

Adsorption Behavior of Cu^{2+} and UO_2^{2+} Ions on Crosslinked Poly[2,2-bis(acrylamido)acetic acid]

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SYNOPSIS

The synthesis of a water-insoluble metal ion complexing resin was carried out by radical polymerization of 2,2-bis(acrylamido)acetic acid. The resin was characterized by elemental analyses, FTIR spectroscopy, and thermal analyses. The ability to bind copper(II), iron(II), iron(III), and uranium(VI) as well as the elution of the metal ions from the loaded resins were studied. For uranyl ions, pH 5 was the optimum sorption pH value. Sorption selectivity from the binary mixture $\text{Cu(II)} + \text{U(VI)}$ was studied at pH 2. The thermal stability is increased by adsorption of UO_2^{2+} . According to these results a coordination mechanism is suggested for sorption of copper and uranium. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

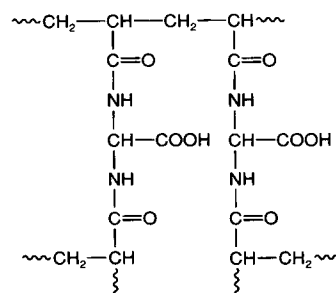
Metal-chelating and ion exchange polymers have been used in hydrometallurgical applications such as recovery of rare metal ions from seawater¹ and removal of traces of radioactive metal ions from wastes.² These methods have found widespread applicability owing to their selectivity.

The rising world prices for metals coupled with the introduction of strict regulations against the pollution of the environment have focused attention on the recovery of metal from lean ores and wastes. Metal extraction based on liquid-liquid contact processes, and liquid-solid contact processes in which the metal is precipitated from a solution or adsorbed on a solid matrix, are the two main types of processes that play a leading role in this separation. Frequently chemically modified polymers are used as synthetic ion-exchange resins. Their main advantages are high chemical and mechanical stability, high ion exchange and high exchange rate. The application of commercial ion exchange resins to metal ions recovery from aqueous solution is a concept that has been extensively studied.^{3,4} Prin-

ciples that are understood in solvent extraction chemistry^{5,6} are applied to the solid-liquid extraction processes.

Many ion exchange substances based on phenol-formaldehyde-ligand copolymers⁷ have been described in the literature together with details of their chelating behavior toward metal ions and selectivity, which is the main feature of chelating ion exchange.⁸⁻²⁰ Today, many routes are available both for the direct and indirect introduction of a chelating function into a high polymer matrix.

In this article the synthesis and uptake properties are reported for Cu^{2+} , Fe^{2+} , UO_2^{2+} , and Fe^{3+} of a resin obtained from 2,2-bis(acrylamido)acetic acid (AmAA), a monomer that contains two double bonds to achieve a network matrix and a metal ion complexing group as a carboxylic or carboxylate group.



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EXPERIMENTAL

Reagents

The chemicals were used without further purification. The metal salts chosen for the present study were analytical reagent grade, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, uranyl acetate $\text{UO}_2\text{Ac} \cdot 2\text{H}_2\text{O}$, iron(II) sulfate $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and iron(III) chloride $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. All solutions were prepared with deionized water.

Preparation of Crosslinked AmAA

The resin was synthesized by radical polymerization dissolving 0.04 mol of AmAA in 70 mL water. Ammonium peroxydisulfate (0.2 mol %) was added under N_2 . The reaction mixture was heated at 70°C for 2 h. After the completion of the reaction, the insoluble water material was filtered, washed repeatedly with water, and dried under vacuum to constant weight. The yield was 89.6%.

Uptake of Cu^{2+} , UO_2^{2+} , Fe^{2+} , and Fe^{3+} Ions

A batch type equilibrium procedure was used to determine the metal ion uptake from aqueous solution by the resin. A 100-mg sample of resin was added to 10 mL of 1 g/L solution of the metal ion. The pH value of the aqueous solution was varied between 0 and 5 depending on the metal ion and it was adjusted with NaOH or H_2SO_4 to the desired constant value. The two phases were shaken at room temperature for 1 h. After shaking, the two phases were separated and the supernatant solution was then analyzed for Cu(II), Fe(II), and Fe(III) using atomic absorption spectrophotometry and, for U(VI), colorimetrically.²¹

The maximum load capacity was defined by contacting 1.0 g of resin with 50 mL aqueous solution containing 1 g/L in uranium or copper. The aqueous solution was separated by decanting and filtration. The process was repeated three times. The metal ions were analyzed in the supernatants as above.

Recovery of Metal Ions

Desorption assays were carried out with the Cu^{2+} and UO_2^{2+} loaded resins at maximum capacity at room temperature (ca. 20°C). The ions were eluted by shaking 0.1 g of resin with 10 mL of 1 M and 4 M H_2SO_4 and 0.25 M and 1 M Na_2CO_3 , respectively, for 1 h. The resin was separated by filtration and the metal ions were analyzed in the supernatants as above.

Measurements

The FTIR spectra were recorded on a Magna Nicolet 550 spectrophotometer. Thermal stability analysis was carried out on a Perkin-Elmer TGA-7 with a heating rate of $10^\circ\text{C min}^{-1}$ under N_2 . Measurements of pH values were performed with a digital Exttech Microcomputer pH-meter. Cu(II), Fe(II), and Fe(III) were analyzed on a Perkin-Elmer 1100 atomic absorption spectrophotometer, and U(VI) was analyzed with a CADAS 100 spectrophotometer.

RESULTS AND DISCUSSION

Synthesis and Characterization

The acrylamide resin was completely insoluble in water and organic solvents. The particle size of the resin immediately after polymerization ranged between 180 and 1000 μm . Subsequently, it was crushed to yield a material with a particle size between 180 and 250 μm . This fraction was employed to study the metal ion uptake properties. The polymerization yield and elemental analyses of the resin are summarized in Table I.

Adsorption Behavior of Metal Ions

The ability of the resin to bind Cu^{2+} , Fe^{2+} , UO_2^{2+} , and Fe^{3+} ions from aqueous solutions is shown graphically in Figure 1. The study was carried out up to pH 2.0 for Fe^{2+} and Fe^{3+} and to pH 4.0 for

Table I Characterization of Resins

		Particle Size (<i>s</i>) (μm)						Elemental Analysis		
500 < <i>s</i> < 1000		250 < <i>s</i> < 500		180 < <i>s</i> < 250		Total Yield		C%	H%	N%
(g)	(%)	(g)	(%)	(g)	(%)	(g)	(%)			
1.5	11.9	4.0	50.5	1.6	20.2	7.1	89.6	48.65	5.15	14.05

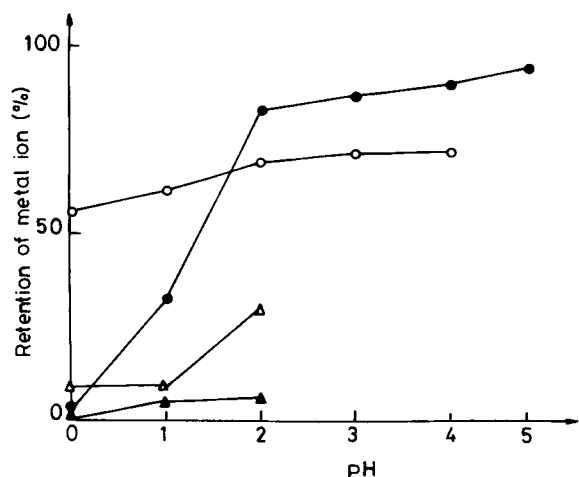


Figure 1 Metal ion uptake as a function of pH. (○) Cu(II); (▲) Fe(II); (●) UO₂(II); and (△) Fe(III).

Cu²⁺ to avoid the hydrolysis of metal ions at higher pH. From the results one can infer that the relative amount of metal ion taken up by the resin increases steadily with increase of the pH of the medium. The retention of Fe²⁺ and Fe³⁺ is lower than 33%, but Cu²⁺ and UO₂²⁺ are significantly adsorbed from pH 1.0 and, at pH 5 95% of UO₂²⁺ was adsorbed from an aqueous solution containing 1 g/L in U(VI). These results are helpful in selecting the optimum pH for a maximum load capacity (see Table II), and a selective uptake for a metal ion from a mixture of different ions.

The rate of UO₂²⁺ sorption of the resin was determined to find the shortest time period for which equilibrium could be carried out while operating as close as possible to equilibrium conditions. The rate of UO₂²⁺ sorption is represented in Figure 2. The resin requires only about 30 min to achieve equilibrium.

The selectivity of metal ion uptake was studied using mixtures of 1.0 g/L solutions of two metal ions. Corresponding to 100% maximum capacity of bound metal ions, the values for each metal ion are summarized in Table III. UO₂²⁺ is bounded preferentially versus Cu²⁺ and Fe³⁺. The highest selectiv-

Table II Maximum Capacity of Load for Cu²⁺ and UO₂²⁺ by Batch Equilibrium Procedure

Metal Ion	pH	mg/g Dry Resin	meq/g Dry Resin
Cu ²⁺	3	59.75	1.88
UO ₂ ²⁺	3	277.22	6.98
UO ₂ ²⁺	5	299.26	7.55

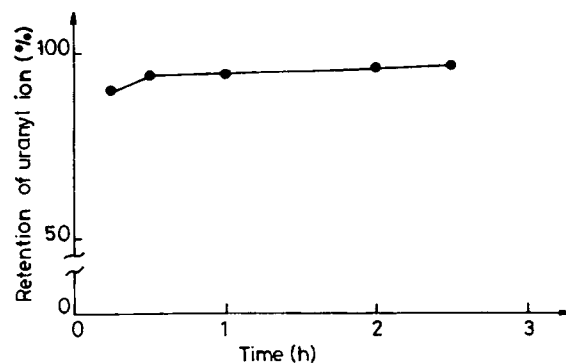


Figure 2 Rate of UO₂²⁺ uptake of the resin at pH 5 contacting 100 mg resin with 10 mL of an aqueous solution of 1 g/L in U(VI) at room temperature.

ity is shown for Fe³⁺ versus Fe²⁺ but the retention is not high, 31 and 6%, respectively (see Fig. 1).

For the regeneration, all Cu²⁺ and UO₂²⁺ containing resin (at maximum load capacity) were treated with 1 M and 4 M H₂SO₄ and 0.25 and 1 M Na₂CO₃. The results are shown in Table IV. Copper is highly eluted in acid medium (>80%) but not in basic medium. On the other hand, UO₂²⁺ is recovered in about 40% in both media. U(VI) in basic media could form a stable carbonate complex, [UO₂(CO₃)₃]⁴⁻.¹⁵

Composition of Resin and Sorption Mechanism

Figure 3 shows the FTIR spectra of the resin alone and saturated with UO₂²⁺ at pH 5 or Cu²⁺ at pH 3. According to the literature²² the peaks in Figure 3(a) can be analyzed as follows at: 1756.1 cm⁻¹ characteristic absorption band of C=O stretching of the monomeric carboxylic acid group; 1665.2 cm⁻¹ the signal due to the carbonyl in the amide groups; 1525.4 cm⁻¹ the N-H deformation in the amide groups; and 1413.6 cm⁻¹ (*w*), 1315.7 cm⁻¹ (*s*) the signals attributed to coupled vibrations involving the C—O stretching and O—H in-plane deformation vibration.

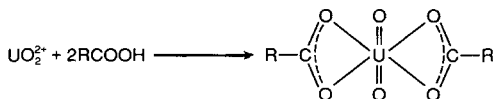
Table III Uptake Metal Ion from Binary Mixture at pH 2

Metal Ions	Uptake	
	mg	%
Fe ³⁺	1.90	29.5
UO ₂ ²⁺	4.54	70.5
Cu ²⁺	2.41	43.9
UO ₂ ²⁺	3.08	56.1

Table IV Metal Ion Elution (%) with Sodium Carbonate and Sulfuric Acid

Metal Ion	pH	H ₂ SO ₄		Na ₂ CO ₃	
		1M	4M	0.25M	1.0M
Cu ²⁺	3	81.8	82.8	2.0	29.9
UO ₂ ²⁺	3	40.1	42.2	39.1	40.0
UO ₂ ²⁺	5	36.7	40.1	37.0	36.7

Comparing trace (b) with (a) in Figure 3, it can be seen that the peak at 1756.1 cm⁻¹ almost disappears, the peaks at 1665.2 and 1525.4 cm⁻¹ move to 1683.4 and 1518.8 cm⁻¹, respectively, and a new peak at 933.1 cm⁻¹ appears, which is identified as the stretching vibration mode of the O—U—O linear structure.²³ These results suggest that the resin operates by a neutral coordination mechanism and not by an ion exchange mechanism, as has been pointed out for similar systems.²⁴



Similarly, from comparing trace (c) with (a) in Figure 3, it can be seen that the peak at 1756.1 cm⁻¹ becomes weaker and changes to 1754.8 cm⁻¹ and the

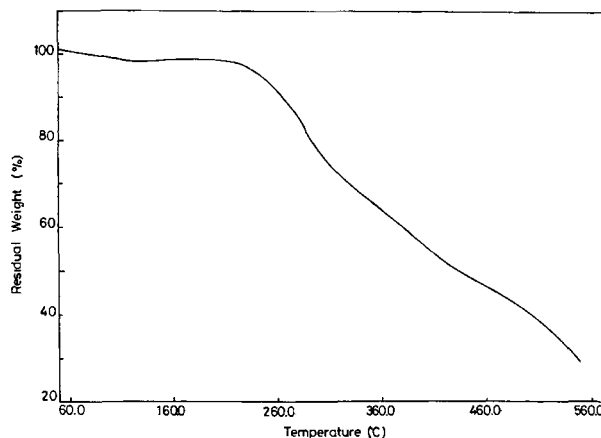


Figure 4 Thermogram of the resin in N₂ atmosphere; heating rate 10°C min⁻¹; weight of resin 1.167 mg.

peaks 1665.2 and 1525.4 cm⁻¹ move to 1671.0 and 1511.2 cm⁻¹, respectively. (In addition, the peak at 1413.6 cm⁻¹ is strengthened and moves to 1397.0 cm⁻¹.)

This is also in agreement with a coordination mechanism for copper where two or more carboxylic groups are involved.

Thermal Stability of Resins

The resin is very stable up to about 250°C (see Fig. 4). To determine the effect of the metal ions ad-

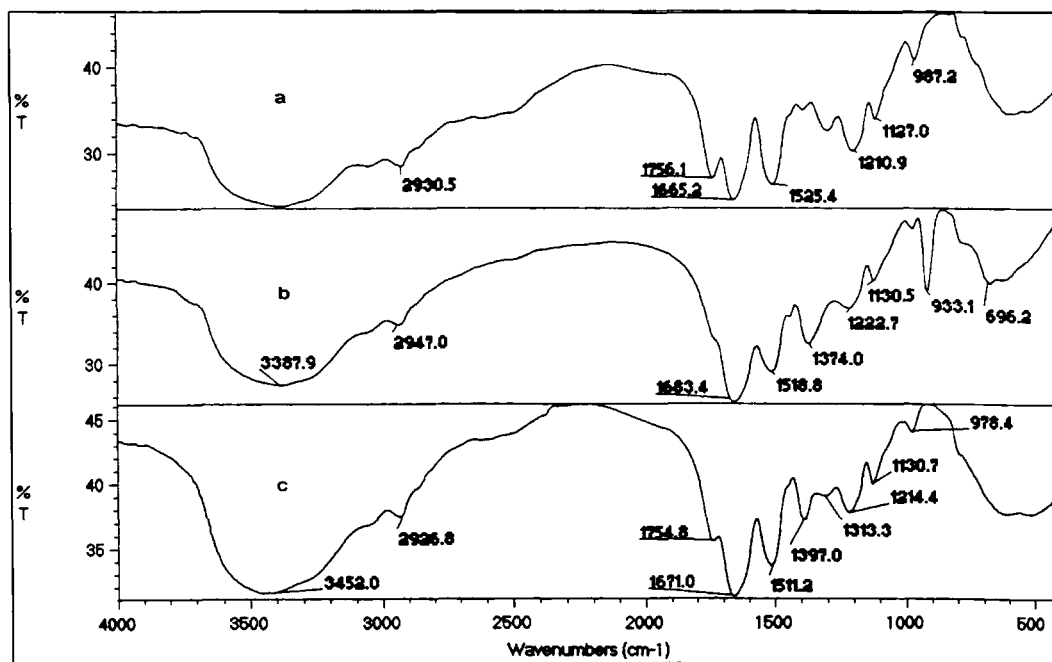


Figure 3 FTIR spectra of: (a) chelating resin; (b) adsorbed UO₂²⁺ at pH 5; and (c) with adsorbed Cu²⁺ at pH 3.

Table V Thermal Stability of Unloaded (R-) and Metal Ion Loaded Resin (R-M²⁺)

R- and R-M ²⁺	pH	Weight Loss (%) at Different Temperatures (°C)					TDT _{10%}
		100	200	300	400	500	
R-	—	0.97	1.35	22.70	43.29	59.67	265
R-Cu ²⁺	3	7.23	9.02	87.87	90.73	97.10	230
R-UO ₂ ²⁺	3	3.64	6.84	11.03	39.53	47.98	293
R-UO ₂ ²⁺	5	0.00	1.47	7.34	29.16	37.61	307

TDT_{10%}, thermal decomposition temperature in which 10% resin weight has been lost.

sorbed on the resin on thermal stability, thermogravimetric analyses were carried out. The resin was loaded according to the maximum capacity (see Table V). UO₂²⁺ increases the thermal stability of the resin. Thermal decomposition temperature in which 10% resin weight has been lost increased by 10% at pH 3 and 16% at pH 5.0, which is in agreement with the higher UO₂²⁺ uptake at the last pH (see Fig. 1).

CONCLUSIONS

AmAA is an excellent monomer to obtain a complexing metal ion resin due to the presence of two double bonds allowing radical polymerization and crosslinking, as well as the presence of a chelating group as carboxylic acid or carboxylate. This resin is very stable up to 250°C, and the UO₂²⁺ adsorbed on the resin increases the thermal stability, perhaps by reason of the metal ion providing a coordination crosslink.

The resin significantly adsorbed Cu²⁺ and UO₂²⁺, particularly the latter at pH 5 at 95%. It does not retain a significant level of Fe²⁺ and Fe³⁺.

It is possible to recover the copper loaded resin by elution with 4M sulfuric acid (82.0%). Uranium is moderately eluted either in basic or acid media (ca. 40%).

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REFERENCES

1. F. Vernon, *Hydrometallurgy*, Wiley, New York, 1979.
2. P. Hodge and D. C. Sherrington, Eds., *Polymer Supported Reaction in Organic Synthesis*, Wiley, Chichester, 1980.
3. S. B. Savvin, *Zh. Anal. Khim.*, **37**, 499 (1982).
4. R. Bogoczek and J. Surowiec, *J. Appl. Polym. Sci.*, **26**, 4162 (1981).
5. J. M. Frechet, *Tetrahedron*, **37**, 666 (1981).
6. G. V. Veseley and V. I. Stemberg, *J. Org. Chem.*, **36**, 2548 (1979).
7. H. P. Gregor, M. Taifer, L. Citarel, and E. Becker, *Ind. Eng. Chem.*, **44**, 2834 (1952).
8. F. Vernon and G. Eccles, *Anal. Chem. Acta*, **72**, 331 (1974).
9. B. S. Patel, G. S. Choxi, and S. R. Patel, *Makromol. Chem.*, **180**, 8791 (1979).
10. A. Latha, B. K. George, K. G. Kannan, and K. N. Ninnan, *J. Appl. Polym. Sci.*, **43**, 1159 (1991).
11. W. H. Chan, S. Y. Lam-Leung, W. S. Fong, and F. W. Kwan, *J. Appl. Polym. Sci.*, **46**, 921 (1992).
12. T. K. Bastía, S. Lenka, and P. L. Nayak, *J. Appl. Polym. Sci.*, **46**, 739 (1992).
13. K. Schipschak, J. Beger, R. Neumann, and H. Wagner, *Angew. Makromol. Chem.*, **199**, 103 (1992).
14. I. Hoskovcová and E. Kálalová, *Angew. Makromol. Chem.*, **198**, 61 (1992).
15. B. L. Rivas, H. A. Maturana, R. E. Catalán, and I. M. Peric, *J. Appl. Polym. Sci.*, **38**, 801 (1989).
16. B. L. Rivas, H. A. Maturana, and I. M. Peric, *Angew. Makromol. Chem.*, **211**, 103 (1993).
17. B. L. Rivas, H. A. Maturana, and E. Pereira, *Angew. Makromol. Chem.*, **220**, 61 (1994).
18. B. L. Rivas, H. A. Maturana, I. M. Peric, and E. Pereira, *Bol. Soc. Chil. Quím.*, **39**, 211 (1994).
19. A. A. Efendiev and V. A. Kabanov, *Pure Appl. Chem.*, **54**, 2077 (1982).
20. C. D. Barnes, R. A. da Silva Neves, and M. Streat, *J. Appl. Chem. Biotechnol.*, **24**, 787 (1974).
21. J. A. Pérez-Bustamante and F. Palomares Delgado, *Analyst (Lond)*, **96**, 407 (1971).
22. *Vogel's Textbook of Practical Organic Chemistry*, 5th ed., B. S. Furniss, A. J. Hannaford, P. W. G. Smith, and A. R. Tatchell, Eds., Longman Scientific and Technical, New York, 1989, p. 1412.
23. M. I. N. Ximenes, O. A. Serra, and G. B. de Barros, *Polym. Bull.*, **30**, 97 (1993).
24. Ch. E. Carraher, *J. Chem. Ed.*, **58**, 921 (1981).

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