

Synthesis of 1,4,8,11-Tetraazacyclotetradecane Monomer by Addition of Acryloyl Chloride and Its Polymer for Specific Transition Metal Binding

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ABSTRACT: 1,4,8,11-Tetraazacyclotetradecane (cyclam) was reacted with acryloyl chloride in a 1 : 2 molar ratio in dichloromethane in the presence of pyridine at 0°C. The modified cyclam was polymerized by adding an azobisisobutyronitrile initiator and irradiated with a UV lamp under reflux for 6 h. Precipitated cyclam containing polymer in the bulk structure was removed from the suspension by filtration. After washing and drying the final polymeric materials were used for transition metal ion adsorption and desorption studies. A Fourier transform IR spectrophotometer and thermogravimetric analyzer were used to characterize the polymeric structure. The affinity of the polymeric material for transition metal ions was used to test the adsorption–desorption of selected ions [Cu(II), Ni(II), Co(II), Cd(II), Pb(II)] from aqueous media containing different amounts of these metal ions (5–800 ppm) at different pH values (2.0–8.0). It was found that the adsorption rates were high and the adsorption equilibrium was reached in about 30 min. The uptake of the transition metal ions onto the polymer from solutions containing a single metal ion was 3.17 mmol/g for Cu(II), 0.98 mmol/g for Cd(II), 0.79 mmol/g for Co(II), 0.78 mmol/g for Ni(II), and 0.32 mmol/g for Pb(II). This polymer showed high affinity for Cu(II) compared to the other metal ions in the single ion solution and in the mixture of transition metal ions. The affinity order of the transition metal ions was Cu(II) \gg Ni(II) > Cd(II) > Co(II) > Pb(II) for competitive adsorption. More than 95% of the adsorbed transition metal ions were desorbed in 2 h in a desorption medium containing 1.0M HNO₃. Poly(cyclam) was found to be suitable for repeated use of more than five cycles without a noticeable loss of adsorption capacity. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1406–1414, 2002

Key words: 1,4,8,11-tetraazacyclotetradecane; removal; transition metal ions; adsorption; metal ion selectivity

INTRODUCTION

Contamination of water sources (e.g., rivers, lakes, and the sea) and industrial water sources

by various toxic metal ions is important because of their toxic effects on living organisms even at very low concentrations.¹ The necessity for the removal of heavy metal ions from wastewater streams of hydrometallurgical and other metal industries and subsequent possible reuse of these valuable metal ions has led to increasing interest in selective sorbents.^{2–4} Metal ions are important for all living organisms and play a crucial role in biology.⁵ In living organisms all major classes of

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biopolymers (proteins, nucleic acids, polysaccharides, and lipids) present a variety of ligands, such as phosphate, carboxylate, amino, and nitrogenous bases for metal binding.⁶ Some metal complexes of the biopolymers are known to be necessary in living organisms, to catalyze certain reactions, to arrange the structure of the biopolymers, and to carry out the transport of electrons and oxygen.⁷ Other classes of metal ions have been shown to be toxic in various concentration ranges, and these should not be allowed to get into the living organism. These metal ions can cause toxicity by displacing native metals from their normal binding sites and binding to macromolecules, thus altering their conformations by affecting oxidative phosphorylation and membrane permeability. Various techniques can be used for the removal of metal ions from aqueous solution, such as extraction, precipitation, dialysis, ion exchange, and complexing agent modified polymers in microbeads and in membrane form.^{8,9} In recent years, selective metal ion removal has been widely carried out using specific ligand modified polymers for the application of ion selective electrodes and preconcentration of precious metal ions.^{10–14} Some of these specific ligands are cyclam, especially for Cu(II), sulfur containing cyclic ligand for Hg(II) and Pb(II), oxygen containing cyclic ligand for Pb(II), and so forth.^{15–18} Ligands such as 1,4,8,11-tetraazacyclotetradecane and its derivatives can be used selectively for some metal ions. These specific ligands are mainly reacted to the polymeric surface via reactive ligands.^{19–22} In this case, the amount of the specific active ligand bound onto the polymeric carrier was limited. When the modified monomer was polymerized in this study, the amount of the ligand on or in the polymeric carrier was increased.

Modified 1,4,8,11-tetraazacyclotetradecane monomer was polymerized and used for the removal of heavy metal ions. Poly(cyclam) polymer was first prepared by photopolymerization of modified 1,4,8,11-tetraazacyclotetradecane monomer. This specific sorbent system in its bulk form was studied in the adsorption–desorption of Cu(II), Ni(II), Co(II), Cd(II), and Pb(II) from aqueous solutions. The adsorption kinetics, pH effects on the adsorption, adsorption capacity of the polymer for metal ions, desorption of metal ions from the polymer, and selectivity of the polymer for the different metal ions were studied.

EXPERIMENTAL

Materials

1,4,8,11-Tetraazacyclotetradecane and acryloyl chloride were purchased from Aldrich (Buchs, Switzerland) and used as received. Copper nitrate [Cu(NO₃)₂], cobalt nitrate [Co(NO₃)₂], nickel nitrate [Ni(NO₃)₂], cadmium nitrate [Cd(NO₃)₂], and lead nitrate [Pb(NO₃)₂] were purchased from BDH (Pole, U.K.). Pyridine and acetone were obtained from Merck AG (Darmstadt, Germany). All other chemicals were reagent grade and were purchased from Merck AG.

Preparation of Poly(Cyclam)

The 1,4,8,11-tetraazacyclotetradecane (1.5 g) was dissolved in 50 mL of CH₂Cl₂ in a three-necked round-bottom flask and nitrogen gas was bubbled inside the solution. Then 1.5 mL of pyridine (for HCl trapping) was added to the solution and 25 mL of a CH₂Cl₂ solution containing 1.2 g of acryloyl chloride was added slowly over 3 h at 0°C and cooled with ice. The reaction medium was stirred at 1000 rpm using a magnetic stirrer. After 6 h, 10 mg of azobisisobutyronitrile initiator was added to the reaction vessel under a nitrogen atmosphere and irradiated by a 200-W high-pressure mercury lamp (Oriol 6137) UV light source. During the irradiation procedure the system was refluxed at the boiling point of CH₂Cl₂ for 5 h. After 5 h the precipitated polymer in its bulk form was filtrated using a gouache (number 4) crucible and washed several times with CH₂Cl₂, acetone, and distilled water to remove all unreacted reagents. The polymeric material was dried in a vacuum oven at 60°C for 6 h and stored in a desiccator until use.

FTIR spectra of the 1,4,8,11-tetraazacyclotetradecane and poly(cyclam) were obtained with a FTIR spectrophotometer (model 520, Nicolet). About 0.02 g of each of the dry ligand and poly(cyclam) was thoroughly mixed with 0.1 g of KBr (IR grade, Merck) and pressed into pellet form. The spectrum was then recorded.

Thermogravimetric analysis (TGA) thermograms of the 1,4,8,11-tetraazacyclotetradecane and poly(cyclam) were obtained using a TGA instrument (model 951, Du Pont). All of the ligand and poly(cyclam) in dried form (about 5 mg) was placed in the crucible and introduced into the system, and then thermograms were recorded under a nitrogen atmosphere at a 25 mL/min flow rate and a heating rate of 10°C/min.

Batchwise Adsorption of Transition Metal Ions

Transition metal ion adsorption from single metal ion aqueous solutions was investigated in batchwise adsorption experiments. The effects of the initial concentration, the adsorption kinetics, and the pH of the medium on the transition metal ion uptake were studied. One hundred parts per million of 20 mL of each single transition metal ion solution was treated with 0.02 g of polymeric material at different pH values in the 2.0–8.0 range, adjusted with HNO₃ and NaOH at 25°C, and then stirred magnetically in a flask at 600 rpm for 1 h. For the metal ion uptake from a single solution, 50 mL of aqueous metal ion solutions with different concentrations (5–800 ppm) were treated for 1 h at room temperature with 0.02 g of poly(cyclam) at pH 6.0 adjusted with NaOH and HNO₃. The polymeric materials were removed from the adsorption medium at the end of the adsorption experiment and the concentrations of the transition metal ions in the aqueous phase were measured by a graphite furnace atomic absorption spectrometer (AAS, GBC 932 AA). The amount of adsorbed transition metal ion was obtained by using the following expression:

$$q = [(C_0 - C_A)V]/m$$

Here q is the amount of metal ion adsorbed onto the polymer; C_0 and C_A are the concentrations of the metal ions in the initial solution and the aqueous phase after adsorption, respectively (ppm); V is the volume of the aqueous phase (mL); and m is the amount of polymer (g).

Transition Metal Ion Selectivity of Poly(cyclam)

Selective adsorption of transition metal ions onto the poly(cyclam) from a mixture was also investigated in a batchwise manner. Solutions (500 mL) containing 0.5 and 1.0 mmol/L of each metal ion in the mixture were treated for 1 h with 0.02 g of polymeric material at a pH of 6.0. All experiments were performed at room temperature in a flask stirred magnetically at 600 rpm. In the second experiments solutions (500 mL) containing 0.5 and 1.0 mmol/L of Ni(II), Co(II), Cd(II), and Pb(II) and 0.005 and 0.01 mmol/L of Cu(II) ions were treated for 1 h with 0.02 g of poly(cyclam) at pH 6.0. After adsorption equilibrium was reached, the concentration of the metal ions in the remaining solution was measured by an AAS.

Regeneration of Resin

To determine the reusability of the poly(cyclam), the regeneration of polymeric material after the

adsorption of transition metal ions was examined using 50 mL of 1.0M HNO₃. Transition metal adsorbed polymeric materials were placed in a desorption medium and stirred at 600 rpm for 2 h at 25°C. The metal ion concentrations released from the polymeric materials into the aqueous phase were measured by an AAS. The regeneration ratio was calculated from the amount of metal ions initially taken up by the polymeric material and the final metal ion concentration in the desorption medium.

RESULTS AND DISCUSSION

Characteristic of Cyclam and Poly(cyclam) Resin

The poly(cyclam) polymer prepared in this study was a highly hydrophilic, swellable, and pH sensitive (swelling ratio 1400% at pH 12.0) structure. A schematic representation of the cyclam monomer and poly(cyclam) synthesis is shown in Figure 1. Cyclam was modified with 2 mol of acryloyl chloride via the amino group onto the cyclam ligand in dichloromethane containing pyridine. FTIR spectra of the cyclam ligand and poly(cyclam) were carried out to clarify the possible structure of the poly(cyclam). Figure 2 gives the FTIR spectra of the cyclam ligand and the poly(cyclam) polymer. The bands at 3070 and 3250 cm⁻¹ in spectrum A in Figure 2 were assigned to cis and trans stretching of N—H, as also pointed out on the chemical structure of the cyclam ligand. These two adsorption bands disappeared when the cyclam was modified and polymerized, as shown in spectrum B in Figure 2. The main characteristic absorption band in the IR region is the amide bond, which was formed between the cyclam monomer and the acryloyl chloride during the modification reaction. The absorption wavenumber of the amide bond is at 1692 cm⁻¹. This absorption band shows that the cyclam ligand was easily modified with acryloyl chloride under these experimental conditions. When the cyclam monomer polymerized, the FTIR absorption bands of the polymeric structure were limited compared to the cyclam ligand absorption bands. This is due to the more rigid structure of the polymer compared to that of the cyclam ligand. The N—H absorption band in the polymeric structure is a very broad band because of the N—H symmetry deformation and the hydrogen bonding occurring between the N—H hydrogen and oxygen atoms in the C=O functional group. In order

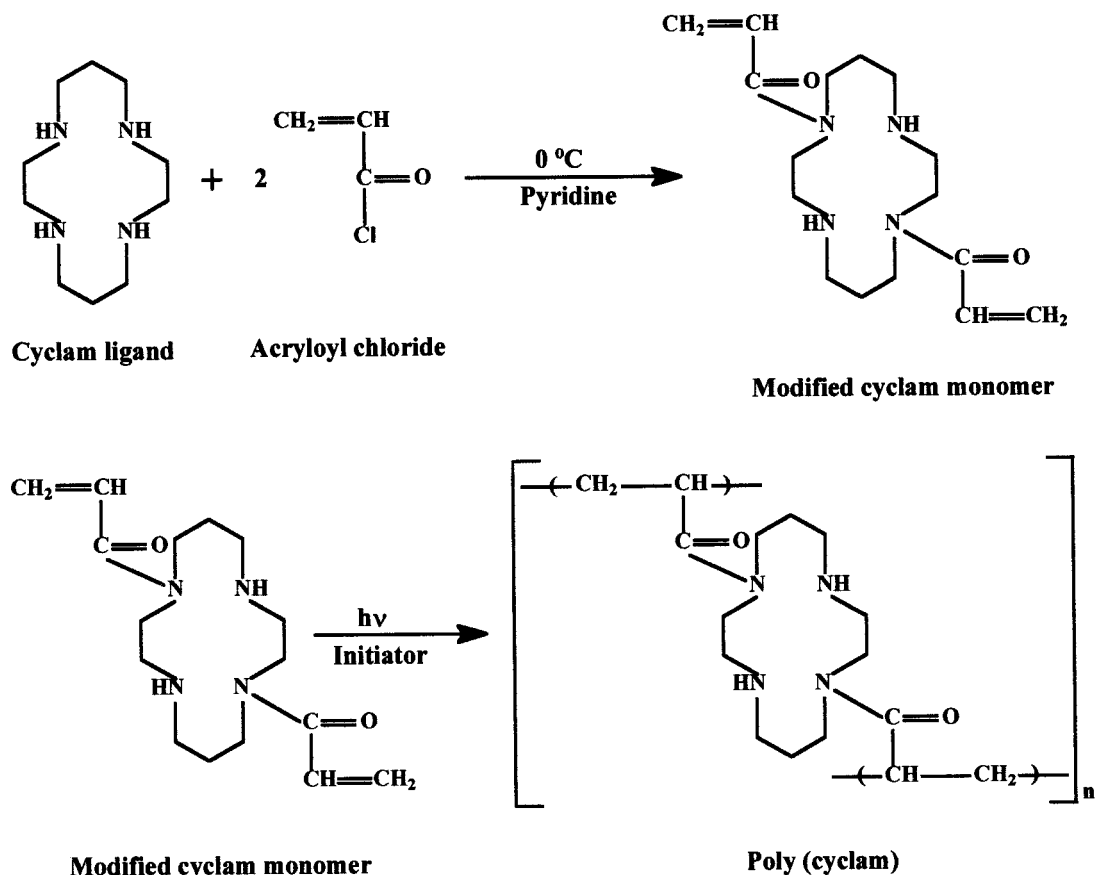


Figure 1 A schematic representation of the modification and polymerization of cyclam ligand.

to clarify the change in the structure and the thermal stability of the polymer, TGA thermograms of the cyclam and poly(cyclam) were obtained. The TGA thermograms of the cyclam ligand and poly(cyclam) are shown in Figure 3. It was found that the degradation temperature of the cyclam had shifted from 209 to 433°C when it occurs in the polymer structure [Fig. 3(A,B)].

Adsorption–Desorption Studies

Adsorption Kinetics

The adsorption kinetics of the transition metal ions [i.e., Cu(II), Co(II), Ni(II), Cd(II), and Pb(II)] onto the poly(cyclam) polymeric powder are given in Figure 4 as a function of time. The initial concentration of the ions within the aqueous phase and the pH were set at 100 ppm and 6.0, respectively. Very high adsorption rates are observed at the beginning of the adsorption, and then the plateau values that characterize adsorption equilibrium are gradually achieved within 45

min for all metal ions. For Pb(II) and Cd(II) the adsorption equilibrium time is longer than for the other transition metal ions. This may be due to the high ionic size of the Cd(II) and Pb(II) ions compared to the other ions studied. However, this is not a very critical limitation. Experimental data on the adsorption kinetics of heavy metal and transition metal ions by various sorbent systems have shown a wide range of adsorption rates. For example, Reed and Matsumoto²³ considered 6 h as a short equilibrium time in their cadmium adsorption kinetic studies in which they used activated carbon as the sorbent. Sarkar et al.²⁴ investigated the effect of the shaking time on the adsorption of heavy metals on silica and reported that the equilibrium adsorption time was 2 h. Shreedhara-Murthy and Ryan²⁵ investigated mercury, copper, cadmium, lead, and uranium adsorption on cellulose–dithiocarbamate resins and reported that the adsorption rates were very low. Salih et al.^{26–28} investigated the adsorption of various metal ions onto different reactive dyes

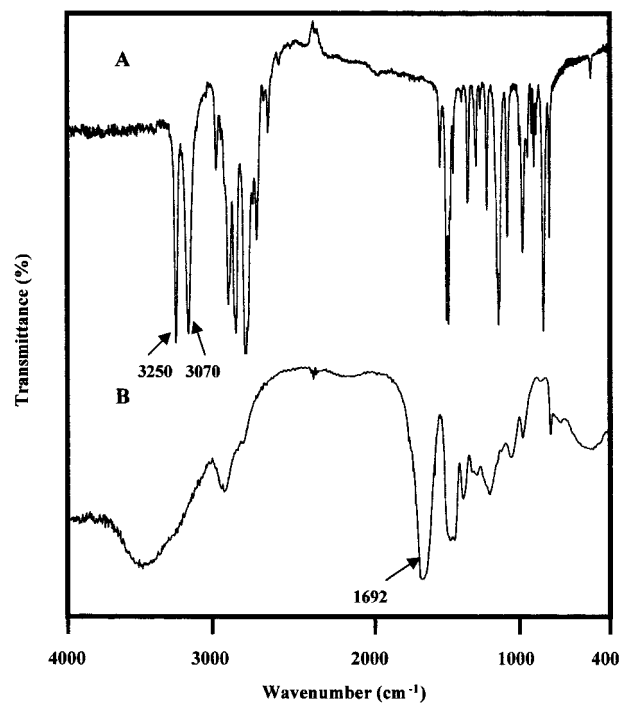


Figure 2 FTIR spectra of the cyclam ligand (spectrum A) and poly(cyclam) (spectrum B).

and dithizone-anchored poly(ethylene glycol dimethacrylate-hydroxyethyl methacrylate) microbeads and reported that the adsorption rates of the metal ions were very fast within 45 min to 2 h. It should be noted that there are several parameters that affect the adsorption rate, such as the stirring rate in the aqueous phase, the structural properties of the sorbent (e.g., porosity, surface area), the amount of sorbent, the ion properties (e.g., ionic radius), the initial concentration of the metal ions, the chelate formation rate, and the presence of other metal ions that may compete with the metal ions of interest for active adsorption sites. Therefore, it is difficult to compare the adsorption rates reported. However, the adsorption rates obtained with the poly(cyclam) polymer seem to be very satisfactory.

pH Effect

The effect of the pH on the metal uptake of the chelating agents on solid polymeric materials is a very important parameter. Ionization of the chelating ligand and the stability of the metal–ligand complexes vary when changing the pH. The effect of the pH on transition metal ion uptake for poly(cyclam) was examined for single metal ion aqueous solutions. The concentration of the metal ions

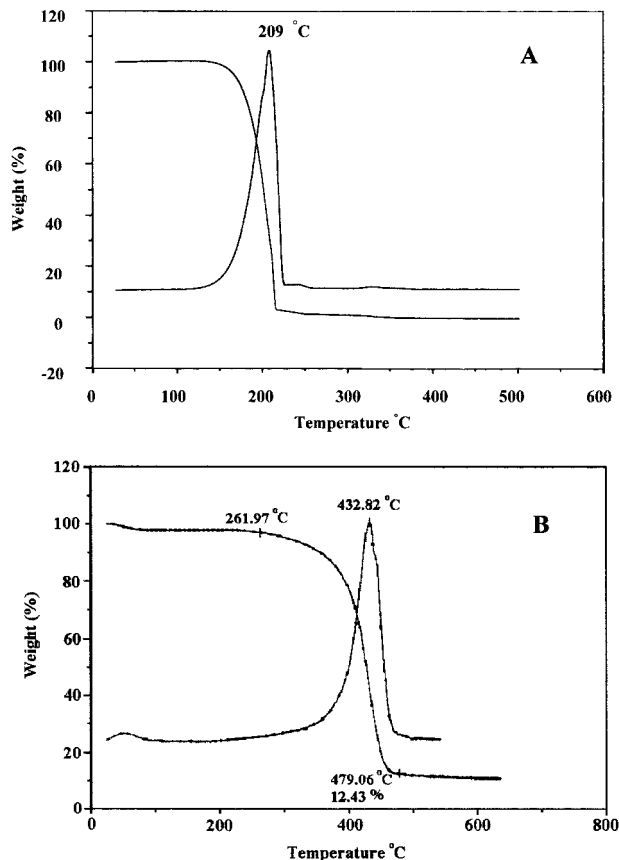


Figure 3 TGA thermograms of (A) the cyclam ligand and (B) poly(cyclam).

involved in this study was chosen to be 100 ppm, the adsorption time was set at 1 h in agreement with our experimental evidence, and the metal

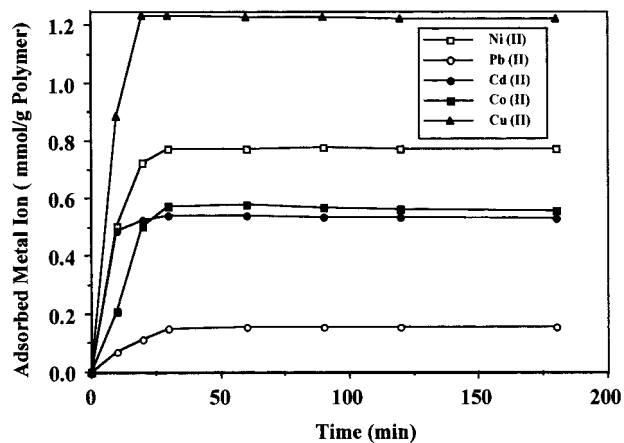


Figure 4 The adsorption kinetics of transition metal ions onto the poly(cyclam) at pH 6.0 and 25 °C with an initial volume of 20 mL, 0.002 g of polymer, and an initial concentration of 100 ppm.

ion uptake from the single metal ion solution was examined for changing pH values. The metal uptakes (mmol) for changing pH values are shown in Figure 5. All of the transition metal ions examined in this study show the same behavior. If the pH was increased, the uptake of the metal ion was also increased. At low pH values the metal ion uptake of all the metal ions studied is very low. For these pH values, some amino groups of the cyclam ligand in the polymeric structure could be protonated and the stability of its metal complexes was decreased, so that the metal ion uptake would be decreased. The most suitable pH values for a maximum uptake of the metal ions studied were found to be 5.0 for Cu(II), 6.0 for Cd(II) and Pb(II), and 7.0 for Ni(II) and Co(II). The metal ion uptakes at these pHs for a 100 ppm initial metal ion concentration were 1.27 mmol/g for Cu(II), 0.54 mmol/g for Cd(II), 0.81 mmol/g for Ni(II), 0.57 mmol/g for Co(II), and 0.18 mmol/g for Pb(II).

Effects of Initial Concentration on Metal Ion Uptake

Figure 6 shows the effects of the initial concentration of the metal ions on the transition metal ion uptake. As presented in Figure 6, with increasing initial metal ion concentrations in the solution, the uptakes of metal ions by the polymer increases almost exponentially at low concentrations up to 200 ppm; then it increases less rapidly

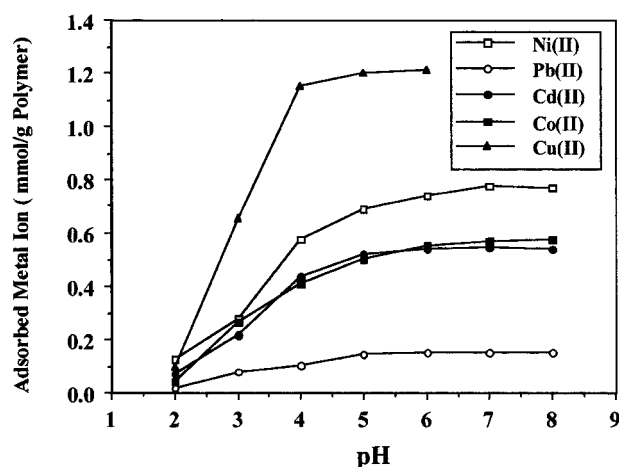


Figure 5 The pH effects of adsorption for the transition metal ions onto the poly(cyclam) at 25°C with an initial volume of 20 mL, an initial metal ion concentration of 100 ppm, and 0.02 g of polymer, and an adsorption time of 1 h.

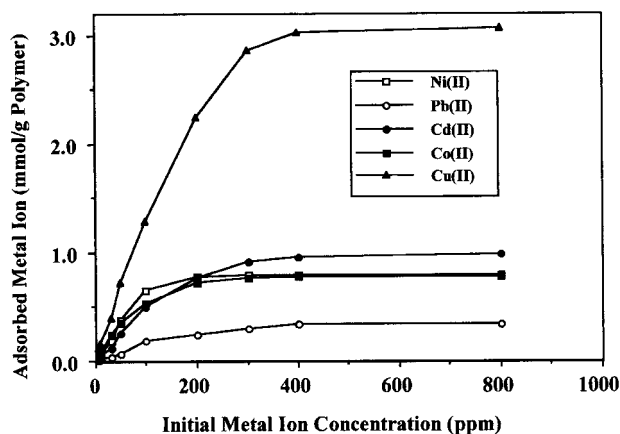


Figure 6 The uptake of the transition metal ions onto the poly(cyclam) at 25°C and pH 6.0 with an initial volume of 50 mL, 0.02 g of polymer, and an adsorption time of 1 h.

and finally approaches a saturation region. It becomes constant when the initial metal ion concentrations are greater than 400 ppm. The metal ion uptakes by the poly(cyclam) are 3.17 mmol/g for Cu(II), 0.98 mmol/g for Cd(II), 0.74 mmol/g for Ni(II), 0.73 mmol/g for Co(II), and 0.38 mmol/g for Pb(II).

Data on the sorption equilibrium of copper, nickel, cobalt, cadmium, and lead for aqueous solutions by different polymer sorbents have previously been reported.^{19,24–29} These data and other reported values cover a very wide range, such as 0.42–2.58 meq/g polymer for Cu(II), 0.12–1.48 meq/g polymer for Ni(II), 0.37–1.32 meq/g polymer for Co(II), 0.23–1.43 meq/g polymer for Cd(II), and 0.09–0.18 meq/g polymer for Pb(II). In this study the poly(cyclam) polymer showed an especially high adsorption capacity for Cu(II) compared to other values in the literature, which was due to the selectivity for Cu(II) of the cyclam ligand in the polymeric structure. The adsorption capacities of the other ions studied are similar to values found in the literature.

Transition Metal Ion Selectivity of Poly(cyclam)

Metal ion selectivity for transition metal ion adsorption onto the polymeric resin or polymeric membrane is very important, especially for ion selective electrode design and for the preconcentration of precious metal ions in a metal ion mixture solution. When the polymeric material selectivity is very high for a single metal ion solution, specific metal ion uptake can be carried out even

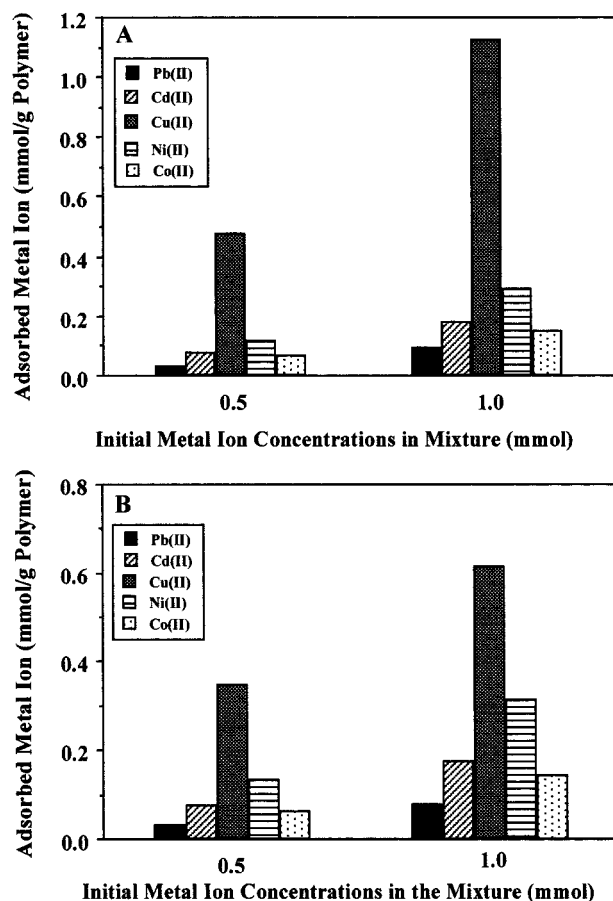


Figure 7 The selectivity of transition metal ions onto the poly(cyclam). The concentrations of (A) all metal ions are 0.5 and 1.0, (B) the Cu(II) ions are 0.005 and 0.01, the other metal ions are 0.5 and 1.0 mmol in the mixture. The adsorption time is 1 h at pH 6.0 and 25°C with 0.02 g of polymer and an initial volume of 500 mL.

if other ions are available in the metal ion mixture at much higher concentrations than the specific metal ion. In this case precious metal ions

can be preconcentrated even when the initial concentration of the precious metal ion is low. In ion selective electrodes for metal ions the selectivity of the membrane in the electrode is a very important parameter when detecting a specific metal ion concentration existing in a metal ion mixture solution at low concentrations. If the electrode membrane shows high selectivity for a cation, the matrix effects that are caused by the other metal ions could be eliminated. For this purpose the selectivity of the synthesized poly(cyclam) resin for Cu(II), Ni(II), Co(II), Cd(II), and Pb(II) metal ions was measured for mixture solutions containing 0.5 and 1.0 mmol of each metal ion. The selectivity of the polymeric resin for these five metal ions in the mixture is shown in Figure 7(A). As seen from Figure 7(A), the Cu(II) ion selectivity is extremely high compared to other metal ions. When the copper concentration was reduced a 100-fold compared to the other metal ions used in this study, the Cu(II) selectivity was still higher than that for the other metal ions (Table I). This behavior is shown in Figure 7(B). Under competitive conditions the adsorption capacities were 1.15 mmol Cu(II)/g, 0.29 mmol Ni(II)/g, 0.19 mmol Cd(II)/g, 0.17 mmol Co(II)/g, and 0.09 mmol Pb(II)/g resin in metal ion mixtures containing 1.0 mmol of each of all metal ion concentrations [Fig. 7(A)] and 0.64 mmol Cu(II)/g, 0.29 mmol Ni(II)/g, 0.18 mmol Cd(II)/g, 0.14 mmol Co(II)/g, and 0.08 mmol Pb(II)/g resin in metal ion mixtures containing 0.01 mmol of Cu(II) and 1.0 mmol of the other metal ion concentrations [Fig. 7(B)]. It was concluded that a membrane formed from this type of resin could be used for the selective determination of the Cu(II) ion and could therefore be used in the design of an electrode with Cu(II) selectivity. The preconcentration of other precious metal ions is under study in our

Table I Selectivity of Transition Metal Ion on Poly(cyclam)

Metal Ion	Initial Conc'n (mmol)	Adsorbed ^a (mmol/g Polymer)	Initial Conc'n (mmol)	Adsorbed ^a (mmol/g Polymer)	Initial Conc'n (mmol)	Adsorbed ^a (mmol/g Polymer)	Initial Conc'n (mmol)	Adsorbed ^a (mmol/g Polymer)
Cu(II)	1.000	1.15	0.050	0.49	0.010	0.64	0.005	0.37
Cd(II)	1.000	0.19	0.050	0.08	1.000	0.18	0.500	0.07
Ni(II)	1.000	0.29	0.050	0.13	1.000	0.29	0.500	0.14
Co(II)	1.000	0.17	0.050	0.07	1.000	0.14	0.500	0.06
Pb(II)	1.000	0.09	0.050	0.04	1.000	0.08	0.500	0.04

^a Data are given as the mean of three parallel studies. A maximum standard deviation is not more than 0.01 for the amount of adsorbed metal ions (mmol/g polymer).

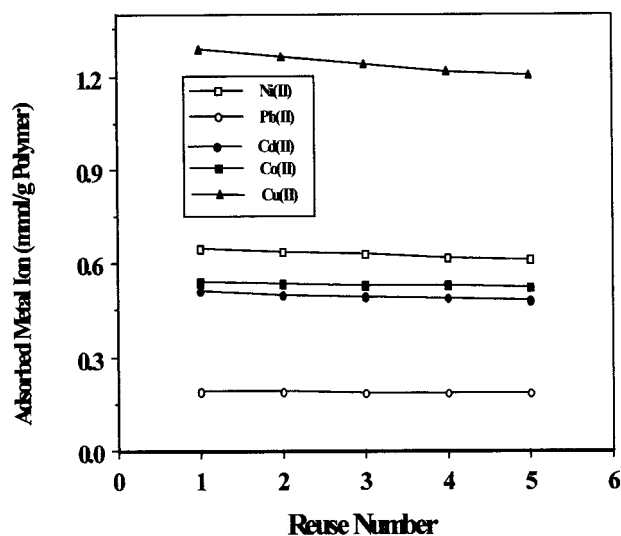


Figure 8 The repeated use of the poly(cyclam) for the transition metal ions with an adsorption time of 2 h and an initial metal ion concentration of 100 ppm for the adsorption at pH 6.0 and 25°C with 0.02 g of polymer at an initial volume of 100 mL.

laboratory using different ion-specific ligand polymers.

Desorption and Repeated Use

Desorption of the adsorbed metal ions from the poly(cyclam) resin was studied in the batchwise system. The polymeric resins loaded with metal ions were placed in a desorption medium containing 1.0M HNO₃, and the amount of metal ions released in 2 h was determined. The desorption ratios for the metal ions used in this study were calculated using the following equation:

$$\text{desorption ratio (\%)} = \frac{\text{amount of metal ions released}}{\text{amount of metal ions adsorbed on resin}} \times 100$$

More than 95% of the adsorbed metal ions were removed in 2 h using a 1.0M HNO₃ solution. Adsorption and desorption studies were repeated 5 times with the same polymeric resin for each of the metal ions. The results for repeated use of the poly(cyclam) resin for the various metal ions are shown in Figure 8. As seen from Figure 8, the adsorption capacities for the metal ions on this polymeric resin did not change noticeably during

the five cycles of the adsorption–desorption operations.

CONCLUSION

Poly(cyclam) resin carrying specific 1,4,8,11-tetraazacyclotetradecane ligand to Cu(II) was used for adsorption–desorption of Cu(II), Ni(II), Co(II), Cd(II), and Pb(II) from aqueous solution under noncompetitive conditions. It was found that the adsorption equilibrium time for the metal ions was very short, being between 30 min and 1 h. The pH for maximum adsorption of the metal ions was between 5.0 and 7.0. The selectivity of this resin for Cu(II) was examined from aqueous solution containing the other metal ions under competitive conditions. The adsorption capacities of poly(cyclam) resin from single metal ion solutions were 3.17 mmol Cu(II)/g, 0.98 mmol Cd(II)/g, 0.74 mmol Ni(II)/g, 0.73 mmol Co(II)/g, and 0.38 mmol Pb(II)/g resin. The poly(cyclam) resin shows the following metal ion affinity order under noncompetitive conditions: Cu(II) ≫ Cd(II) > Ni(II) > Co(II) > Pb(II). Under competitive conditions the adsorption capacities were 1.15 mmol Cu(II)/g, 0.29 mmol Ni(II)/g, 0.19 mmol Cd(II)/g, 0.17 mmol Co(II)/g, and 0.09 mmol Pb(II)/g resin for a metal ion mixtures containing 1.0 mmol of each of all metal ion concentrations and 0.64 mmol Cu(II)/g, 0.29 mmol Ni(II)/g, 0.18 mmol Cd(II)/g, 0.14 mmol Co(II)/g, and 0.08 mmol Pb(II)/g resin for metal ion mixtures containing 0.01 mmol of Cu(II) and 1.0 mmol of the other metal ion concentrations. The poly(cyclam) resin shows a high selectivity for Cu(II) ion in solution containing a mixture of metal ions, even if the Cu(II) ion concentration is a 100-fold lower than that of the other metal ions. In competitive metal ion adsorption the metal ion affinity order was Cu(II) ≫ Ni(II) > Cd(II) > Co(II) > Pb(II). Repeated adsorption and desorption cycles showed the feasibility of using the poly(cyclam) resin for metal ion adsorption. It was concluded that this type of polymer could be used for the preconcentration of Cu(II) from a mixture and the membrane form of poly(cyclam) might be used for selective Cu(II) ion analysis in an ion selective electrode.

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