

Vinyl resins with retention properties for heavy metal ions

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SUMMARY

Resins with carboxylic pendant groups were synthesized. The resins were characterized by elemental analyses and FT-IR spectroscopy, and the ability to bind copper(II) and uranium(VI) by batch method at different pH was studied. Uranium(VI) is adsorbed at pH 3 and pH 4 above 88%. The maximum capacity of load for uranium(VI) is higher than IRA-400, a commercial resin. Elution assays for Cu(II) and U(VI) from the loaded resins with sulfuric acid and sodium carbonate were also carried out.

INTRODUCTION

Polymer-metal complexes are of great current interest (1,2). The formation of chelates, adducts and polymers has widely been used for concentration, separation and extraction of metal ions (3-9). Thus, chelating resins have other applications as in environmental protection, water treatment, chemical analysis (10-13). A majority of the chelating sorbents reported so far are based on polymeric organic matrices, mostly hydrophobic polymers. The use of polymer-supported binding groups to selectively remove one component from a multicomponent solution is important in the recovery and concentration of metal ions from aqueous solution and offer an ideal alternative to liquid extractants because of their long-term stability and ease of continuous operation (1,3).

This paper reports the preparation and application of a chelating resin based on a hydrophilic poly(acrylamide) derivative by radical polymerization of 2-acrylamido glycolic acid and varying the extent of crosslinking. The sorption ability of the resins towards copper(II) and uranium(VI), sorption rate and desorption behaviour were investigated.

EXPERIMENTAL PART

Materials: 2-Acrylamido glycolic acid, (AGA), N,N'-methylene-bis-acrylamide (MBA) and ammonium peroxydisulfate (APS) were used without further purification.

Preparation of CAGA crosslinked sorbents: The crosslinking reagent, MBA of concentrations (2, 6, 10, 15 mol%) was added to the aqueous solution containing the monomer, AGA (0.02 mol) and the radical initiator, APS (0.2 mol%). The reaction was kept under N₂ at 70°C for 30 min. The resin was filtered

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off, washed with water repeatedly, and dried in vacuo. The dried resin was grinded and the 250-500 μm size portion was used in all the experiments.

Determination of the chelating capacities at different pHs: The chelating capacities of the resins were determined using the batch method. A 100 mg sample of resin was added to 10 ml of a 1g/l solution of the metal ion. pH was adjusted with NaOH or H_2SO_4 until the desired constant value. Then the metal ion content of the supernatant was monitored by atomic absorption spectrometry for Cu(II) and by colorimetry for uranium(VI) (14) and, from the difference, the amount of metal ion extracted was calculated.

The maximum capacity of load was carried out contacting 1.0 g of resin with 50 ml aqueous solution containing 1.0 g/l in uranium. The mixture was stirred for 2 h at 25°C. The aqueous solution was separated by decanting and filtration, and washed with water. This process was repeated three times. The metal ions were determined in the supernatants.

Metal ion elution: The loaded resin with the metal ion at optimum pH was contacted with sulfuric acid and sodium carbonate at different concentrations. The mixture was stirred for 1 h. The resin was separated by filtration and the metal ions were analyzed in the supernatants as above.

Measurements: FT-IR spectra were recorded by a Bruker IFS-25 spectrophotometer.

Copper(II) was analyzed by a Perkin Elmer 306 Atomic Absorption spectrophotometer and uranium(VI) on a CADAS 100 spectrophotometer. pH measurements were carried out with a digital Extech microcomputer pH-meter.

RESULTS AND DISCUSSION

The resins were synthesized by radical polymerization of AGA at 70°C for 30 min in the presence of a crosslinking agent such as MBA (2-15 mol%). All the resins were insoluble in water and in common organic solvents.

The particle size(s) of the resins immediately after the polymerization is shown in Table 1. All the resins have a particle size between 500 and 1000 μm . The resins were crushed to yield a material with a particle size between 250 and 500 μm . This fraction was used to study the metal ion binding capacity of the resins.

The FT-IR spectra for 4 resins were basically the same, showing a band at 1751 cm^{-1} due to the carbonyl in the acid groups and a band at 1670 cm^{-1} due to the carbonyl in the amide groups (see Figure 1).

Table 1. Yield and distribution of the particle size.

Resin	Particle size (μm)						Total Yield(g)
	500 < s < 1000		250 < s < 500		125 < s < 250		
	(g)	(%)	(g)	(%)	(g)	(%)	
1	5.825	71.5	1.688	20.6	0.645	7.9	8.198
2	8.285	74.1	2.089	18.7	0.801	7.2	11.175
3	6.044	65.5	2.424	26.3	0.762	8.3	9.230
4	6.422	62.9	2.572	25.2	1.208	11.8	10.202

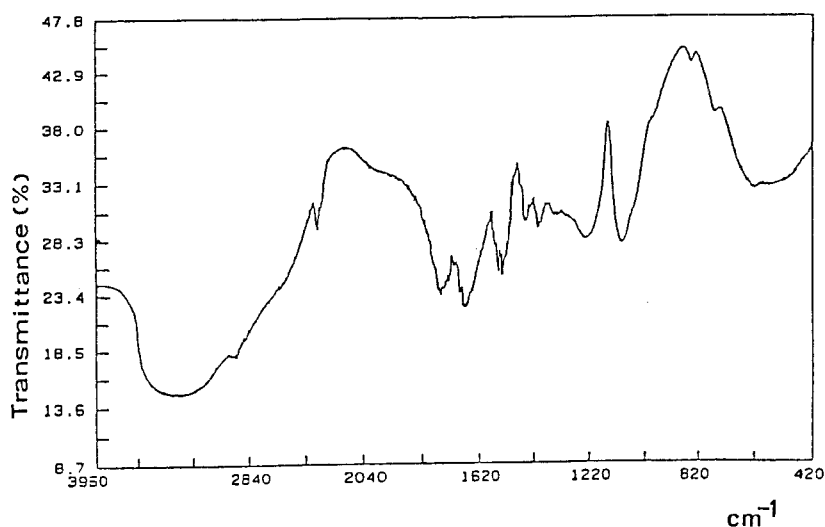


Figure 1. IR spectrum of the resin 2.

Elemental analyses and the C/N mol ratio are summarized in Table 2. These results show that the higher the C/N ratio mol ratio, the lower the MBA content, as expected.

Table 2. Characterization of the CAGA resins.

Resin	MBA (mol%)	Elemental analysis			(C/N) ratio
		C(%)	H(%)	N(%)	
1	2	38.34	6.56	10.81	4.138
2	6	37.91	6.31	10.98	4.028
3	10	36.31	6.35	10.66	3.974
4	15	32.60	5.55	10.23	3.718

Binding ability of the CAGA resins for Cu(II) and U(VI).

The binding capacity of the CAGA resins at different pH as well as the maximum load capacity (MLC) for Cu(II) and U(VI) by the batch method were carried out. The aqueous solutions were not buffered because it is known that buffers complex the metals somewhat producing a shift in equilibrium other than that produced by the acid. The pH was determined initially, knowing that it would change upon addition of the resin.

The results of the effect of pH on the amount of metal ion distributed between two phases are summarized in Tables 3 and 4 for copper(II) and uranium(VI) respectively. Adsorbability of a metal ion on a resin is expressed in term of the distribution coefficient, defined as (15):

$$K_d = \frac{\text{amount of metal ion in the resin}}{\text{amount of metal ion in solution}} \times \frac{\text{volume solution (ml)}}{\text{weight of resin (g)}}$$

Table 3. Distribution coefficients (ml/g) for the CAGA resins at different pH for copper(II).

Resin	pH				
	0	1	2	3	4
1	4.5	21.8	91.2	142	146
2	3.7	14.5	95.3	158	162
3	0.1	22.2	22.5	129	135
4	0.1	0.7	83.5	116	118

Table 4. Distribution coefficients (ml/g) for the CAGA resins at different pH for uranium(VI).

Resin	pH				
	0	1	2	3	4
1	10.4	22.2	105.0	826.2	1463.1
2	10.0	22.0	95.7	852.1	1463.1
3	9.5	18.6	102.0	834.3	1513.2
4	7.2	20.2	91.6	740.2	1233.1

Examination of the results showed that the adsorption of both copper(II) and uranium(VI) on resins derived from AGA increases as pH increases, with a slight dependence on crosslinking within experimental error.

Adsorption, from a 1.0 g/l aqueous solution, for copper(II) and uranium(VI) reached a maximum value by about 50% and 95% respectively at pH 4. Moreover, a negligible adsorption for copper(II) was observed in contrast to the uranium(VI) uptake at pH < 1. Thus, the results of this study are helpful in selecting the optimum pH for a selective uptake of a metal ion from a mixture of the metal ions considered.

The results of the maximum capacity of copper(II) and uranium(VI) determined at pH 4 are summarized in Table 5.

Table 5. Maximum capacity of adsorption for copper(II) and uranium(VI).

Resin	Cu(II) ^{a)}	U(VI) ^{a)}
1	1.6 (50.8)	7.1 (282)
2	1.8 (57.2)	7.2 (285)
3	1.5 (47.7)	7.2 (286)
4	1.3 (41.3)	7.2 (285)
IRA-400	--	6.4 (254)

a) In meq/g-dry resin; in parenthesis expressed in mg/g-dry resin.

All the resins adsorb copper(II) lower than 1.8 meq/g-dry resin but they retain significant amounts of uranium(VI). Four resins have a greater adsorption capacity for uranium(VI) than IRA-400, a commercial resin which contains quaternary ammonium groups.

The time dependence of adsorption of copper(II) and uranium(VI) from aqueous solutions at pH 4 are shown in Tables 6 and 7 respectively. Examination of these results indicates that copper(II) requires a shaking time longer than 1 h for the establishment of the equilibrium. On the other hand, the adsorption of uranium(VI) requires only about 15 min, whereas IRA-400 reaches the equilibrium slowly.

Table 6. Attainment of equilibrium for copper(II) expressed in percentage.

Resin	Time (min)				
	15	30	60	120	180
1	40.2	41.3	47.7	54.5	56.9
2	49.2	51.0	54.8	56.7	60.3
3	67.0	68.3	69.3	69.5	69.9
4	35.2	37.5	40.3	45.5	54.4

Table 7. Attainment of equilibrium for uranium(VI) expressed in percentage.

Resin	Time (h)				
	15	30	60	120	180
1	95.4	95.3	95.3	95.2	95.5
2	94.9	94.7	94.7	94.7	95.2
3	94.4	94.3	94.3	94.5	94.2
4	97.4	94.7	92.5	94.3	94.5
IRA-400	37.8	44.1	50.1	54.9	57.1

The copper(II) and uranium(VI) adsorbed on the resins were eluted by shaking 0.1 g of the resin with Na_2CO_3 or H_2SO_4 at different concentrations, at room temperature (about 20°C) for 1 h. The results are summarized in Tables 8 and 9.

Table 8. Uranium(VI) elution (in %) with 0.25 M sulfuric acid and sodium carbonate.

Resin	H_2SO_4		Na_2CO_3	
	0.25 M	1.0 M	0.25 M	1.0 M
1	38.3	42.9	19.5	36.8
2	17.4	20.9	13.7	32.9
3	31.4	39.0	22.9	34.9
4	23.0	33.1	21.7	28.7

Table 9. Copper(II) elution (in %) with 0.25 M and 1.0 M sulfuric acid and sodium carbonate.

Resin	H_2SO_4		Na_2CO_3	
	0.25 M	1.0 M	0.25 M	1.0 M
1	52.5	79.8	0.0	0.2
2	65.7	87.8	0.0	0.1
3	42.5	80.3	0.1	0.2
4	55.6	71.7	0.1	0.3

In basic medium, little uranium is eluted because the resins are not able to form stable complex carbonate. From the loaded resin 1 it is possible to elute 42.9% of uranium(VI) by 1 M H_2SO_4 medium. On the other hand, copper(II) is not

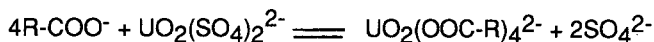
eluted by Na_2CO_3 medium but it is eluted above 70% after one contact with 1 M H_2SO_4 .

Copper(II)-Uranium(VI) binary mixture

In order to know the ability of resin **2** to bind the metal ion from Cu^{2+} - UO_2^{2+} mixtures, 0.1 g-dry resin **2** was contacted at pH 4.0 with 10 ml of an aqueous solution containing 1.0 g/l in each metal ion. Sorption selectivity, defined as the percent of sorbed amount of U(VI) in respect to the total sorbed amount of metal, both ions Cu(II) (58.4%) + U(VI) (87.3%) is 59.9%. The K_d Cu(II) and U(VI) are 140 and 687 respectively.

Cu(II) and U(VI) from resin **2** were eluted in 89.4% and 86.4% in 4M H_2SO_4 respectively. Accordingly, Cu(II) sorption does not affect the sorption and elution of U(VI).

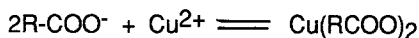
In respect to the metal ion sorption mechanism, it is established that uranyl ions can be complexed by either sulfate or bisulfate ions to produce anionic sulfate complexes which are affected by the pH and sulfate concentrations in aqueous solution (16). Consequently, these sulfate complexes can react with the carboxylic moieties of the resins according to the following overall reaction:



Thus, a more stable complex than $\text{UO}_2(\text{CO}_3)_6^{4-}$ is formed, because of the lower extent of uranium recovery in sodium carbonate media.

On the other hand, it is known that a carboxylic group is able to form complexes. Hence, they do not react as standard ion exchangers within a rather wide pH interval, and copper uptake may also take place only under formation of the coordination bonds (17).

The overall reaction is:



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