Metal ion extraction behavior of poly([2(methacryloyloxy)ethyl]trimethylammonium chloride-*co*-acrylic acid) resin

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SUMMARY

The crosslinked poly([2-(methacryloyloxy)ethyl]trimethyl ammonium chloride-*co*-acrylic acid) was tested as adsorbent for Cd(II), Hg(II), Zn(II), Pb(II), Cr(III), and U(VI) by batch equilibrium procedure. At pH 5.0 the adsorbent retained 74% (1.865 meq/g) of U(VI) with a maximum capacity of load of 2.7 meq/g (108 mg/g). The resin-U(VI) equilibrium was achieved around of 1 h which is considered adequate for a heterogeneous reaction. It showed a high selectivity for U(VI) respect to all the other metal ions both from competitive and non-competitive conditions. The recovery of the resin was over 65% by H_2SO_4 and Na_2CO_3.

INTRODUCTION

Metals are among the most commonly encountered and difficult to treat environmental pollulants. They are introduced into the environment during industrial processes, refining of ores, mining, combustion of fossil fuels, disposal of industrial and domestic waters, *etc*. (1-2). 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. Chemical precipitation has been traditionally proposed to remove metal ions from aqueous solutions. However, metal removal in the precipitation-coagulation systems is, in many cases, insufficient to meet strict regulatory requirements. According to that, adsorption has been shown to be an efficient alternative (3-4). However, the need to reduce the amount of metal ions in these media and the subsequent re-use, has led to an increasing interest in ion exchange materials (5-12), in particular to those called "ion-specific resins", which under proper operating conditions, are selective for one ionic species only (13-17). Among the more important properties of such ion exchangers should be included high capacity, high selectivity, and fast kinetics. Unfortunately, the last ones are competitives and it is necessary achieve a balance to yield adequate resins.

These polymeric substances usually have a polyelectrolyte character and a very large number of sorption sites per macromolecule, which may be different in their chemical nature or not. Owing to electrostatic and steric effects, these substances display a large range of complexation properties, the respective microscopic stability constants being different for the different sorption sites even when they are chemically homogeneous.

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Specific sorbents consist of a ligand (*e.g.* ion exchange material or chelating agents) which interact specifically with the metal ions, and a carrier matrix, which may be an inorganic material (*e.g.* silica, glass, or aluminium oxide) or polymer microbeads (*e.g.* poly(styrene), cellulose, poly(acrylic acid) poly(4-vinylpyridine), poly(methylmethacrylate)) (18-19).

The aim of this paper is the investigation of retention properties by batch equilibrium procedure under different experimental conditions of crosslinked poly([(2-(methacryloyloxy)ethyl]trimethyl ammonium chloride-*co*-acrylic acid) for metal ions with impact in the environment as Cu(II), Cd(II), Hg(II), Pb(II), Zn(II), Cr(III), and U(VI).

EXPERIMENTAL PART

Starting materials: All reagents and solvents were purchased from commercial sources and were used as received. The crosslinked resin MTAC-AA was prepared by radical polymerization using a mixture of [2-(methacryloyloxy)ethyl]trimethyl ammonium chloride (MTAC) (0.05 mol, 8.72 g), acrylic acid (AA) (0.05 mol, 3.60 g), N,N'-methylene bis acrylamide (MAAm) (6 mol%, 462.5 mg) and ammonium peroxydisulfate (APS) (0.5 mol%, 57.05 mg).

Batch metal-uptake experiments: The batch metal uptake experiments were performed using standard metal salt ($Cu(NO_3)_2$, $CdCl_2$, $HgCl_2$, $Zn(NO_3)_2$, $Pb(NO_3)_2$, $Cr(NO_3)_3$, and $UO_2(CH_3COO)_2$ 1g/L at pH range 1-5 depending of the metal ion. All experiments were performed in flasks mounted on a shaker at 25°C. The capacities for Cu(II), Cd(II), Zn(II), Hg(II), Pb(II), Cr(III), and U(VI) under non-competitive and competitive conditions were determined as a function of the pH. Batches of 0.1 g resin were used, together with a mixture of 10 ml of metal solution. After a shaking time of 1 h, the samples were filtered, washed with water, and dried in vacuum at 50°C. Batch metal-uptake experiments under competitive conditions were performed with the following metal ion mixtures: U(VI)-Cu(II), U(VI)-Pb(II), and U(VI)-Cu(II)-Pb(II). Batches of 0.1g resin was used together with a mixture of 10 ml of each metal solution (0.5 g/L). After a shaking time of 1 h, the samples were further handled as describes for the non-competitive experiments.

To obtain the maximum adsorption capacity for U(VI), 50mL of an aqueous solution 1 g/L were shaken with 1.0 g of the resin for 1 h at 25°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 U(VI) colorimetrically at $\lambda = 655$ nm was determined.

In the regeneration experiments, (0.10-2.0 M) H_2SO_4 and (0.25-2.0 M) Na_2CO_3 were tested for its stripping potential. Batches of 1.0 g resin were loaded with uranyl acetate solution (50 ml of the metal solution 1.0 g/L) at pH 5.0 by shaking for a period of 1 h. The loaded resin was washed with water and the filtrates collected. This procedure was repeated three times.

RESULTS AND DISCUSSION

The croslinked poly([2-(methacryloyloxy)ethyl] trimethylammonium chloride-*co*-acrylic acid) was synthesized by radical copolymerization by using ammonium peroxydisulfate, and N,N-methylene bis acrylamide as initiator and crosslinker agent respectively. It was completely insoluble in water and in common organic solvents as methanol, ethanol, chloroform, acetone, dimethylformamide, *etc*.

The sorption properties by the resin towards Cu(II), Hg(II), Cd(II), Zn(II), Pb(II), Cr(III), and U(VI) were assayed by a batch method at different pH values (see Table 1).

Table 1. Sorption in percentage and in meq ( ) of metal ions on MTAC-AA at different pH. Concentration of metal ion: 1.0 g/L.

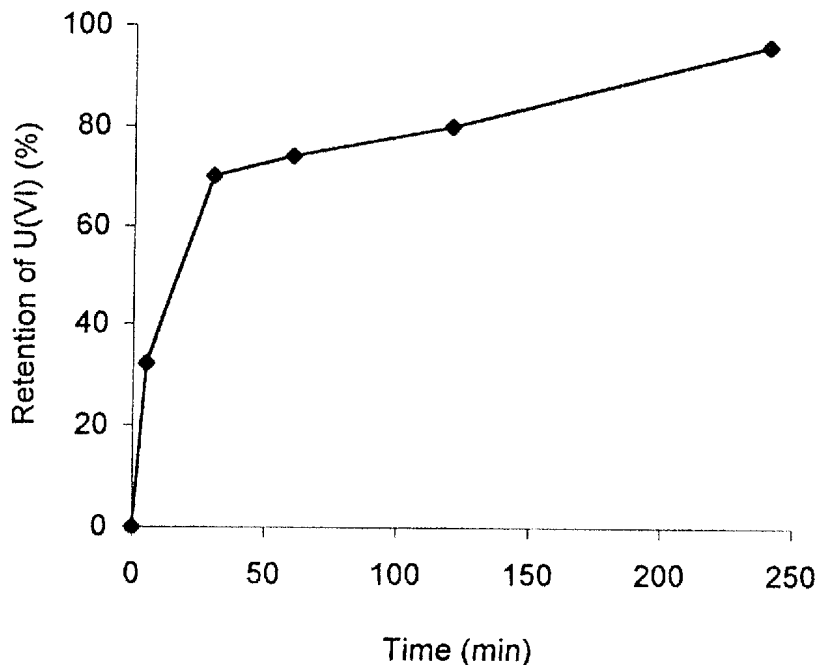| Metal ion	pH			
	1	2	3	5
Cu(II)	0.0		0.0	0.0
Cd(II)	3.9 (0.069)		0.0	0.0
Zn(II)	14.0 (0.367)		0.0	0.0
Pb(II)	8.6 (0.083)		2.0	5.2 (0.05)
Hg(II)	0.0	17 (0.169)		
Cr(III)	0.0		19.6 (1.133)	25.0 (1.445)
U(VI)	0.0		65.0 (1.638)	74.0 (1.865)

In these experiments, buffer solutions deliberately were not used to avoid any possible interferences coming from the components of the buffer.

The highest increase on the metal ion sorption of U(VI) occurs between pH 3 and 5. At the last pH the resin adsorb 74% (1.865 meq) of U(VI) but only 25% (1.445 meq) Cr(III) and 5.2% (0.050 meq) Pb(II). All the other metal ions were not adsorbed. According to these results the following runs were carried for U(VI) at pH 5.0.

The adsorption rate of U(VI) was relatively fast, the time required to attain the equilibrium conditions is about 60 min which is considered adequate assuming that it is a heterogenous system (see Figure 1).

The maximum adsorption capacity for U(VI) is 2.7 meq/g resin (108 mg/g resin) after three contacts. The uptake of U(VI) ions would occur through the carboxylate groups, specially at higher pH, where the concentration of carboxylate groups responsible for the U(VI) sorption is higher, and/or ammonium groups by forming an adduct at lower pH (10). It is not possible discard the simultaneous extraction of uranyl ions by both ligand groups.

Adsorption capacity of U(VI) is presented in Figure 2 as a function of the initial concentration in the aqueous phase at pH 5 after the contact with 0.1 g of the resin. The amount of U(VI) ion adsorbed per unit mass of the resin increase during the first 60 min as increase their initial concentration from 2.1 mmol/L to 12.6 mmol/L.

Figure 1. Time course of uranyl ion interactions with MTAC-AA at pH 5.
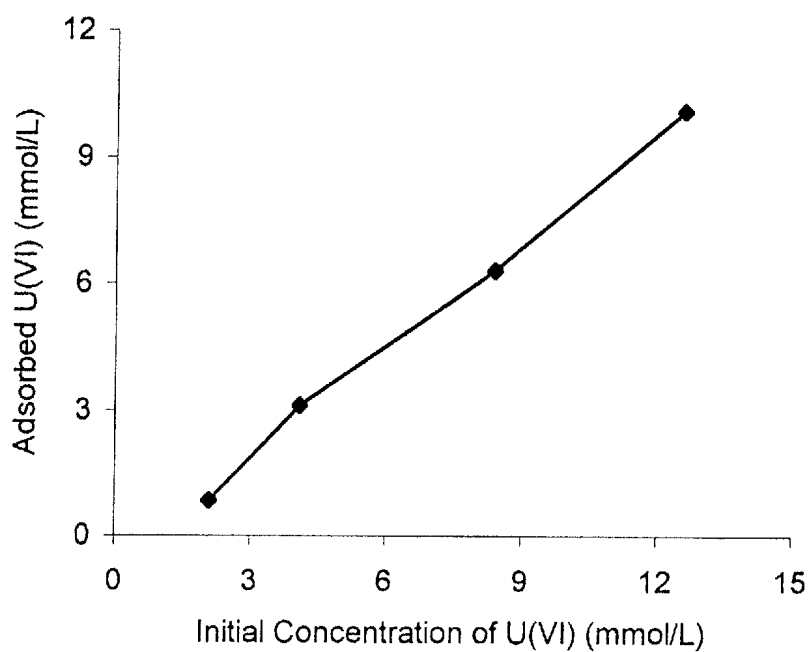
Figure 2.   Effect of the U(VI) initial concentration on the sorption ability (%) at pH 5 and contact time : 1 h.

The sorption selectivity from binary and tertiary metal ion mixtures at pH 5.0 was studied. Hg(II) was not studied due to that precipitates at higher pH than 2.0. On the other hand, Cu(II) ions often are together in lixiviation medium but the retention was always lower 20%. The adsorptivity was determined by observing the concentration of the ions in the aqueous phase. The selectivity, S was determined according to the following relationship:

$$S = \log K_d U(VI) - [\log K_d Pb(II) + \log K_d Cu(II)] \qquad 1)$$

where the distribution coefficients (K_d) of metal ions between the sorbent phase and the sorption medium at equilibrium, was calculated by using the following expression:

$$K_d = \frac{\text{Adsorbed metal ion (mg)/Amount of polymer (g)}}{\text{Amount of metal ion in solution (mg)/Volume of solution (mL)}} \qquad 2)$$

The selectivity sorption for U(VI) was particularly high respect to Cu(II), S = 0.5, and for Pb(II) S = 1.9. On the other hand, the ternary metal ion mixture shows a higher selectivity for U(VI) respect to the Pb(II) and Cu(II) separately ($K_d Pb(II)$ = 4.7 mL/g and $K_d Cu(II)$ = 4.6 mL/g) but it is 0.03 considering both metal ions.

To recover the resin, nitric acid and sodium carbonate at different concentrations were added to the U(VI)-loaded resin (see Figure 3). In both media, the elution after only one contact is high close to 70% for 2.0M solutions of nitric acid and sodium carbonate. It shows that the MTAC-AA resin can be used again for U(VI).
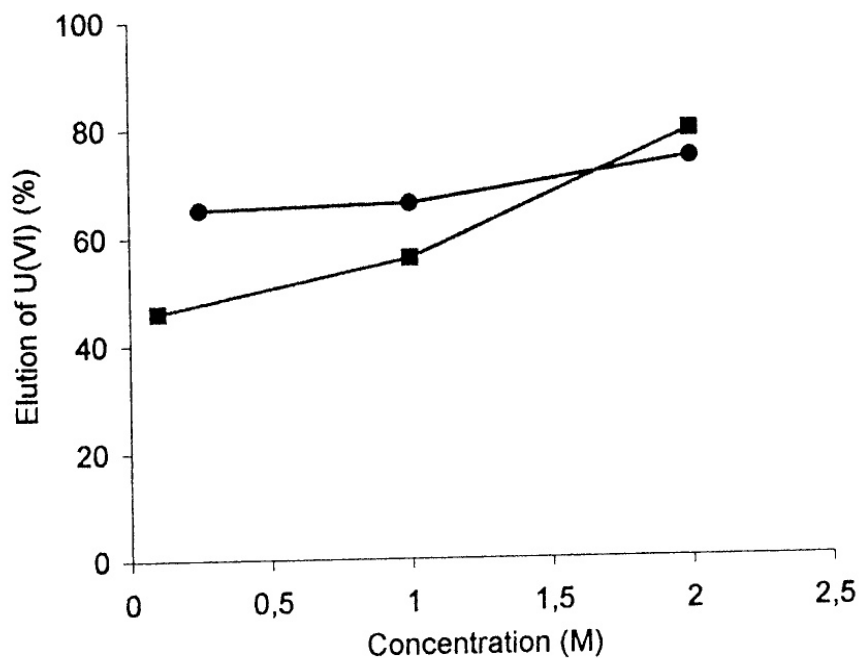
Figure 3. Recovery of the resin by elution (%) of U(VI) ion with (■) sufuric acid and (●) sodium carbonate. Sample 0.1 g.

To determine the effect of U(VI) adsorbed on the thermal stability of the MTAC-AA resin, thermogravimetric analyses were carried out. The resin was loaded with U(VI) at pH 5 according to their maximum capacity. For temperatures to 200°C for both resins the weight-loss was less than 10%. Therefore, the weight-loss increase strongly up to 96.0% (for unloaded) and 76.4% (for uranium loaded-resin) at 500°C (see Figure 4). The presence of the uranyl ions increased the thermal stability particularly at highest temperatures.
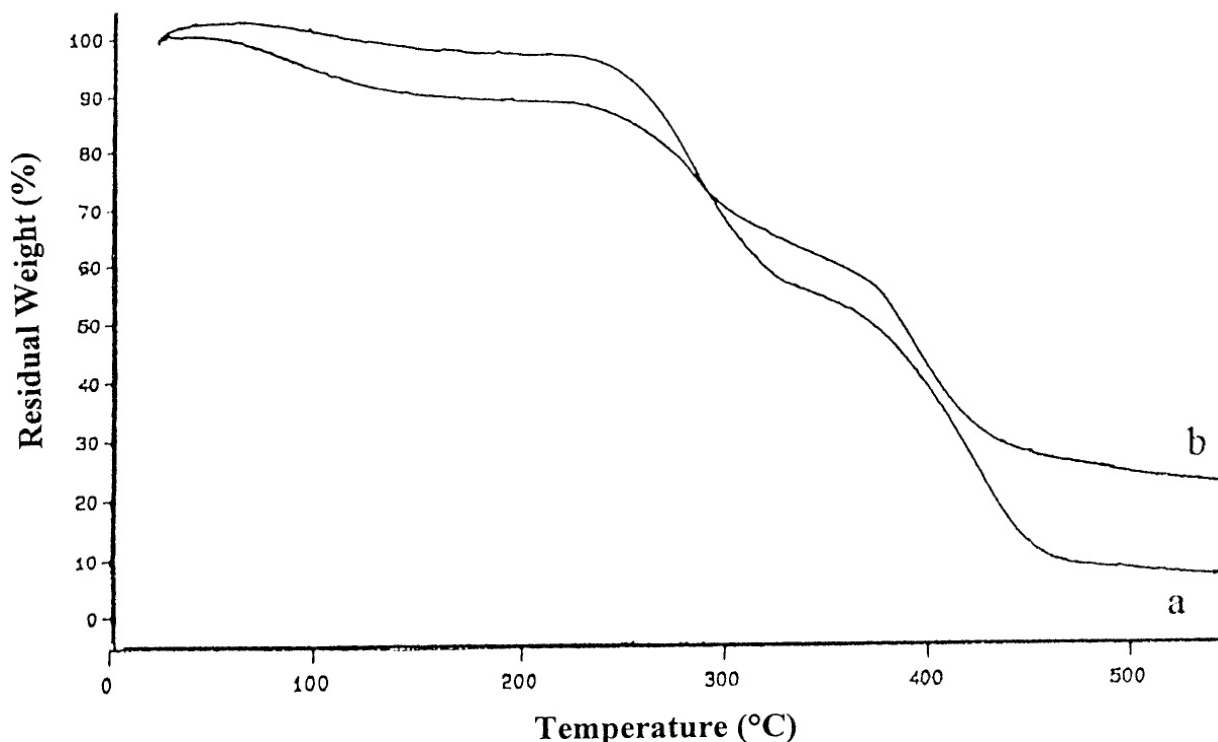
Figure 4. Thermal behavior under N_2 of the (**a**) unloaded and (**b**) uranium loaded resin. Heating rate 10°C/min.

CONCLUSIONS

Crosslinked poly([2-(metahacryloyloxy)ethyl]trimethyl ammonium chloride-*co*-acrylic acid) resin showed a higher affinity (74%, 0.94 meq) for U(VI) respect to Cu(II), Hg(II), Cd(II), Zn(II), Pb(II), and Cr(III), particular at pH 5. That means that basically the carboxylate groups are involved in the polymer-metal interaction. The polymer-U(VI) equilibrium was achieved during 60 min. Besides, it should be possible to separate U(VI) from a binary mixtures U(VI)-Cu(II), U(VI)-Pb(II) and ternary mixture U(VI)-Cu(II)-Pb(II). Finally, the presence of the uranyl ions in the MTCA-AA resin increased the thermal stabilty particularly at 500°C.

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