

High-Retention Properties for Hg(II) Ions of a Resin Containing Ammonium and Pyridine Groups

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ABSTRACT: The metal-ion uptake behavior of the chelating resin poly([(3-(methacryloylamino)propyl) trimethyl ammonium chloride-co-4-vinyl pyridine]) has been investigated. The resin is obtained by radical copolymerization in a yield of 99.6%. The hydrophilic resin shows a high retention capacity and selectivity toward Hg(II) ions in the presence of Cu(II), Pb(II), Cd(II), Zn(II), and Cr(III) ions. A retention of Hg(II) higher than 99% is observed after 5 min. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2595–2599, 2002

Key words: chelating resin; metal-ion extraction; mercury ions

INTRODUCTION

The presence of the metal ions in the environment is one of the major concerns because of their toxicity to many life forms. Metal ions can be removed by adsorption on solid carriers. There are nonspecific adsorbents, such as activated carbon, metal oxides, silica, and ion-exchange resins,^{1–3} and specific ones that are considered among the most promising techniques.^{4–8} These specific sorbents consist of a ligand, which can specifically interact with the metal ion, and the carrier, which may be an inorganic material or polymer microbead. The latter carrier matrices have attracted the most interest because they are easily produced in a wide range of compositions, and can be modified by polymer analogous reactions to introduce a new ligand. Metal-ion selectivity of synthetic organic molecules has also been the subject of extensive investigations.^{9–11} These studies used synthetic cyclic molecules, cryptans, and crown ethers, to demonstrate that the selectivity of these chelators toward inorganic ions is

similar to that observed in the biological systems, and it is also possible to remove selected metal ions from complex solutions using polymers with preorganized recognition sites that have been templated to bind specific metal ions. It also needs to control polymeric properties to ensure the preparation of nonswelling, porous, and rigid but not brittle polymers.

One of the most dangerous metal ions is mercury. The high volatility of mercury and its compounds, as well as its high stability and persistence in the environment, increasing water solubility and ease with which they can be adsorbed by soils and suspended solids in natural waters, are responsible for the continuous global cycling of Hg on the planet. Although the toxicity of mercury and its compounds has been known since ancient times, the metal has always been regarded as a toxic, undesirable substance, and its massive use in widely diverse industrial activities such as power plants, chlorine and caustic soda production, paint and pesticide manufacturing, and mining, makes it a ubiquitous element in nature.^{12,13}

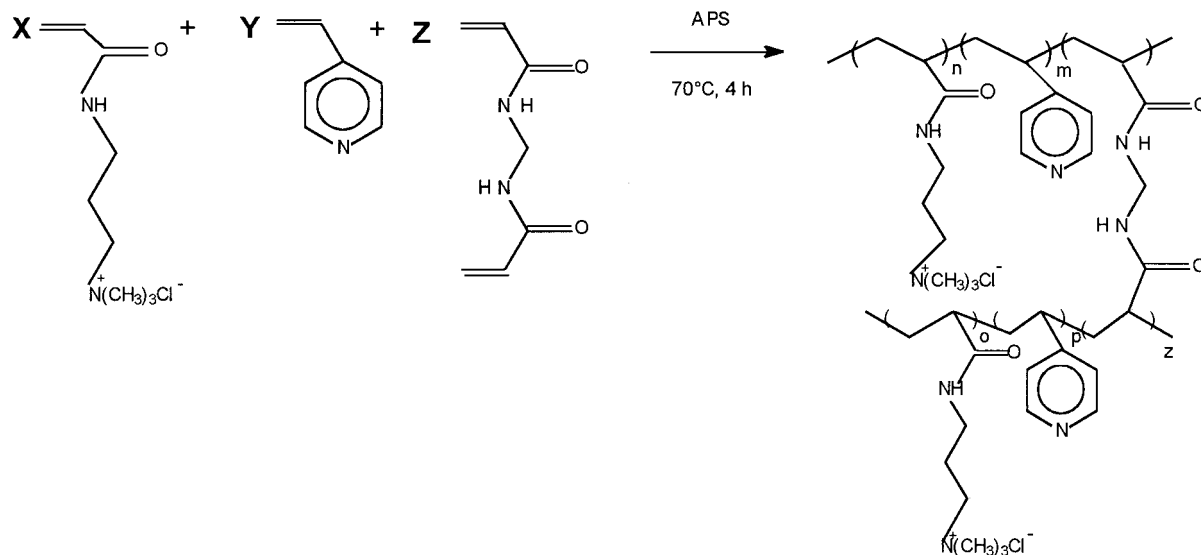
In the last few years, we have prepared water-insoluble adsorbents with varying swelling capacities and metal ions, particularly Hg(II).^{14–18}

The aim of this study is to synthesize a resin containing ammonium and pyridine groups with

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Scheme 1

high affinity and selectivity to bind metal ions, particularly mercury (II).

EXPERIMENTAL

Reagents

[3-(Methacryloylamino)propyl] trimethyl ammonium chloride (MAPT; Aldrich, Milwaukee, WI), *N,N*-methylene-bis-acrylamide (MBA; Merck, Darmstadt, Germany), and ammonium peroxydisulfate (APS; Merck) were of commercial grade and used without further purification. 4-Vinylpyridine (4-VPy; Aldrich) was purified by distillation. Reagent-grade metal ions were used and solutions were prepared by dissolving appropriate weights of the nitrate salt in twice-distilled water. The following metal salts were employed: $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Nitric acid (65%), perchloric acid (70%), and sodium hydroxide standard solutions were used.

Synthesis of the Adsorbent Resin

Equimolar amounts of MAPT (7.7 g) and 4-VPy (3.7 g) were polymerized in bulk with APS (0.5 mol %) and MBA (6 mol %) as initiator and crosslinking reagent, respectively, at 70°C by 24 h. The resin was dried under vacuum until constant weight. The yield was 99.6%, of which 96.2% corresponded to a size fraction over 1000 μm . Therefore, the dried resin was ground,

sieved, and the 180- to 250- μm portion used in the sorption experiments.

Sorption of Metal Ions on the Resin

A batch equilibrium type procedure was used to determine the metal-ion uptake from an aqueous solution containing 1.5×10^{-2} mmol in the metal ion. The resin-to-metal ion ratio (in mmol) was 20 : 1. The pH of the aqueous solution (10 mL) varied between 1 and 7, depending on the metal ion. The two phases were stirred by a mechanical shaker at 20°C for 1 h. Then, the two phases were separated, and the supernatant solution was analyzed for Hg(II), Cd(II), Zn(II), Cu(II), Pb(II), and Cr(III) ions, by atomic absorption spectrophotometry (AAS).

Maximum Adsorption Capacity (MAC) for Cu(II) and Hg(II)

To obtain the MAC, 50 mL of an aqueous solution were shaken with 0.5 g of the resin for 2 h at 20°C. The mixture in the flask was filtered and washed with water, and the filtered solution was transferred into a calibrated flask. The process was repeated three times, the volume was made up to 250 mL, and then the metal ion in the filtrate was determined.

Separation of Hg(II) from Mixtures

The following mixtures were evaluated: Cu(II)–Pb(II) (7.5×10^{-3} mmol of each metal ion), Cu(I)–Pb(II)–Zn(II) (5×10^{-3} mmol of each metal

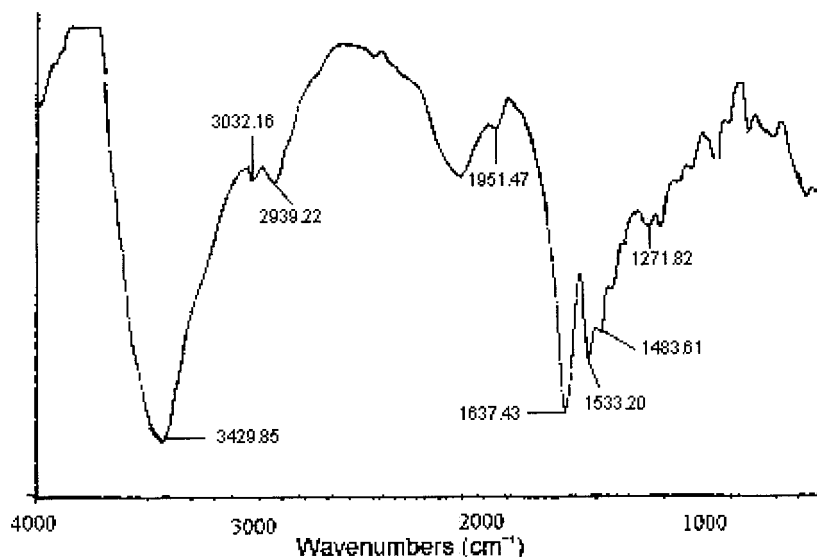


Figure 1 FTIR spectrum of the resin poly(MAPT-co-4-VPy).

ion), and Pb(II)–Zn(II)–Hg(II) (5×10^{-3} of each metal ion). Thus, 10 mL of an aqueous solution containing the metal ion mixture was contacted for 1 h with 0.1 g of dry resin. The pH was adjusted to 1 or 3, then the resin was filtered and washed repeatedly with deionized water. The metal ions were analyzed in the filtrates by AAS.

Optimization of Adsorption Time for Hg(II)

The time required for the solid-liquid system to achieve the equilibrium conditions was determined by placing 10 mL of 1 g/L aqueous solution of Hg(II) with 0.1 g of the resin. At each time the supernatant was separated and the mercury ion determined.

Measurements

The FTIR spectrum was recorded with a Magna Nicolet 550 spectrophotometer (Nicolet Instruments, Madison, WI). Thermal stability was performed on a Polymer Laboratories (UK) STA 625 thermoanalyzer with a heating rate of $10^\circ\text{C min}^{-1}$ under N_2 . The pH was measured with a digital Extech Microcomputer pH-meter (USA). The metal ions were analyzed on a Unicam Solar Series spectrometer (UK).

RESULTS AND DISCUSSION

The crosslinked poly(MAPT-co-4-VPy) resin was prepared by radical polymerization (Scheme 1). The resin was completely insoluble in water and

in organic solvents. The yield was 99.6%. The particle size of the resin, immediately after polymerization, was higher than $1000 \mu\text{m}$ (96.2%). Subsequently, the resin was crushed to yield a material with a particle size between 180 and $250 \mu\text{m}$. This fraction was used to study the metal-ion binding capacity.

The FTIR spectrum shows the most characteristic absorption bands (in cm^{-1}) at 3429 (N–H, secondary amide), 3032 (C=C, pyridine ring), 2939 (C–H), and 1637 (C=O, amide) (see Fig. 1).

The resin contains an ammonium group, which would increase the swelling capacity but—significantly—not the binding capacity, and the pyridine group, which would act as ligand group for the different metal ions.

The metal-ion uptake behavior of the resin was tested under both competitive and noncompetitive conditions as a function of pH.

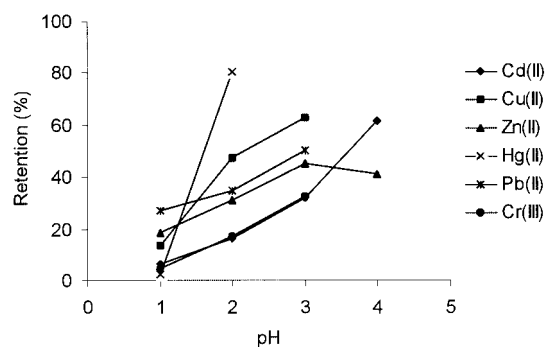


Figure 2 Effect of the pH on the metal ion retention under noncompetitive conditions. Time = 1 h and $T = 20^\circ\text{C}$.

Table I Metal Ion Retention Behavior from Mixture of Metal Ions and Selectivity

Mixture of Metal Ions	Retention (%)				Retention (meq/g resin)				Selectivity (S)
	Cu(II)	Pb(II)	Zn(II)	Hg(II)	Cu(II)	Pb(II)	Zn(II)	Hg(II)	
Cu(II)–Pb(II)	76.2	52.6	—	—	0.114	0.078	—	—	$0.46_{\text{Cu(II)/Pb(II)}}$
Cu(II)–Pb(II)–Zn(II)	81.8	60.5	37.1	—	0.082	0.060	0.036	—	$0.44_{\text{Cu(II)/Pb(II)}}$ $0.84_{\text{Cu(II)/Zn(II)}}$
Pb(II)–Zn(II)–Hg(II)	—	31.4	14.1	91.9	—	0.032	0.014	0.092	$1.35_{\text{Hg(II)/Pb(II)}}$ $1.85_{\text{Hg(II)/Zn(II)}}$

The resin, metal-to-ion 20 : 1 ratio, was tested to avoid the precipitation of the metal salts. The uptake results under noncompetitive conditions are given in Figure 2. Metal nitrate was used for all the experiments. The resin clearly showed the highest affinity with Hg(II), with a maximum of 0.24 meq/g dry resin at pH 3, corresponding to 80% of the initial concentration. The Hg(II) uptake is hardly pH dependent because at pH 1 it is lower than 3%. The capacities for the other divalent ions Cu(II), Cd(II), Zn(II), and Pb(II) are also pH dependent and relatively low. The highest values correspond to Cu(II) (0.20 meq/g dry resin, 62.7%, at pH 5) and Cd(II) (0.10 meq/g dry resin, 61.4%, at pH 7). The only one trivalent cation, Cr(III), also shows a low retention, lower than 33%. Cr(III) ions were not investigated at higher pH to avoid the precipitation. It is important to establish that at pH 3, the retention under noncompetitive conditions for Hg(II) ions is very high compared with that of all the other di- and trivalent metal ions.

Three competitive experiments were carried out with the resin: one at pH 3 with the ternary mixture of divalent cations Pb(II)–Zn(II)–Hg(II), and the others at pH 5 with the binary and ternary mixtures: Cu(II)–Pb(II) and Cu(II)–Pb(II)–Zn(II) (see Table I). The metal-ion retention val-

ues are referred to the total concentration of the metal ions in the initial solution.

The selectivity S is given by the difference in distribution coefficient for different metal ions and was determined according to the following equation:

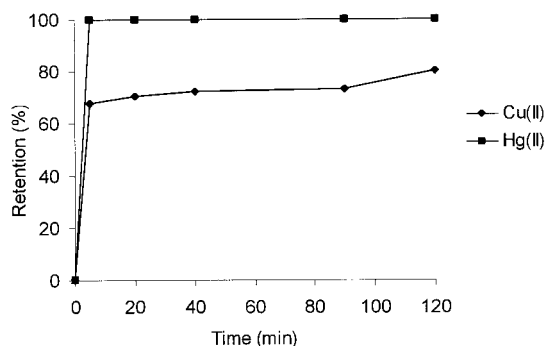
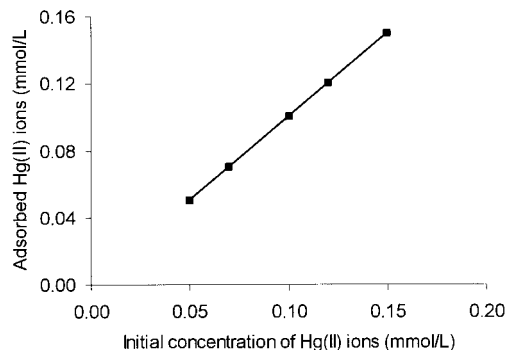
$$S = \log K_d(M_1) - \log K_d(M_2)$$

where K_d is the distribution coefficient of the respective metal ions M_1 and M_2 .¹⁹

The high preference of the resin for the adsorption of Hg(II) may be attributed to at least two factors: stability constant for complex formation and conformational requirements.

Kinetic experiments were performed with the resin for Hg(II) at pH 3 and for Cu(II) at pH 5. The fastest kinetic was observed for Hg(II) because the retention, after 5 min, was 0.306 meq/g dry resin but for copper(II) it was increased from 0.210 meq/g dry resin (67.9%) after 5 min and up to 0.246 meq/g dry resin (79.9%) after 2 h (see Fig. 3).

Hg(II) adsorbed on the adsorbent for an initial concentration of Hg(II), ranging from 100 to 308 ppm at 20°C and pH 3, is shown in Figure 4. For this concentration range, the retention of Hg(II) was always 100%. However, Cu(II) showed a dif-

**Figure 3** Effect of the time on the retention of Hg(II) and Cu(II) ions at pH 2 and 5, respectively.**Figure 4** Effect of the initial concentration of Hg(II) ions on the retention. pH 2, time = 1 h, and T = 20°C.

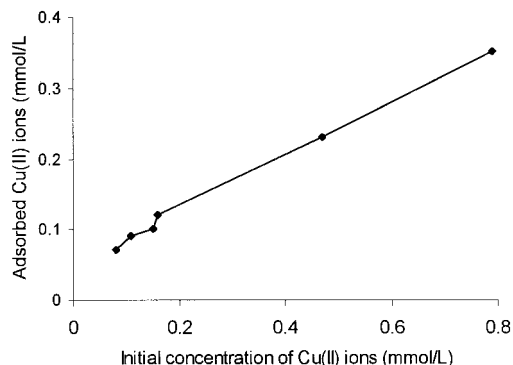


Figure 5 Effect of the initial concentration of Cu(II) ions on the retention. pH 5, time = 1 h, and T = 20°C.

ferent behavior. The percentage of adsorbed Cu(II) decreased from 85.8% to 44.2% by increasing the initial concentration of Cu(II) from 50 to 500 ppm (see Fig. 5). These results indicate that the removal of Cu(II) is highly concentration dependent. Besides, this would imply that the type of adsorption isotherm behavior for both metal ions would be different.

Because of the low adsorption capacity of the other metal ions, particularly at pH 3 and 5, the maximum load capacity was determined only for Cu(II) at pH 5 and Hg(II) at pH 3. It was 0.110 meq/g dry resin (60%) and 1.78 meq/g dry resin (96.6%), respectively.

To determine the effect of the metal ion adsorbed on the thermal stability of the resin, thermogravimetric analyses were carried out. The resin was loaded with the metal ion at the defined pH. For comparison, the thermal behavior of the resin without metal ion was also included. The resin was very stable up to 200°C with a weight loss lower than 7%; at 300°C it increased up to 27.3%. The divalent cations Cu(II), Pb(II), and Hg(II) showed a similar thermal behavior. No important difference among them, compared with the resin, was observed. Cd(II) showed a different behavior. In all the temperature ranges studied, the resin–Cd(II) material showed a higher thermal stability compared with that of the unloaded resin. This would imply that Cd(II) could interact in way different from that of Cu(II), Pb(II), and Hg(II). The latter would interact through an interchain complex and the former by an intrachain complex.

CONCLUSIONS

The present investigation has shown that the radical polymerization of [3-(methacryloylamino)pro-

pyl] trimethyl ammonium chloride with 4-vinyl pyridine has a yield of 99.6%. The resin showed high affinity for Hg(II) ions at pH 3, and selectivity toward other di- and trivalent cations. The resin–Hg(II) ion equilibrium was achieved in close to 5 min, which is considered fast for a heterogeneous reaction. The 4-vinylpyridine group is the most important moiety to interact with the metal ions, probably forming complexes, although the participation of the ammonium group, which would increase the swelling capacity to facilitate the interaction of the active sites with the metal ions, was not relevant.

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