

Adsorption Behavior of Metal Ions by Amidoxime Chelating Resin

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ABSTRACT: The adsorption properties of poly(acrylamidoxime) chelating resin for Cu(II), Cd(II), Hg(II), Zn(II), Pb(II), Cr(III), and U(VI) are investigated by the batch technique. Based on the research results of the binding capacity effect of the pH value on sorption kinetic experiments, it is shown that this resin has higher binding capacity to uranyl ions, fast kinetics, and very good selectivity from binary metal ion mixtures with Cu(II) and Pb(II). The uranyl ion sorption strongly depends on the pH value of the solution. The highest value of 99% is at pH 5, but at pH 1 there is no retention. The adsorbed UO_2^{2+} can be eluted by sulfuric acid and sodium carbonate. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 1994–1999, 2000

Key words: adsorption; metal ions; chelating resin; amidoxime groups

INTRODUCTION

Polymeric substances with the ability to complex metal ions are very common and have both natural and industrial sources. Humic acids, polysaccharides, clays, and resin materials are examples of substances whose capability of binding metal ions is of great interest from the scientific and technological point of view. Chelating resins represent an important category of synthetic polymers of wide applicability to selectively remove metal cations. These materials usually have a polyelectrolyte character and a very large number of sorption sites per macromolecule, which may be different in their nature or not. These substances display a large range of complexation properties that are due to electrostatic and steric effects. In those resins the copolymer is usually styrene-divinylbenzene and the chelating agent is a func-

tional group (like iminodiacetic, sulfonic acid, amide, amine, amidoxime, etc.) that forms strong complexes with such ions.^{1–3}

The high metal ion selectivities of chelating exchangers are attributed not only to electrostatic forces but also to coordination bonds in metal-chelating groups. The commercial resins Chelamine (Fluka), Bio-Rex-70 (which contains amine and carboxylic groups), and Chelex 100 (Bio-Rad Laboratories; which contains iminodiacetic groups) correspond to examples of ion-exchange resins that contain groups with a strong ability to bind heavy metal ions.

Extensive investigations were carried out with chelating resins containing amidoxime groups. Verraest et al.⁴ demonstrated that Inuline modified with an amidoxime group formed stable complexes with Cu(II). Colella et al.⁵ also demonstrated that poly(acrylamidoxime) can be successfully used for the preconcentration of trace metals from aqueous solutions.

Ferreira et al.⁶ studied the complexation equilibrium of copper, lead, and zinc by using Duolite ES-346, which is a crosslinked copolymer (polystyrene-divinylbenzene) with an amidoxime-che-

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lating group. An increase in the pH favored the metal ion complexation.

One of the best examples of the applicability of chelating resins for the concentration of trace elements is the recovery of uranium from seawater.⁷⁻¹⁰

As in our recent articles,¹¹⁻¹⁵ the objective of this study was to investigate the sorption behavior for metal ions, particularly for uranium(VI).

This present work reports on the sorption of copper, mercury, lead, cadmium, zinc, chromium, and uranium from aqueous solutions with a commercial resin. Copper frequently exists in wastewaters generated in plants that treat mineral ores; almost all of the other metals are usually associated with copper minerals or impact the environment as mercury.

EXPERIMENTAL

Materials and Reagents

The chelating resin used was poly(acrylamidoxime), which was obtained from Polysciences, Inc. Copper nitrate, cadmium chloride, mercury chloride, lead nitrate, zinc nitrate, chromium nitrate monohydrate, and uranyl acetate (Merck, Darmstadt, Germany) as the sources of metal ions were analytical reagent grade and used as received.

Sorption Equilibrium Procedure

Batch studies were employed in all the sorption runs. The sorption equilibrium experiments included the effect of the pH value on sorption, determination of the maximum binding capacity, kinetics sorption, and selectivity sorption of uranyl ions from binary mixtures with copper(II) and lead(II) ions.

Sorption Procedures

Dried samples (0.1 g each) of the chelating resin were equilibrated by 1 h in 10 mL of metal ion solutions at 25°C. The various metal ion solutions were adjusted to the desired pH value with nitric acid or sodium hydroxide prior to equilibrium. The loaded sample resins were filtered and washed with distilled water. The concentrations of metal ions in the filtrate were determined by atomic absorption spectroscopy, except the uranyl ions that were determined by spectrophotometry. Batch metal uptake experiments under competi-

tive conditions were also carried out. The following metal ion mixtures were made: batches of 0.1 g resin were added together with a mixture of 10 mL of each metal ion solution (0.5 g/L). After shaking for 1 h the samples were further handled as described above for noncompetitive conditions. To obtain the maximum sorption capacity for U(VI), 50 mL of an aqueous solution (1 g/L) were shaken with 1 g of dry resin for 1 h at 25°C. The mixture in the flask was filtered and washed with distilled water and transferred into a calibrated flask. The process was repeated 3 times, the volume was made up to 250 mL, and the U(VI) was determined by spectrophotometry.

Batch studies were carried out with the resin to determine the optimum duration necessary for maximum complexation. The resin (0.1 g) with 10 mL of U(VI) solution (1 g/L) were mixed and stirred at pH 5 for the desired time.

The binary mixtures U(VI)-Cu(II) and U(VI)-Pb(II) were evaluated. Thus, 10 mL of an aqueous solution at pH 5 containing 0.5 g/L of each metal ion were contacted by 1 h with 0.1 g of dry resin. Then the resin was filtered and washed repeatedly with deionized water. The metal ions were analyzed in the filtrates as described above.

Removal of Uranium(VI)

The resin loaded with uranyl ions (0.1 g) was stirred with H₂SO₄ (10 mL, 1-3M) or Na₂CO₃ (10 mL, 0.25-1M). The desorbed uranyl ions were collected and estimated as above.

Instruments and Apparatuses

A Julabo air-bath shaker was used for shaking the solution at a desired temperature. The pH was measured with a digital Extech microcomputer pH meter. A Perkin-Elmer 3100 atomic absorption spectrometer was used for the determination of single and mixed metal ions. Uranyl ions were determined by a CADAS 100 spectrophotometer. The FTIR spectra of the samples were recorded with a Magna Nicolet 550 spectrophotometer. The thermograms of the resin and uranium loaded resin were recorded on an STA 625 thermoanalyzer (Polymer Laboratories). Approximately 5 mg of the dry sample was heated at a 10°C/min heating rate under a dynamic nitrogen atmosphere.

RESULTS AND DISCUSSION

The commercial resin poly(acrylamidoxime) was used as received without further treatment. The

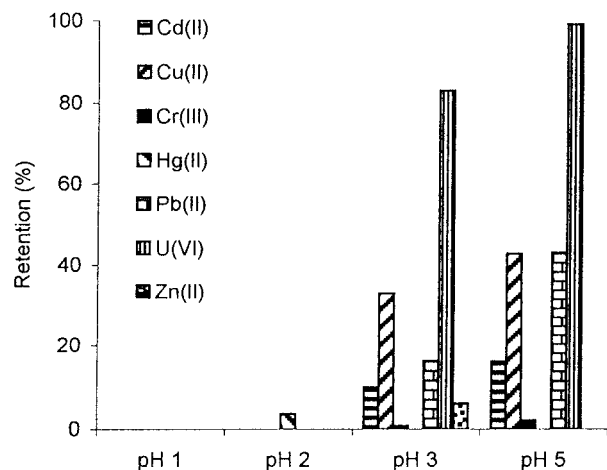
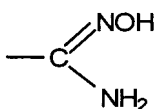


Figure 1 The effect of the pH on the adsorption of various metal ions by 0.1 g poly(acrylamidoxime) resin and 1 g/L metal ions for 1 h at 25°C.

resin contains amidoxime-chelating groups having the following formula:



The amidoximes exist predominantly in the *syn*-hydroxyamino form that is stabilized by an intramolecular hydrogen bond. The compounds behave in water as bases. The amidoximes may coordinate as a nonionic group, but they generally undergo a metal-assisted hydroxyl proton dissociation upon coordination (i.e., the latter type of coordination is expected for copper(II) at pH 6). Besides, this chelating group has a high and efficient selective adsorption ability for uranium(VI). Therefore, the retention behavior of this resin for certain metal ions like Cu(II), Cd(II), Zn(II), Hg(II), Pb(II), Cr(III), and U(VI) was examined at various pH values and the results are shown in Figure 1. The retention increases as the pH increases and the higher retention was observed for Pb(II) and U(VI) at pH 5. At low pH (< 3.0) the competition of H⁺ ions for the resin sites in-

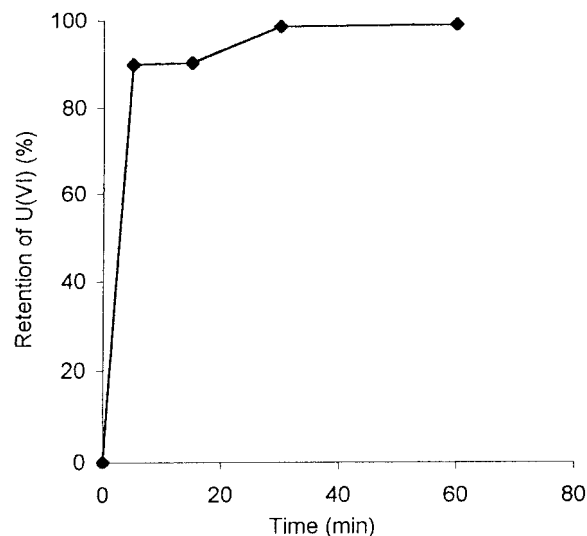


Figure 2 The adsorption rate behavior of uranyl ions on poly(acrylamidoxime) resin at pH 5.

creases and the resin's chelating ability is greatly reduced. An increase in pH decreases the competition of H⁺ ions for the resin sites and complexation of the metal ion is favored. The high selectivities may be attributed not only to electrostatic forces but also to coordination bonds in metal-chelating groups.

Figure 2 shows adsorption rates of U(VI) onto the resin from a 1 g/L aqueous solution at a constant pH of 5. High adsorption rates are observed at the beginning, and then the plateau values (i.e., adsorption equilibrium) are gradually reached within 10–40 min. Adsorption of U(VI) is quite fast. However, in an adsorption process there are several parameters that determine the adsorption rate, such as the agitation rate in the aqueous phase, the amount of the sorbent, the sorbent structural properties, and the metal ion properties (i.e., hydrated ionic radius, initial concentration of metal ion, etc.). Therefore, this result was expected only for the selected experimental conditions.

Table I shows the effects of the initial concentration of uranyl ions on the adsorption capacity of the resin. The amount of U(VI) adsorbed by the

Table I Uranium(VI) Ion Adsorption Capacity of Resin at pH 5

U(VI)						
Initial solution (mmol/L)	0.25	0.50	2.49	4.98	9.97	19.94
Adsorbed (mmol/L)	0.20	0.40	2.40	4.80	9.20	13.90

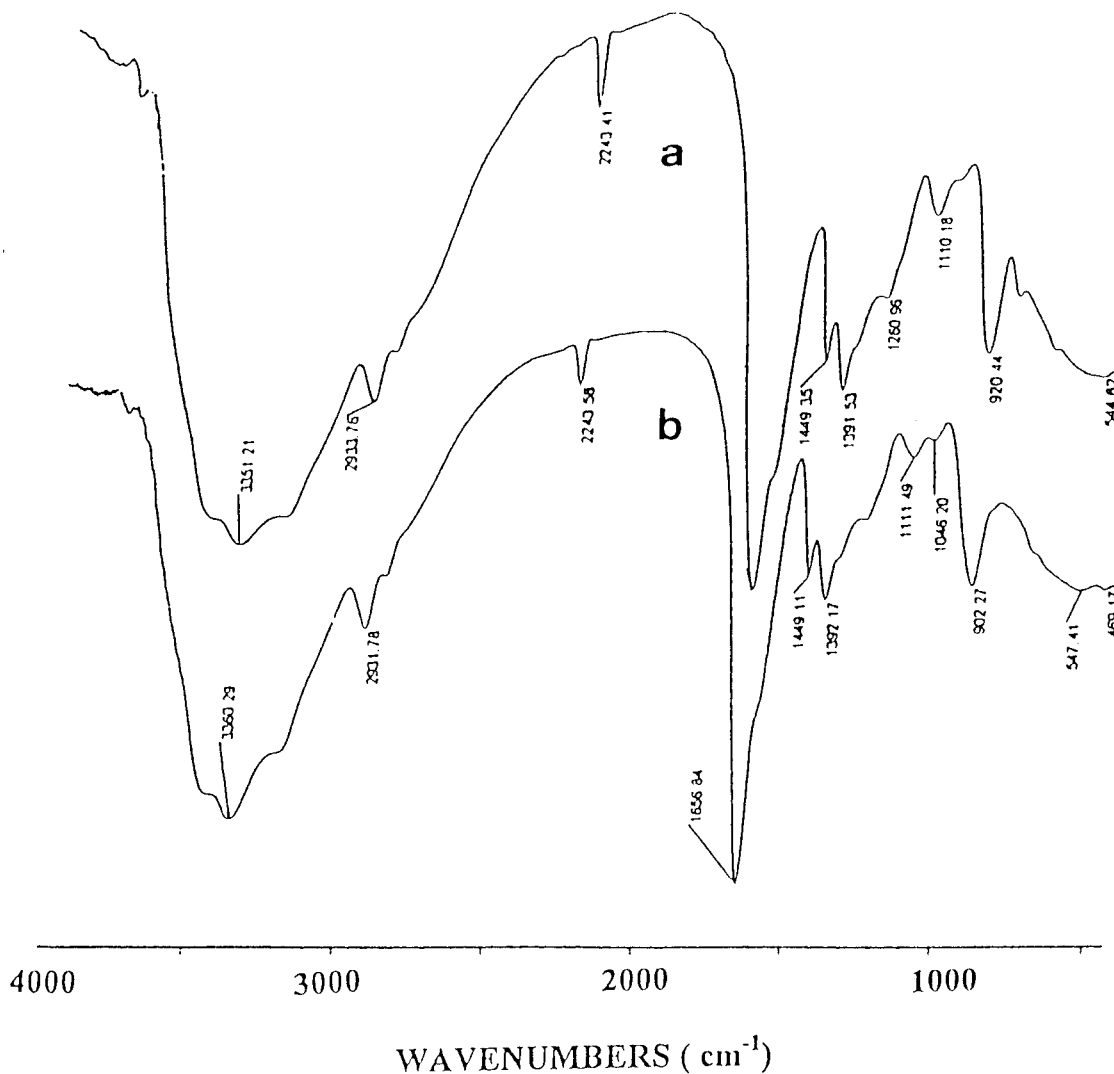


Figure 3 FTIR spectra of the (a) unloaded and (b) uranyl ions poly(acrylamidoxime) resin.

resin increased according to the increased initial concentration of uranyl ions up to a 2 mM concentration (99%). But for a 4 mM solution only 70% was retained, which represents the initial saturation of the active points that are available for uranyl ions on the resin.

The resin exhibited affinity for U(VI) and Pb(II), particularly for U(VI), but no affinity for all the other metal ions. In particular, the adsorption of uranium increased with increasing the pH and the highest values was found to be 2.5 meq/g resin. This result indicates that the macroreticular chelating resins that contain amidoxime groups are more advantageous for the recovery of uranium(VI).

Moreover, the maximum load capacity for uranyl ions was determined at pH 5, demonstrating

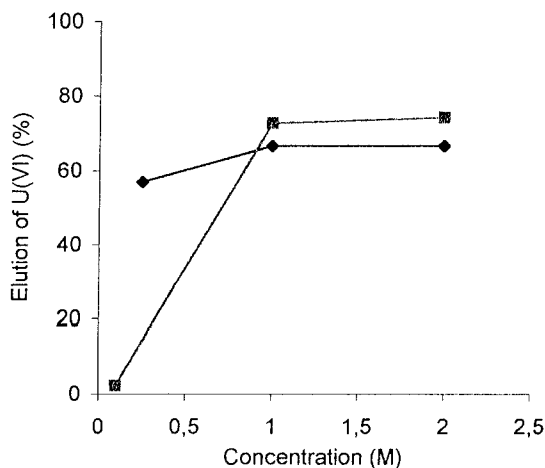
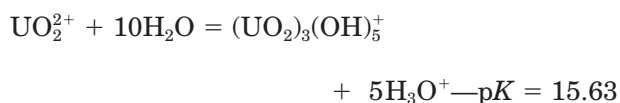
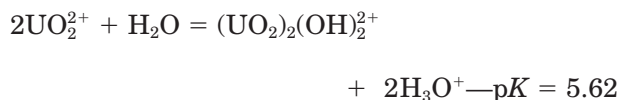


Figure 4 The uranyl ion elution behavior with (■) sulfuric acid and (◆) sodium carbonate.

that after three contacts with an aqueous solution containing 1 g/L in uranium, the amidoxime sites were practically saturated because the retention was 98% (3.7 meq/g dry resin).

The adsorption of uranyl ions from binary mixtures demonstrated that the distribution coefficients were always higher with respect to copper(II) and lead(II). The log K_d for U(VI) was 2.4, for Cu(II) was 2.0, for U(VI) was 4.9, and for lead(II) was 2.2. Therefore, the selectivities of uranium(VI) with respect to copper(II) and lead(II) were 0.4 and 2.7, respectively.

Nevertheless, the partial hydrolysis in acidic media of the amidoxime groups to hydroxamic acid or carboxylic acid was reported^{7,16} and the capability of binding uranyl ions was very high. Uranyl ion species are easily hydrolyzed into various forms previously described by Baes and Mesmer.¹⁷ The equilibria of hydrolysis are as follows:



Consequently, the pH at which hydrolyzed forms appear decreases as the metal ion concentration increases. The major form of hydrolyzed uranyl species is the $(\text{UO}_2)_3(\text{OH})_5^{5+}$ form, whose ionic size is much greater than the free form.

The FTIR spectroscopy also corroborated the involvement of the amidoxime groups in the interaction with uranyl ions. Thus, the bands placed between 3350 and 3400 cm^{-1} , which are assigned to an antisymmetric and a symmetric stretching mode, respectively of NH_2 groups are narrowed, and the peak at 920 cm^{-1} , which is assigned to the N–O stretching mode, disappears and appears as an absorption signal at 902 cm^{-1} , which is attributed to the stretching vibration mode of the U–O–O linear structure¹⁸ (see Fig. 3).

In order to repeatedly reuse the resin for the recovery of uranium, uranium adsorbed on the resin must be easily eluted with a certain kind of eluent. The elution was investigated by the batch method. The results are shown in Figure 4. The uranium(VI) adsorbed on the resin was eluted at close to 73% by sulfuric acid and 67% by sodium

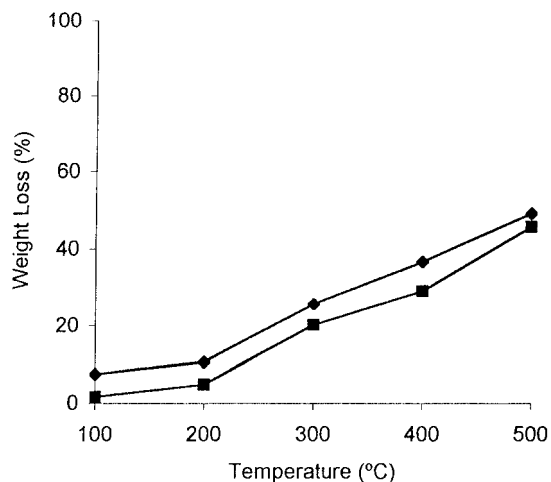


Figure 5 Thermograms of the (◆) unloaded and (■) loaded poly(acrylamidoxime) resin with uranyl ions. The heating rate was 10°C/min under nitrogen.

carbonate with a 1M aqueous solution, but the uranium(VI) was not eluted with 0.25M sulfuric acid. Meanwhile, there was no important effect of the concentration of sodium carbonate on the uranium(VI) desorption. Uranyl ions in basic media could form a stable carbonate complex, $[\text{UO}_2(\text{CO}_3)_3]^{4-}$.¹⁹

Thermogravimetric analyses were carried out to determine the effect of U(VI) adsorbed on the thermal stability of the resin. The resin was loaded with U(VI) at pH 5 according to the maximum load capacity. The metal ion had no important effect on the thermal stability. In both compounds, a weight loss of less than 10% was observed at 200°C. It increased with the temperature up to approximately 36% at 400°C, but it was lower than 50% at 500°C (see Fig. 5).

CONCLUSIONS

Poly(acrylamidoxime) formed stable complexes with uranyl ions as the pH was increased; the highest value of 99% (2.5 meq/g dry resin) was found at pH 5. The sorption equilibrium was achieved relatively fast within the 40 min. It showed an adequate selectivity from binary mixtures with copper(II) and lead(II). The maximum load capacity for uranium(VI) was very high (98%, 3.7 meq/g dry resin). The FTIR of the loaded resin showed the characteristic absorption band at 902 cm^{-1} , which is attributed to linear uranyl. Because at pH 1 the uranium(VI) was not ad-

sorbed, the treatment with 2*M* sulfuric acid allowed the elution of 75% of the uranyl ions adsorbed on the resin; 67% of the adsorbed uranium(VI) was eluted by 1*M* sodium carbonate. The uranyl ions had no observed important effect on the thermal properties.

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