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Dual sorption of metal-ions on a crosslinked resin of 2-acrylamidoglycolic acid and 4-vinylpyridine

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SUMMARY

A resin containing 4-vinylpyridine and 2-acrylamidoglycolic acid was synthesized by radical polymerization with subsequent crosslinking by N,N'-methylene-bis-acrylamide. The resin was characterized by elemental analyses and FT-IR spectroscopy. The ability of this resin as well as both crosslinked homopolymers to bind Cu(II), Fe(II), Fe(III) and U(VI) was studied at different pHs depending on the metal ion. From pH = 2 U(VI) was sorbed above 96% from an aqueous solution of 1.0 g/L. A dual sorption mechanism to U(VI) depending on the pH is suggested. The elution of the metal ions from the loaded resins was assayed with H_2SO_4 and Na_2CO_3.

INTRODUCTION

Polymers as metal ion complexing agents have been extensively studied (1-19) and have also been important use in solvent extraction chemistry. Chelating adsorbents are usually employed in analytical chemistry to preconcentrate metal ions and to separate the analytes from interfering concomitants prior to their determination by an instrumental method. The chelating ligand can be linked to an insoluble polymer matrix by covalent binding or by adsorption (20). Frequently, principles that are applied in liquid-liquid extraction processes are extrapolated to solid-liquid extraction processes by the synthesis of resins with different ligands.

Because of the existence of a wide range of synthesis methods it is not surprising that the exchanger physical form may vary from rock-hard material to soft gel. Desirable properties of chelating exchangers are (21): (a) high capacity for the metal ion(s) of interest, (b) high selectivity, (c) fast kinetics, (d) high mechanical strength and thoughness of the exchanger particles. Unfortunately the last two properties are competitive.

In the present investigation, 2-acrylamidoglycolic acid was copolymerized with 4-vinylpyridine to obtain a chelating resin. The binding ability for Cu(II), Fe(II), Fe(III), and U(VI) ions by batch equilibrium procedure was assayed. The chelating properties were compared with both homopolymers, and the recovery of the resin was assayed in acidic and basic media.

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EXPERIMENTAL PART

Materials

Analytical grade reagents 4-vinylpyridine (4-VPy), 2-acrylamidoglycolic acid (2-AmGA), copper sulfate pentahydrate $CuSO_4 \cdot 5H_2O$, uranyl acetate $UO_2Ac_2 \cdot 2H_2O$, iron(II) sulfate $FeSO_4 \cdot 7H_2O$ and iron(III) chloride $FeCl_3 \cdot 6H_2O$ were used. All solutions were prepared with deionized water.

Preparation of sorbents

Homopolymers: The reference homopolymers of 4-VPy and 2-AmGA, were obtained by radical polymerization. 4-VPy (0.2 mol) was polymerized in bulk with AIBN (1 mmol) and a mixture of isomeric divinylbenzenes (DVB) (12 mmol) at 70°C for 1 h. 2-AmGA (0.2 mol) was polymerized with ammonium persulfate (APS) (1 mmol) and N,N'-methylene-bis-acrylamide (MBA)[a] (12 mmol) as crosslinking agent.

Copolymer: 4-VPy (0.1 mol) and 2-AmGA (0.1 mol) were copolymerized in presence of APS (1 mmol) and MBA (12 mmol) at 70°C for 1 h. All the resins were washed repeteadly with water, and dried in vacuum until constant weight. The dried resins were ground and the of 180 - 250 μm particle size fraction was used in all the experiments.

Sorption of metal ions on the resins

A batch type equilibrium procedure was used to determine the metal ion uptake from aqueous solution by the resin. The pH of the aqueous solution varied from 0 up to 5 depending on the metal ion. The two phases were shaken in a mechanical shaker at room temperature for 1 h. After shaking, the two phases were separated, and the supernatant solution was analyzed for Cu(II), Fe(II), Fe(III) by using atomic absorption spectrophotometry and for U(VI) colorimetrically (22). The amount of metal ion in the supernatant substracted from the initial amount added gave the amount of metal ion adsorbed on the resin.

Desorption of metal ions

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

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[a] Systematic name: N-(acrylamidomethyl)acrylamide

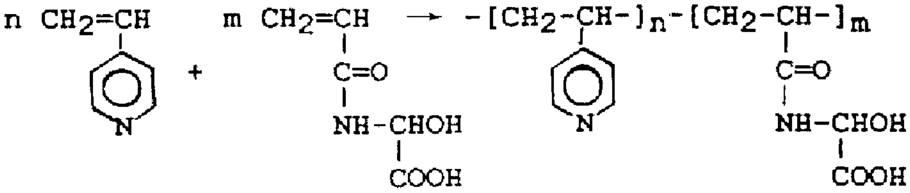
Measurements

Cu(II), Fe(II), Fe(III) were analyzed by a Perkin Elmer 1100 atomic absorption spectrophotometer, and U(VI) was analyzed by a CADAS 100 spectrophotometer. pH measurements were carried out with a digital Extech Microcomputer pH-meter. FT-IR spectra were recorded by a Magna Nicolet 550 spectrophotometer.

RESULTS AND DISCUSSION

Synthesis and characterization of the resins

The preparation of poly(4-vinylpyridine-*co*-2-acrylamidoglycolic acid) was carried out as shown in Scheme 1. The monomer ratio in the feed was 1:1 (mol/mol).



4-VPy 2-AmGA 3

Scheme 1

Also, reference homopolymers of 4-VPy and 2-AmGA were synthesized. The resins were crosslinked, i.e., poly(2-acrylamido glycolic acid) **1** and poly(4-vinylpyridine-*co*-2-acrylamido glycolic acid) **3** with N,N'-methylene-bis-acrylamide (MBA), and poly(4-vinylpyridine) **2** with divinylbenzene, The resins were insoluble in water and organic solvents. The particle size of the resins after the polymerization ranged from 500 up to 1000 mm. Consequently, the resins were crushed to yield a material with particle sizes from 180 to 250 mm. This fraction was used to study the analytical parameters.

The polymerization yield, elemental analysis, and N/C molar ratios of the resins are summarized in Table 1.

Table 1. Yield, elemental analysis, and N/C molar ratio of the resins.

Resin	Yield	Empirical formula	%Calculated[a] C	N	N/C[b]	% Found C	N	N/C[b]
1	95	$C_5H_7O_4N(MBA)_{0.06}$	42.2	10.2	0.207	37.9	11.0	0.248
2	91	$C_7H_7N(DVB)_{0.06}$	80.2	12.4	0.132	75.7	13.3	0.150
3	92	$(C_5H_7O_4N)_n(C_7H_7N)_m(MBA)_{0.12}$	57.4	11.7	0.174	54.9	12.1	0.175

a) calculated percentage of C, N is based on the value of n = m =1
b) expressed in molar ratios

Sorption capacities for metal ions (batch method)

pH has two kinds of influence on metal sorption: an effect on the solubility and speciation of metal ion in aqueous solution, and on overall charge of the sorbents. It is well known that uranyl ion is easily hydrolyzed which depends on the pH and uranium concentration (23).

The affinities of these resins for Cu(II), Fe(II), Fe(III), and U(VI) were investigated by a batch operation as outlined above. Unbuffered systems were utilized because it is known that buffers complex the metal ions causing a shift in equilibrium other than that caused by the acid (24). The meq. of the metal ions taken up by the resins, as a function of the initial pH are reported in Table 2 for each resin under comparable initial conditions.

Examination of the uptake data by the resins (Table 2) shows that resin **2** does not retain either Fe(II) or Fe(III) significantly (<0.36 meq/g-resin), but these metal ions were sorbed by **1** and **3**. This result is in agreement with the knowledge that Fe(II) and Fe(III) resp., have very low affinity for tertiary nitrogen atoms as in the resin **2**, and also that the ability to form complexes of Fe(III) is greater than that of Fe(II), as in resins **1** and **3**, where carboxylic groups are involved.

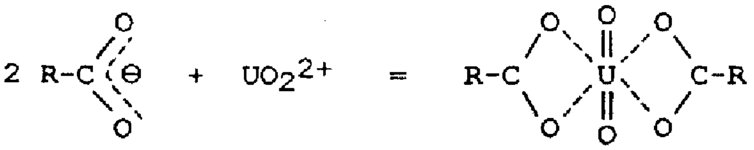
Table 2. Metal ions uptake (meq/g) by resins as a function of pH. Resin (0.10 g) in 10 mL aqueous metal ion solution (1 g/L), 25° for 1 h.[a]

			pH values			
Resin	0	1	2	3	4	5
			Fe(II)			
1	0.03	0.12	0.57	---	---	---
2	0.12	0.12	0.21	---	---	---
3	0.05	0.14	0.54	---	---	---
			Fe(III)			
1	0.15	1.46	2.28	---	---	---
2	0.09	0.18	0.36	---	---	---
3	0.10	0.52	2.28	---	---	---
			Cu(II)			
1	0.14	0.56	1.50	1.85	1.87	1.89
2	0.12	0.09	0.74	0.15	0.43	0.52
3	0.06	0.17	1.21	1.65	1.56	1.68
			U(VI)			
1	0.24	0.46	1.29	2.25	2.36	2.46
2	0.95	2.27	1.91	1.75	1.26	0.48
3	0.11	1.87	2.49	2.43	2.51	2.45

[a] Due to the precipitation of the corresponding Fe(II) and Fe(III) hydroxides, sorption up to pH 2 was tested.

The sorption of Cu(II) on resins **1** and **3** increases with increasing pH. This result suggests that the increase in pH promotes complexation with Cu(II) ions, where carboxylate and/or pyridinic groups may be involved (25,26). The sorption behaviour on resin **2** is different, it passes through a maximum (pH ~ 2), then levels off. This can be explained by considering that complexation with Cu(II) changes, for example, the acid-base properties of the resin due to the increase in the coordination number of the copper ions with increasing pH (25).

The uptake of U(VI) suggest that the sorption of this metal ion takes place by a different mechanism. It is known that the uranyl ions are sorbed by anion exchange resins as a sulfato complex (25). In this context, the pyridinic groups in resin **2** are protonated at low pH which is necessary to sorb the disulfatedioxouranate(II) complex. In contrast, in resin 1 a complexation mechanism is possible (27), where the higher the pH the higher the concentration of carboxylate groups, which would be responsible for the sorption of the uranyl ions according to:



In this context, resin **3** contains at least two sorbing sites: pyridine and carboxylic groups, which have different energies of adsorption. It could be proposed that the sorption or the chelation of the uranyl ion first occurs on the higher energetic groups (e.g. pyridine groups) and after the saturation of the pyridine groups on the carboxylic groups. The sorption could also occur with simultaneous sorption or chelation of both sorbing groups from neighbouring polymers chains (28,29), as observed in Fig. 1.

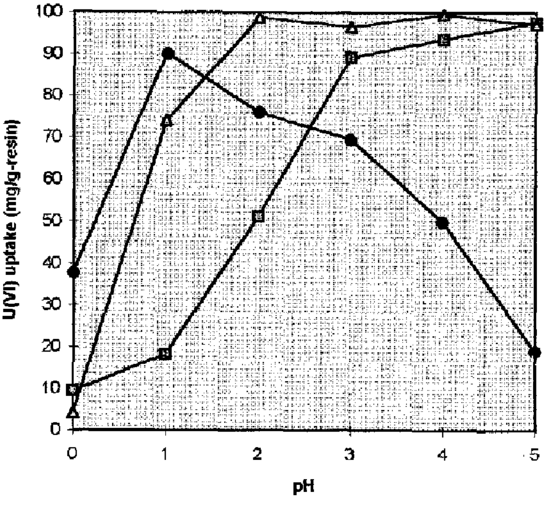


Figure 1. Uranium(VI) sorption behaviour of resins **1**(●), **2**(□) and **3**(△)

The maximum retention capacity for uranyl ions was determined as described in the experimental part. The results are summarized in Table 3.

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

Resin	pH	meq/g-resin	mg/g-resin
1	3	3.6	142.8
2	1	3.8	146.8
3	1	2.9	115.0

FT-IR spectroscopy

The FT-IR spectrum of resin **3** (Figure 2a) shows a broad band from 3700 to 2800 cm^{-1}, assigned to the overlapping peaks of stretching vibrations of aliphatic C-H, aromatic C-H, amide N-H, and carboxylic O-H bonds. Resin **3** also displays coupled strong bands at ~ 1670 cm^{-1} which may be assigned to C=O stretching of carboxylic and amide groups. The medium intense band at ~ 1540 cm^{-1} may be assigned to asymmetric carboxylate stretching coupled with the amide N-H deformation, and the weak band at ~ 1330 cm^{-1} to the symmetric carboxylate stretching. The bands at 1200 cm^{-1} and ~ 1110 cm^{-1} may be attributed to O-H in plane deformation and C-O stretching, respectively.

On coordination (Figure 2b) with UO_2^{2+}, resin **3** displays a new band at 910 cm^{-1} with a subsequent attenuation of the assigned carboxylate bands (1540 cm^{-1}, 1330 cm^{-1}) indicating involvement of carboxylate groups in coordinating with UO_2^{2+}.

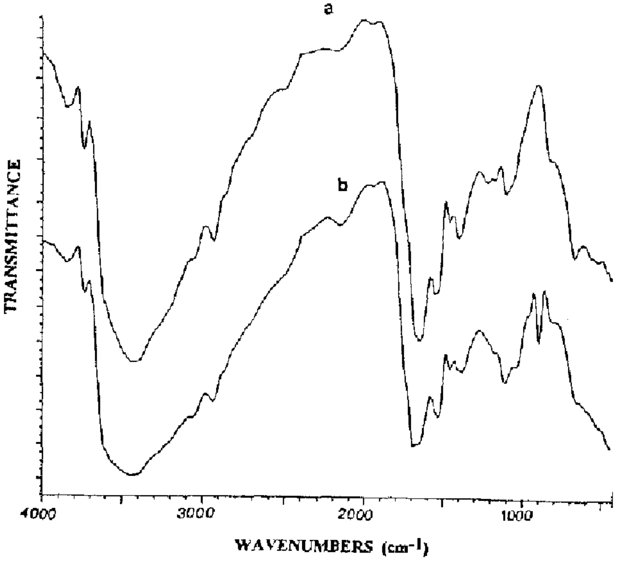


Figure 2. FT-IR spectra of resin **3**, unloaded (**a**) and loaded with uranium(VI) (**b**).

Elution assays

In order to recover the resins, sulfuric acid and sodium carbonate solutions at different concentrations were added to U(VI) - loaded resins (see Table 4).

With all the resins, increasing the H_2SO_4 or Na_2CO_3 concentration increased the eluted uranium. With the Na_2CO_3 solution the $[UO_2(CO_3)_3]^{4-}$ complex is probably formed. When an ion-exchange mechanism is involved, a lower elution of uranium is observed presumably due to the higher stability of the adduct formed between the pyridinic groups (resin **2**) and the disulfatedioxouranate(II) complex. On the other hand, uranium is eluted to a higher extent, when complexation is involved (resins **1** and **3**).

Table 4. Acid and basic elution (%) of uranium.

	H_2SO_4		Na_2CO_3	
Resin	1M	4M	0.25M	1M
1	54.7	72.3	30.5	32.4
2	34.1	42.2	34.6	29.4
3	46.7	65.6	31.4	32.2

CONCLUSIONS

The resins containing 4-vinylpyridine and 2-acrylamidoglycolic acid showed a strong ability to bind U(VI) toward Fe(II), Cu(II), and Fe(III) over the pH range studied. This capacity was higher than both crosslinked homopolymers. 4-Vinylpyridine and carboxylic acid moieties participated in U(VI) sorption. At higher pH, the carboxylate groups should be responsible for the sorption of the uranyl ions and at lower pH should be the protonated pyridine groups.

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