fast decomplexation, although diffusion of the desorbing metal ions from the swollen structure becomes difficult. For this reason, polymers, whose swelling rates do not change so much in different pHs, must be preferred to conduct the regeneration at reliable rates. Actually, we didn't study optimization of the rates of metal desorptions. However, in our case, the percentage difference of the swelling ratios at pHs 2 and 5.5 is about 6% (Fig. 1) and not so much.
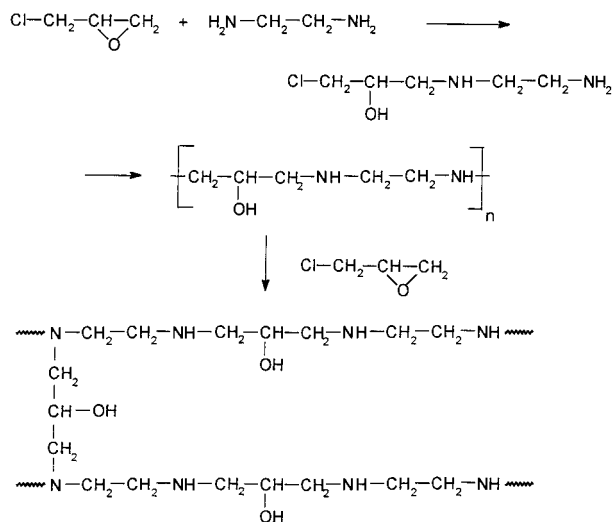
Scheme 1
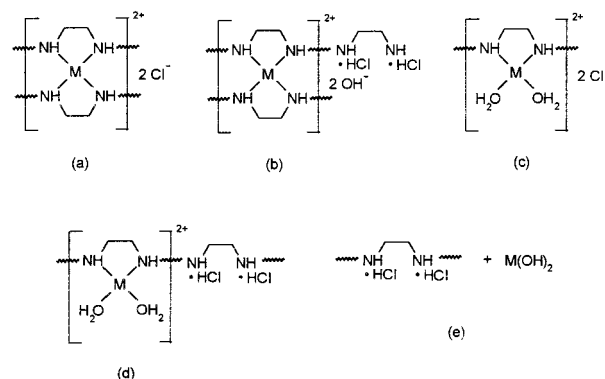
Scheme 2

Metal Sorption Characteristics

All the amino groups in the crosslinked polymer do not participate in complexation with metal ions. Inevitably, some portion of amines remains unreacted. To represent the intrinsic activity of the polymer, we have introduced a new quantity, "accessible amine content." This can be found by treating the polymer sample with excess HCl solution and back-titration of the excess acid with NaOH solution.

In our case, accessible amine content was found to be 11.4 (mmol/g dry resin). This corresponds to 67.7% of the theoretical amine content.

In ideal conditions, four or six amino groups may coordinate with one metal ion to give planar, tetrahedral, or octahedral complexes. With the ligands in crosslinked polymers, to attain such high coordinations is quite difficult due to restriction of the chains' flexibilities. In our case, for true coordination, at least two amino groups must coordinate with one metal ion. Once a metal ion attaches to one of the amino groups, the neighboring amino group in the 1,2-diaminoethane unit must also be involved in coordination for formation of a stable five-membered chelate.

Maximum loading experiments (Table I) indicate that accessible amine content/metal ion ratios are about 2 : 1 for $Fe(III)$ and $Cr(III)$ ions

and 3.5–4 for $Cu(II)$, $Ni(II)$, and $Co(II)$ ions. This result generally establishes the above assumption. As a consequence, formation of tris chelates is prohibited by steric factors, and the most plausible types of metal complexation must be (a), (c), or (e) in Scheme 2.

But the situation still remains quite complicated due to the different behavior of metal ions. For instance, $Fe(III)$ and $Cr(III)$ precipitate, as $Fe(OH)_3$ and $Cr(OH)_3$, respectively, in the presence of ethylenediamine in water, so interaction with $Fe(III)$ may run in accordance with Scheme 2(e). But in the case of $Cu(II)$, both types of interaction are possible because, with ethylenediamine, $Cu(II)$ forms both $Cu(OH)_2$ and $Cu(en)$-$(OH)_2$, depending on the concentration of ethylenediamine, so chelatation of $Cu(II)$ with the polymeric ligand may be as shown in Scheme 2(b) or 2(e). In general, metal uptakes occur by chelate formation or precipitation of metal hydroxides on the surface of polymer particles.

Kinetic experiments indicate that metal sorptions are reasonably fast and that equilibria establish within 30–35 min at pH 4.3 (Fig. 2).

Regarding pH-dependent metal sorptions (Fig. 3), it can be deduced that it is not possible to separate any metal ion from the mixtures selectively, and the amounts of sorbed metal ions increase with increasing pH.

Anion Binding Ability of the Polymer

The most important feature of the polymer is its anion binding ability. This fact has already been known from the complex-forming behavior of ethylenediamine, which is the monomeric analogue of the polymer. By a series of experiments, we have clearly demonstrated that Cl^-, SO_4^{-2}, and NO_3^- anions are bonded to the polymer at high levels, as shown in the Table II.

These experiments were deliberately carried out without using buffer solutions to avoid probable interferences arising from the buffer compo-

Table II   Anion Binding Characteristics of the Crosslinked Polymer

Metal Salts Used	Anion	PH of the Mixture	Sorbed Anion (mmol/g Resin)	Accompanying Cation (mmol/g Resin)
$CuCl_2 \cdot 6H_2O$	Cl^-	5.1	10.0	5.1
$NiSO_4$	SO_4^{2-}	6.2	4.8	4.6
$Cd(NO_3)_2$	NO_3^-	4.7	6.9	3.7
$Cd(CH_3COO)_2$	CH_3COO^-	4.6	6.7	3.5

nents because anions of the buffer especially may be competitive in the sorption of anions.

Comparing the sorbed anion contents with accompanying metal cations, their ratios are almost the same as in their free salts, at least for the anions studied.

Recovery of the Metal Ions and Regeneration of the Polymer

The metal ions were eluted and recovered by leaching with $1M$ HCl solutions. This process provides decomplexation of metal ions sorbed. With the exception of $Cd(II)$, decomplexations are visually followed by disappearance of their characteristic colors, and the aqueous solutions become colored. However, within 30 min, we observed that polymer particles remain colored, which means incomplete decomplexation. Indeed, metal contents of the resulting acid solutions are $10-40\%$ of the sorbed amounts. To speed up, the decomplexation, we also used more concentrated acid ($5M$) solutions. However, the effect was reversed in the cases for $Fe(III)$ and $Cr(III)$ ions. This can be ascribed to anionic complex forming ability of $Cr(III)$ ions, which can be bonded to aminium cations as complex salts.[16] We found that a suitable way of desorbtion is to repeat the leaching by acids in moderate concentrations ($1M$).

CONCLUSION

The crosslinked polymer presented has high metal-uptake abilities. Being an all amine-ligating polymer, it sorbs metal ions by forming cationic complexes, which carry counteranions for $CuCl_2$, $Cd(NO_3)_2$, $Cd(CH_3COO)_2$, and $NiSO_4$ salts.

Being also an anion binder, this polymer provides a means of complete removal of some transition metal salts from aqueous solutions. Hydrophilicity of the structure does not change during complexation, due to formation of charged metal complexes, and this causes high metal uptakes.

Although we did not recycle the used polymer more than three times, hydrolytic stability of simple aliphatic amines implies that the polymer can be recycled many times without losing its original activity.

As a consequence, due to its anion binding ability, this material is superior to classical ion exchangers and might be of interest for water purification.

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