Polymer Bulletin 30, 633–639 (1993)

Polymer Bulletin

Preparation and uranyl sorption of extractant resin containing ammonium groups

B. L. Rivas*, H. A. Maturana, I. M. Peric, and H. Lopez

Facultad de Ciencias Químicas, Universidad de Concepción, Casilla 3-C, Concepción, Chile

SUMMARY

An extractant resin was synthesized by radical polymerization of [3-(methacryloyl amino)propyl] trimethyl ammonium chloride in presence of N,N'-methylene-bis-methacrylamide as crosslinker agent at different concentrations. All the resins are insoluble in water. The resins showed high affinity and selectivity for uranium. The resins do not retain significantly copper (< 6%). Elution assays with sulfuric acid and sodium carbonate, were also carried out.

INTRODUCTION

An extractant resin is an important polymer which removes metal ions from aqueous solution. For this purpose, various types of extractant groups have been introduced into network polymers. Although these extractant resins take up almost all transition metal ions in high yield, they do not have sufficient selectivity for metal ions. Therefore, interest in selective ion-exchange resins has largely grown in the last few years. One approach to achieve that is preparation of crosslinked polymers with functional groups as specific extractants (1).

For the purification and recovery of uranium, various kinds of extractant resins have been studied (2-7). From this view-point, attempts to synthesize polymers with selective binding ability for uranyl ion have been reported: resins as poly(phosphonic acid) (8), polymer supported cyclic hexaketone (9). We have also reported the uranium sorption properties of resins synthesized by modification of poly(ethyleneimine) (10-13).

In this paper the synthesis of the water-insoluble resins by radical polymerization of [3-(methacryloylamino)propyl] trimethyl ammonium chloride (MPTA), initiated by ammonium peroxydisulfate using different concentrations of N,N'-methylene-bis-acrylamide as crosslinker, is reported. The sorption properties for copper(II) and uranium(VI); elution assays; maximum load sorption for uranium(VI) were also studied.

EXPERIMENTAL PART

Materials and reagents:

[3-(methacryloylamino)propyl] trimethylammonium chloride (MPTA), N,N'-methylene-bis-acrylamide (MBA) and ammonium peroxydisulfate (APS) were

---

*Corresponding author

used without further purification. Analytical grade reagents of uranyl acetate and copper(II) sulfate pentahydrate were used.

Synthesis of the extractant resin:

Crosslinked poly[3-(methacryloylamino)propyl] trimethylammonium chloride (CMPTA) was obtained as follows: Monomer (MPTA) (0.02 mol) was polymerized with (MBA) (2, 6, 10 and 15 mol%) using APS (0.2 mol%) in 30 ml water. The reaction was kept under N_2 during 30 min at 70°C. The crosslinked resin was washed repeatedly with water, dried under vacuum till constant weight and crushed to 250-500 mesh.

Sorption of metal ions on the CMPTA resins:

A batch type equilibration procedure was used to determine the metal ions adsorbed from solution at different pH by the crosslinked resin. The two phases were shaken at room temperature for 1 h. Then the supernatant solution was analyzed for copper(II) and uranium(VI) by atomic absorption spectrophotometry and colorimetry (14) respectively.

Determination of the maximum capacity of sorption for uranium

A 250 ml beaker containing dry resin (1.0 g) and uranyl acetate aqueous solution (50 ml) (equivalent to 1.0 g uranium/L) was placed in a thermostatically controlled bath at 25°C. The mixture was shaken for 2 h. The aqueous solution was separated by decanting and filtration and washed with water. This process was repeated three times using the same resin. Uranium(VI) was analyzed by the spectrophotometric method (14), and the uranium (VI) adsorbed in the resin is determined from the difference.

Uranium Elution:

The resin loaded with uranium at pH 2.0 was contacted with sulfuric acid or sodium carbonate at different concentrations. The mixture was stirred for 1 h. The resin was separated by filtration and the uranium was analyzed by colorimetry (14).

Measurements:

Copper(II) was analyzed in a Perkin-Elmer 306 Atomic Absorption Spectrophotometer and uranium(VI) was analyzed on a Gilford 250 Spectrophotometer.

RESULTS AND DISCUSSION

Preparation of CMPTA-crosslinked resins:

The resins were prepared by solution radical polymerization of MPTA at 70°C during 30 min using BMA as crosslinker (2-15 mol%) and APS as initiator giving a crosslinked structure which has the following idealized structure:

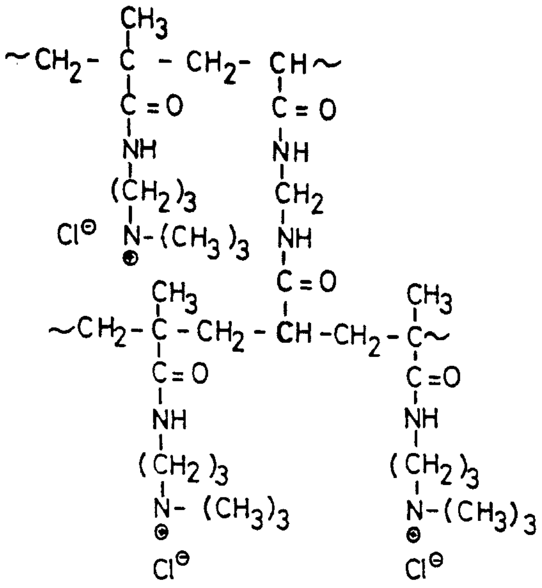

Table 1 compiles the properties of four resins which differ in the concentration of BMA in the feed. The yield immediately after the polymerization reaction is between (84% - 86%). But during the working-up procedure to a granular product, some resin is lost, mostly as finest grained solid. According to the analytical data and N/C ratio there is not an important effect of the BMA concentration on the structure properties of the resins under the polymerization reaction conditions.

Table 1. Characterization of the CMPTA resins

RESIN	MBA (mol %)	Elemental Analysis C (%)	H (%)	N (%)	N/C mol ratio
1	2	40.87	10.10	10.58	0.2219
2	6	38.70	10.44	9.97	0.2208
3	10	38.10	10.11	9.63	0.2166
4	15	38.95	9.98	10.10	0.2223

Study of metal ions sorbed on the CMPTA resins:

This study was carried out basically to compare the affinity and selectivity of the CMPTA for copper(II) and uranium(VI).

Sorption parameters:

The time required to reach equilibrium was determined by measuring the uranium(VI) concentration in the aqueous solution (pH 2.0) at different times (see Figure 1). A shaking time of 0.5 h sufficed for almost complete adsorption of uranium(VI), but a period of 1 h was adopted in further experiments.

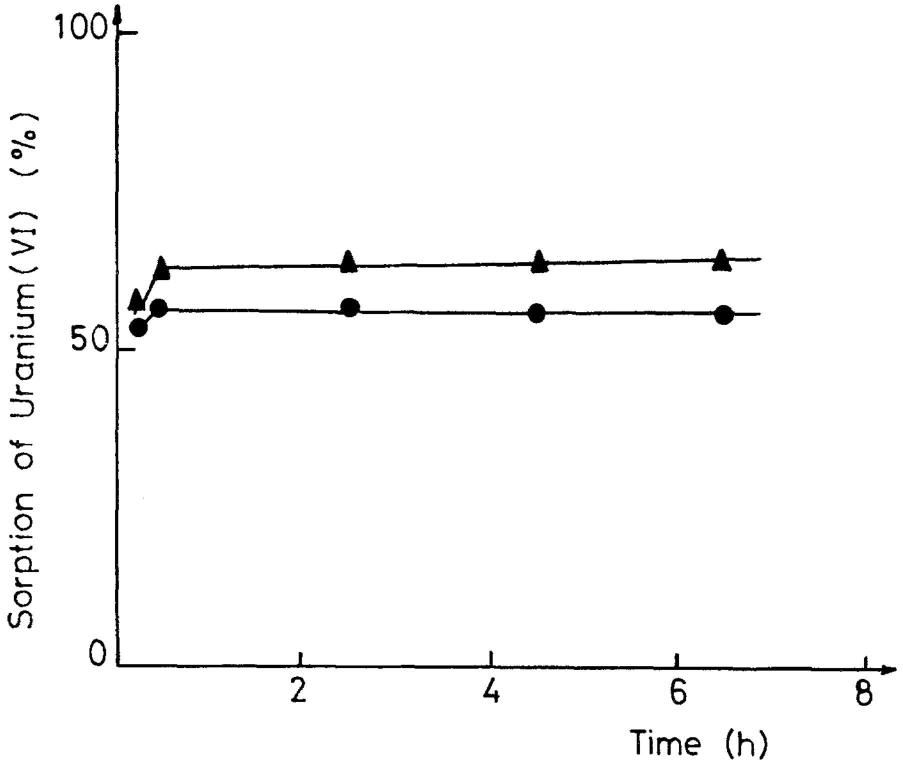

Fig. 1. Kinetics characteristics of the resins 1 (-•-) and 4 (-▲-) towards UO^{2+} at pH 2.0.

Effect of pH on degree of sorption (Batch method):

The sorption properties for the resins were assayed by a batch method at different pH. The four resins almost show the same sorption behaviour for uranium(VI) (see Table 2). The sorption for uranium(VI) increases from pH 0 to 2.0 and decreases sharply from pH 2.0 to pH 4.0. All the resins show the optimum sorption for uranium(VI) at pH 2.0 (53-63%). Therefore, pH 2.0 was selected for subsequent work.

Table 2. Sorption (%) of uranium(VI) on CMPTA resins

RESIN	pH				
	0	1	2	3	4
1	6.0	41.8	56.2	15.7	19.7
2	7.7	44.1	57.4	18.8	16.4
3	5.0	46.9	53.1	14.9	16.9
4	4.1	50.4	63.5	16.0	16.8

The same resins do not retain significantly copper(II) (< 6%) in the pH range assayed.

All the resins show good selectivity for uranium(VI). As an example, the sorption properties of resin 4 were compared. It adsorbs uranium(VI) over the entire pH range, with a maximum sorption (63.5%) at pH 2.0, but not copper(II) (see Figure 2). The maximum capacity of sorption (MCS) for uranium(VI) was determined at pH 2.0 and the values vary between 4.6 to 5.0 meq uranium(VI)/g-dry resin (see Table 3). These values are lower than those observed under the same experimental conditions for IRA-400, a commercial resin (6.7 uranium(VI)/g-dry resin).

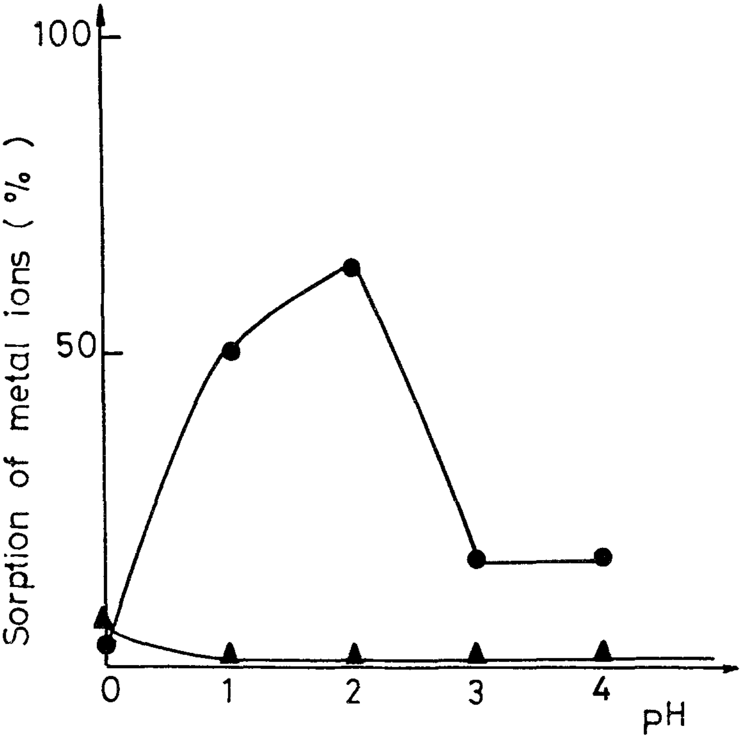

Fig. 2. Effect of pH on the sorption for UO^{2+} (-•-) and Cu^{2+} (-▲-) by resin 4.

Table 3. Maximum capacity of sorption for uranium(VI)

RESIN	1	2	3	4
RESIN (meq/g)	4.6	4.8	4.8	5.0

It is established that uranyl ion can be complexed by either sulfate or bisulfate ions to produce anionic sulfate complexes which depends on pH value and sulfate concentration in aqueous solution (15). Consequently, these sulfate complexes can exchange with chloride ions in the strong basic resins:

$$2(\overset{+}{R_4N})Cl^- + [UO_2(SO_4)_2]^{2-} ==== (\overset{+}{R_4N})_2[UO_2(SO_4)_2]^{2-} + 2Cl^-$$

Elution assays:

This study was done in order to choose a suitable reagent able to release uranium(VI) from the resin. Thus, uranium(VI) sorbed on the resin was eluted with 10 ml of sulfuric acid (0.25M and 1.0M) and sodium carbonate (0.25 M and 1.0 M). For both eluents, increasing the concentration of the acid or basic media, increases the elution of uranium(VI) (see Table 4). Sodium carbonate 1.0 M released after one contact between 75 to 85% of uranium(VI) which is higher than that of sulfuric acid of 1.0 M, due to that a more stable complex carbonate $[UO_2(CO_3)_3]^{4-}$ is formed.

Table 4. Uranium elution (%) with sulfuric acid and sodium carbonate at different concentrations.

RESIN	H_2SO_4		Na_2CO_3	
	0.25 M	1.0 M	0.25 M	1.0 M
1	34.6	69.4	60.8	82.7
2	36.8	73.7	51.5	75.9
3	36.0	73.7	53.5	80.7
4	36.1	75.9	55.3	84.7

In addition, the resin-uranyl ion equilibrium is relatively fast considering that the equilibrium occurs in heterogeneous phase. According to the sorption behaviour it should be possible to separate uranium(VI) from copper(II) in all pH range tested and particularly at pH 2.0. It is possible to partially recover uranium-loaded resins with 1.0 M sodium carbonate.

ACKNOWLEDGEMENTS

The authors thank FONDECYT (Grant Nº 92-0243) for financial support.

REFERENCES

1. J. Stamberg, J. Seidl, J. Rahm, J. Polym. Sci., **B31**, 15 (1958).
2. H. Kise, H. Sato, Makromol. Chem., **186**, 2449 (1985).
3. J. Kennedy, R.V. Davies, Chem. Ind. (London), 378 (1956).
4. H. Egawa, T. Nonata, M.I. Kari, J. Appl. Polym. Sci., **29**, 2045 (1984).
5. J. Kennedy, G.E. Ficken, J. Appl. Chem., **8**, 465 (1958).
6. G. Manecke, J. Danhauser, Makromol. Chem., **56**, 208 (1962).
7. J. Kennedy, E.S. Lane, B.K. Robinson, J. Appl. Chem., **8**, 459 (1958).
8. M. Marhol. K.L. Chen, Talanta, **21**, 751 (1974).
9. I. Tabushi, Y. Kobuke, T. Nishiy, Nature, **280**, 665 (1979).
10. B.L. Rivas, J. Bartulín, Bol. Soc. Chil. Quim., **31**, 37 (1986).
11. B.L. Rivas, K.E. Geckeler, Adv. Polym. Sci., **102**, 171 (1992).
12. B.L. Rivas, H.A. Maturana, R.E. Catalán, I.M. Perich, J. Appl. Polym. Sci., **38**, 801 (1989).
13. B.L. Rivas, H.A. Maturana, U. Angne, R.E. Catalán, I.M. Perich, Polym. Bull. **16**, 305 (1986).
14. J.A. Pérez-Bustamante, F. Palomares Delgado, Analyst, **96**, 407 (1971).
15. C.D. Barnes, R.A. da Silva Neves, M. Streat, J. Appl. Chem. Biotechnol., **24**, 787 (1974).

Accepted May 4,1993 K