

# Synthesis, Characterization, and Properties of a Selective Adsorbent to Mercury(II) Ions

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**ABSTRACT:** A resin containing 3-(dimethylamine)propyl acrylate and 4-vinylpyridine was synthesized by radical polymerization (in 1:1 mole ratio). Ammonium persulfate (0.5 mol %) and N,N'-methylene-bis-acrylamide (2 mol %) were used as initiator and crosslinking reagents, respectively. The resin was characterized by Fourier transform infrared (FTIR) and ultraviolet-visible (UV-Vis) spectroscopy. The ability to bind Hg(II), Cd(II), Zn(II), Pb(II), Cu(II), and Cr(III) as well as the maximum adsorption capacity and elution of Hg(II) ions from the loaded resin was studied. Sorption selectivity from ternary mixture Hg(II), Cd(II), and Zn(II) was studied at the optimum sorption pH value. At pH 2 the adsorbent retained 98% of Hg(II); the retention of the other metal ions was lower than 20%. The elution assay was made in HClO<sub>4</sub> solutions. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2559–2563, 2002

**Key words:** complexing resin; retention properties; selectivity; mercury ions

## INTRODUCTION

Metals are among the most commonly encountered and difficult to treat environmental pollutants. They are introduced into the environment during industrial processes, refining of ores, mining, disposal of industrial and domestic waters, etc. Therefore, the removal of metal ions has attracted considerable interest for several applications, including improved analyses, concentrating trace metal ions from dilute solutions, economy, remediation, and general concern for eliminating noxious metals from waters that may enter natural waters.

In particular, the search for metal ion-specific resins has been increased.<sup>1–15</sup> Since such a wide range of materials and methods of synthesis are possible, it is not surprising that the exchangers' physical form may vary from rock-hard material to soft gel. The desirable properties of the material are the high capacity for the metal of interest, high selectivity, fast kinetics and high mechanical strength and toughness of the particles. On the separation of desired metal ions by chelating resin from a solution containing various metal ions, the selectivity is one of the most important functions. The choice of ligand introduced into the resin plays a significant role in achieving the selectivity. The high metal ion selectivity of chelating exchangers is attributed not only to electrostatic forces but also to coordination bonds in metal chelating groups. The commercial resin Chelamine (Fluk), Bio-Rex-70, and Chelex 100 correspond to examples of ion-exchange resins

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that contain groups with a strong ability to bind heavy metal ions.

Accordingly in the current work, 3-(dimethylamine)propyl acrylate was copolymerized with 4-vinylpyridine to obtain a chelating resin. The binding ability for environmentally relevant metal ions such as Hg(II), Cd(II), Zn(II), Pb(II), and Cr(III) ions by batch equilibrium procedure was assayed. Retention properties, maximum capacity, selectivity retention behavior, and elution assay are discussed.

## EXPERIMENTAL

### Materials

3-(Dimethylamino)propyl acrylate (DAPA) (Aldrich), 4-vinylpyridine (4-VPy) (Aldrich), ammonium persulfate (APS) (Fluka), and *N,N'*-methylene-bis-acrylamide (MBA) (Aldrich) were of commercial grade, and used without further purification. Reagent grade metal ions were used, and metal ion solutions were prepared by dissolving appropriate weights of copper nitrate trihydrate, cadmium nitrate tetrahydrate, zinc nitrate hexahydrate, mercury nitrate monohydrate, lead nitrate, and chromium nitrate nonahydrate (Merck, UCB) in deionized water. Nitric acid (65%) (Merck) and sodium hydroxide (98%) (Riedel de Haën) standard solutions were used.

### Synthesis of the Adsorbent Resin

DAPA (0.04 mol) was polymerized in bulk with 4-VPy (0.04 mol), APS (0.5 mol %), and MBA (2 mol %) as initiator and crosslinking reagents, respectively, at 70°C for 24 h under N<sub>2</sub>. The resin was washed with deionized water, and dried under vacuum to constant weight. Yield 40%.

### 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  $1.9 \times 10^{-3}M$  in the metal ion by the resin (0.1 g). The pH of the aqueous solution (10 mL) varied between 1 and 5 depending on the metal ion. The pH was adjusted by using dilute nitric acid or sodium hydroxide solution. The two phases were shaken by a mechanical shaker at room temperature for 1 h. After shaking, the two phases were separated, and the supernatant solution was analyzed for Cu(II),

Cd(II), Zn(II), Hg(II), Pb(II), and Cr(III) by atomic absorption spectrophotometry.

### Maximum Adsorption Capacity for Hg(II)

To obtain the maximum adsorption capacity for Hg(II), 50 mL of an aqueous solution were shaken with 1 g of the resin for 1 h at room temperature (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 was determined by atomic absorption spectrophotometry.

### Separation of Hg(II) from Ternary Mixture

The following ternary mixture was evaluated: Hg(II)–Cd(II)–Zn(II). Thus, 10 mL of aqueous solution containing  $6.3 \times 10^{-4}M$  of each metal ion were contacted for 1 h with 0.1 g of dry resin. The pH was adjusted at 1.0, then the resin was filtered and washed repeatedly with deionized water. The metal ions were analyzed in the filtrates by atomic absorption spectrophotometry.

### Desorption of Hg(II)

Desorption assays were carried out with the Hg(II)-loaded resin at maximum capacity. The ion was eluted by shaking 0.1 g of the resin with 10 mL of 1 and 4M of HClO<sub>4</sub> for 1 h. The resin was separated by filtration and the metal ion was analyzed in the supernatant as above.

### Measurements

Cu(II), Cd(II), Zn(II), Hg(II), Pb(II), and Cr(III) were analyzed on a Unicam SOLAAR M Series atomic absorption spectrometer. The pH were measured with a digital H. Jurgens & CoO. pH meter. The FTIR spectra were recorded on a Magna Nicolet 550 spectrophotometer.

## RESULTS AND DISCUSSION

The ability of the pyridine ring and amine groups to form complexes with different metal ions is well known. The aim of this paper is obtain a resin containing a pyridine unit and another one unit as 3-(dimethylamino) propyl acrylate, which would give potential ligand groups and would increase the hydrophilicity—hence favor the polymer–metal ion interaction.

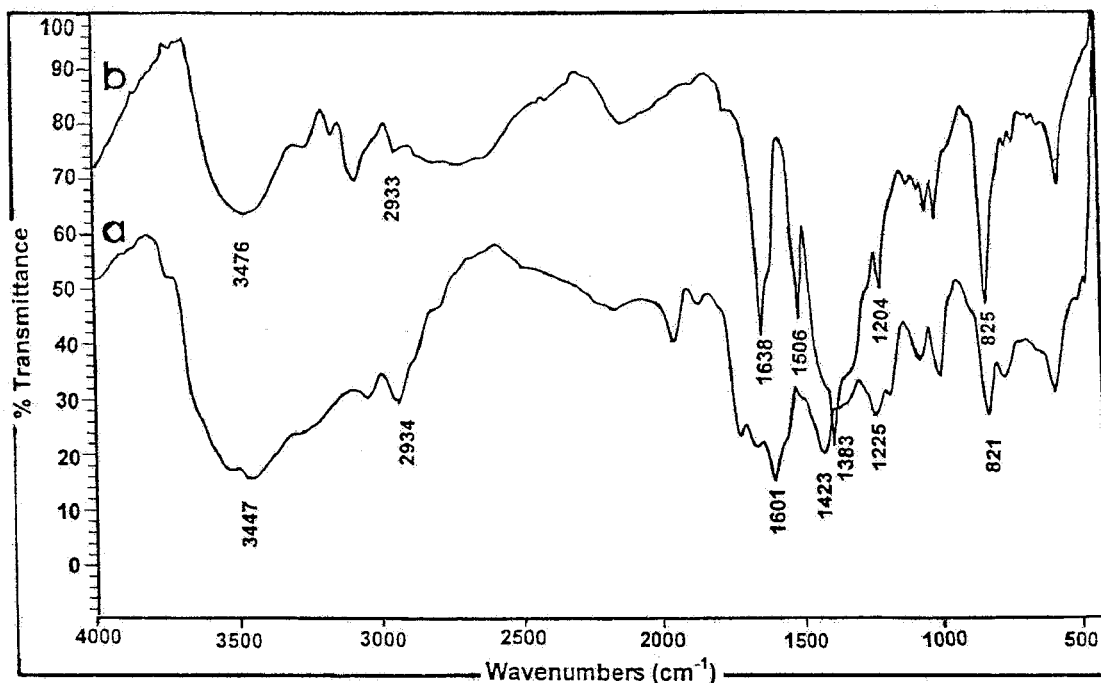
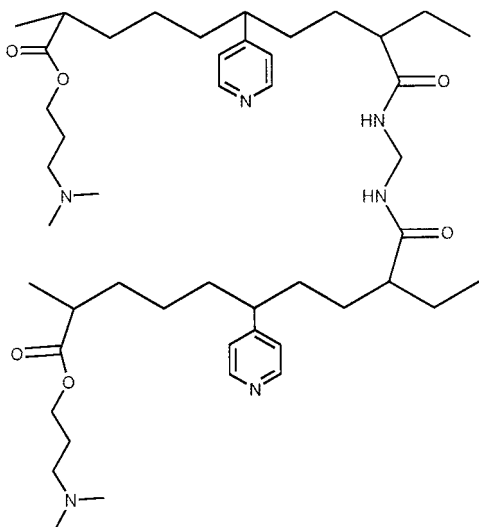


Figure 1 FTIR spectra of the resin DAPA-4VPy (a) and DAPA-4VPy-Hg(II) (b).

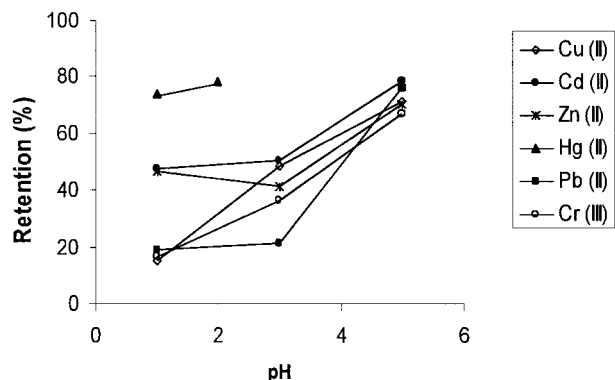
The crosslinked resin was prepared by radical polymerization. The resin was completely insoluble in water and inorganic solvents. The yield was 40%. The particle size of the resin immediately after the polymerization was higher: 1000  $\mu\text{m}$  (99%) and 1000–500  $\mu\text{m}$  (1%). Subsequently, 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 general structure of the DAPA-4VPy resin is as follows:



The FTIR spectra of the unloaded resin show, among other characteristic absorption signals (in  $\text{cm}^{-1}$ ) at 3447 (N—H stretching) corresponding to the secondary amide, 3040 and 1946 ( $\text{C}_{\text{sp}^2}$ —H) corresponding to the aromatic ring of pyridine, 1718 (stretching of C=O carbonyl ester group), and 1600 (C—N) corresponding to the stretching signal of pyridine [see Fig. 1(a)].

The sorption properties of the resin toward Hg(II), Cd(II), Zn(II), Pb(II), Cu(II), and Cr(III) were assayed by a batch equilibrium procedure at different pH values. The results are shown in Figure 2.

At pH 1, the resin presents a low retention capacity for all metal ions. At this pH the amino groups are protonated and the metal ions compete with the protons. The metal ion retention increases as the pH increases, achieving values ranging between 60 and 75%. This can be attributed to the fact that the amino groups are not protonated and hence the metal ion interactions are favored. At pH 2 the resin shows important sorption capacity (85%) and particularly high selectivity for Hg(II). This high preference of the resin for the adsorption of Hg(II) may be attributed to at least two factors, i.e., stability constants for complex formation and conformational requirements. The interaction of the mercury ions with the pyridine

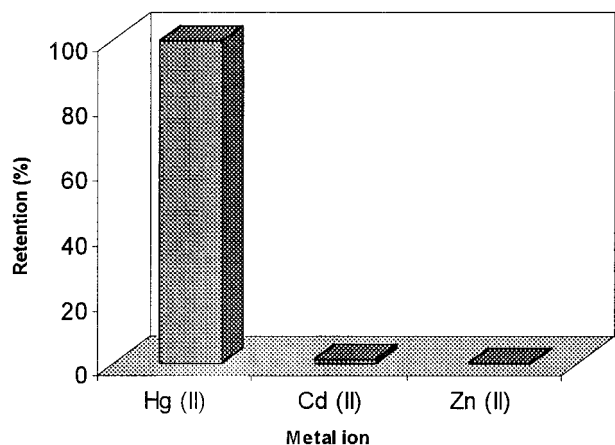


**Figure 2** Effect of the pH under noncompetitive conditions of DAPA-4VPy.

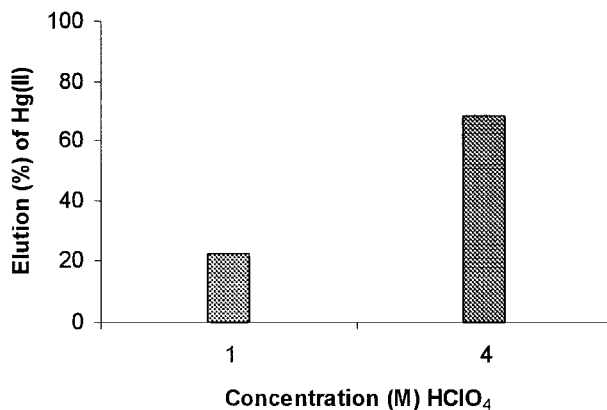
moiety is corroborated by the shifting of the (C—N) absorption band and by the presence of the signal at  $1383\text{ cm}^{-1}$  [(see Fig. 1(b)).

The maximum retention capacity determined after three contacts is 76.9% [0.44 meq of Hg(II) ions/g of dry resin].

The selectivity sorption from the ternary metal ion mixture containing mercury ions was then studied. The resin was suspended for 2 h in an aqueous solution containing equal amounts ( $6.3 \times 10^{-4}\text{ mol L}^{-1}$ ) of three kinds of metal ions: Hg(II)—Cd(II)—Zn(II). The metal ions were analyzed in the filtrated by AAS. The results are summarized in Figure 3. The sorption of mercury(II) ions (98%) is increased with respect to that under noncompetitive conditions and was not affected by the presence of the other metal ions. These results show a high selectivity of the DAPA-4VPy resin for mercury(II) with respect to cadmium(II) and zinc(II) ions. It is well



**Figure 3** Retention behavior of DAPA-4VPy from a mixture of three metal ions at pH 2.



**Figure 4** Elution behavior of Hg(II) from DAPA-4VPy with 1 and 4M HClO<sub>4</sub> at pH 2.

known that Hg(II) ions form tetrahedral, bicoordinated, lineal, and tetracoordinated stable complexes. The bicoordinated complexes show a high covalent character. The affinity of Hg(II) ions to form complexes with nitrogen ligands in aqueous solution is higher than those heavy metal ions.<sup>16</sup> Nevertheless, Hg(II), Cd(II), and Zn(II) have similar electronic properties, they have little analytical analogies.

In order to recover the DAPA-4VPy resin, desorption assays were carried out with the Hg(II)-loaded resin at maximum retention capacity (pH 2). The ion was eluted by perchloric acid at different concentration (see Fig. 4). The elution of Hg(II) ions after only one contact ranged between 20 and 68% depend of the perchloric acid concentration. The highest value correspond to 4M HClO<sub>4</sub>.

In addition, the resin containing 4-vinylpyridine and 3-(dimethylamino) propyl acrylate showed a strong ability to bind Hg(II) at pH 1 and 2. Resin shows a remarkable selectivity for Hg(II) toward Cd(II) and Zn(II) ions at pH 1 in ternary mixture. The maximum load capacity for Hg(II) was high (76.9%, 0.44 meq/g dry resin) at pH 1. The FTIR spectra display the interaction of pyridinic groups with Hg(II). The removal of Hg(II) ions with 4M HClO<sub>4</sub> was of 68%.

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