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Separation Science and Technology

Publication details, including instructions for authors and subscription information:
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To cite this Article Hirotsu, Takahiro , Takagi, Norio , Katoh, Shunsaku , Sugasaka, Kazuhiko , Takai, Nobuharu , Sen, Manabu and Itagaki, Takaharu(1987) 'Selective Elution of Uranium from Amidoxime Polymer. II', Separation Science and Technology, 22: 11, 2217 — 2227

To link to this Article: DOI: 10.1080/01496398708068609

URL: http://dx.doi.org/10.1080/01496398708068609

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SEPARATION SCIENCE AND TECHNOLOGY, **22**(11), pp. 2217-2227, 1987

Selective Elution of Uranium from Amidoxime Polymer. II

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Abstract

A separative elution of uranium from an amidoxime polymer which had been immersed in seawater was examined on its relation with the flow rate of acidic eluent. The elution with 0.5 *M* HCl at S.V. $< 1\ h^{-1}$ or with 1.0 *M* HCl at S.V. $< 3\ h^{-1}$, which was started from the elution by 16.5 L/L_p of 0.1 *M* HCl at S.V. $< 3\ h^{-1}$, provided an eluate containing more than 80% of uranium adsorbed and separating from other metal ions except Fe(III) and Cu(II). The efficiency of uranium elution was hardly affected by the scale of the system employed. Acid consumption, which occurred predominantly in the elution with 0.1 *M* HCl, was $\sim$1.4 mol/L_p. The results suggest that this elution method is promising in the recovery of uranium from seawater.

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INTRODUCTION

In the recovery of uranium from seawater, the adsorption method has been accepted as the most promising (*1*). The process characteristic of this method is principally an adsorption of uranium on an adsorbent from seawater followed by an elution of uranium from the adsorbent. It has been already demonstrated that a polymer bearing amidoxime groups exhibits a high selective adsorptivity toward uranium in seawater (*1–4*). In a previous paper (*5*) an elution of uranium with acidic eluents from the amidoxime polymer, which had been immersed in seawater for a prescribed period, was examined in relation to the pH dependence of elution of the metal ions. Various metal ions such as Mg(II), Ca(II), Fe(III), Ni(II), Cu(II), and Zn(II) as well as UO_2(VI) were adsorbed onto the polymer. Fortunately, the elution pH values of these metal ions are appreciably different from each other; thus, the following elution was tentatively applied to the column method: By initial elution with 0.1 *M* HCl, Mg(II), Ca(II), Ni(II), and Zn(II) are eluted completely, and by the succeeding elution with 0.5–1.0 *M* HCl, an eluate of enriched uranium is obtained. The eluate of uranium is contaminated with both Cu(II) and Fe(III), but the concentrations of these metal ions are low enough so that separation and concentration of uranium in this eluate could be successfully followed (*6*). Furthermore, this elution treatment of amidoxime polymer with HCl solutions hardly affects its adsorptivity to uranium in seawater, assuring repeated utilizations of this polymer. Therefore, this elution method of uranium from amidoxime polymer is promising in the recovery of uranium from seawater.

In the present study the separative elution of uranium from an amidoxime polymer was examined in detail on its relation with the flow rate of acidic eluents. Based on these results, elution on a large scale was explored from a practical point of view.

EXPERIMENTAL

Materials

An amidoxime polymer crosslinked with both divinylbenzene (5 wt%) and tetraethyleneglycol dimethacrylate (35 wt%) was prepared by the method described in a previous paper (*7*). The polymer was treated with a 1 *M* NaOH solution at room temperature for 24 h for the purpose of conditioning it for adsorption of uranium in seawater (*8*).

The amidoxime polymer was immersed in seawater under the same conditions as in a previous paper (*5*) to afford Polymer Samples A and B for elution experiments. The major metal ions adsorbed on these samples from seawater were Mg(II), Ca(II), Fe(III), Ni(II), Cu(II), Zn(II), and UO_2(VI).

Elution of Metal Ions by the Column Method on a Small Scale

Polymer Sample A (20 mL) was washed well with distilled water and loaded in a column (inner diameter, 1 cm; height, 30 cm). An elution with 0.5–1.0 *M* HCl was performed by starting from an elution with 0.1 *M* HCl of 16.5 L/L_p (where L_p denotes the volume of polymer sample loaded; therefore L/L_p is the bed volume), as described in a previous paper (*5*). Mg(II), Ca(II), Ni(II), and Zn(II) are eluted with 0.1 *M* HCl of 16.5 L/L_p, and Fe(III), Cu(II), and UO_2(VI) are collected by the succeeding elution with 0.5–1.0 *M* HCl. These elution behaviors were examined in relation to their dependence on the flow rate. Distilled water was used for these experiments.

Elution of Metal Ions by the Column Method on a Large Scale

An elution apparatus carrying four columns (inner diameter, 7 cm; height, 150 cm), shown schematically in Fig. 1, was used. The valve operation permits selection of two flow directions of eluent (upward and downward) and two linkages of columns (in series and in parallel). The eluent was passed through the columns at a constant flow rate, and the eluate was divided into several fractions of a given volume (10–20 L) after pH measurement. The polymer sample, which had been immersed for 40 d in seawater (*5*), was directly loaded into the columns connected in parallel and washed with water until the washings showed minimal concentrations of Mg(II) and Ca(II). After washing, the columns were connected in series and the elution experiments were performed under conditions similar to those described above. The water used for these experiments was a city water which was not distilled.

Measurements

The concentrations of uranium in the solutions were determined with an Aloka Model FMT-3B Fluorimeter, and those of the other metal ions were determined with a Perkin-Elmer Model 403 and a Hitachi Model 170-70 Zeeman-Effect Atomic Absorption Spectrophotometer.

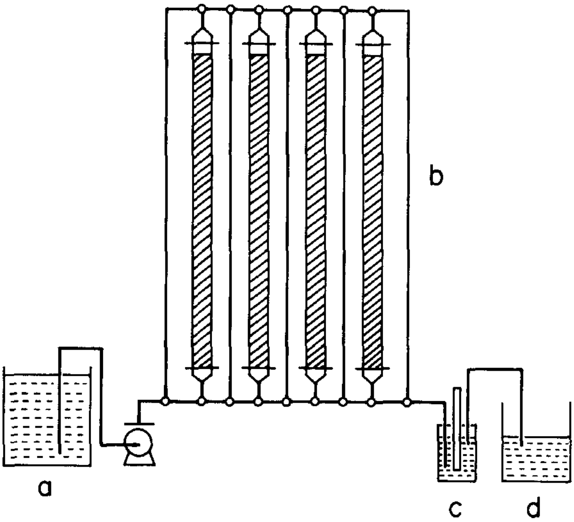

FIG. 1. A schematic diagram of a large-scale elution apparatus. Units: supply of eluent (a), columns (b), pH measurement (c), and fractional collection of eluate (d).

RESULTS AND DISCUSSION

An amidoxime polymer exhibits high selective adsorptivity toward uranium in seawater, but at the same time it adsorbs alkaline-earth and the first-row transition metal ions from seawater (*5*). The quantities of metal ions adsorbed on the present amidoxime Polymer Samples A and B are listed in Table 1. Therefore, separative elution of uranium with hydrochloric acid solutions by a column method was examined preliminarily in the previous paper (*5*), and it was found that uranium can be eluted separately from the metal ions except for Fe(III) and Cu(II). In the present study, elutions of metal ions are examined on their dependence upon the flow rate of eluent.

Dependence of Elution of Metal Ions upon the Flow Rate

As shown in a previous paper (*5*), Mg(II), Ca(II), Ni(II), and Zn(II) are readily eluted with 0.1 *M* HCl in a region of elution volume, E.V., $\leqslant$ 16.5 L/L_p. Then, the extent of elution of metal ions in this region was examined for their dependence on the flow rate. The results are listed in Table 2. The elutions of Mg(II), Ca(II), Ni(II), and Zn(II) go up to more

TABLE 1
Amounts of Metal Ions Adsorbed on Amidoxime Polymer Samples[a] Employed for Elutions

	Amount adsorbed			
	Sample A		Sample B	
Metal ion	μg/g	μg/mL$_p$	μg/g	μg/mL$_p$
Mg(II)	22×10^3	4.1×10^3	22×10^3	4.2×10^3
Ca(II)	22×10^3	4.1×10^3	24×10^3	4.6×10^3
Fe(III)	440	83.1	587	111
Ni(II)	150	28.3	142	26.9
Cu(II)	66.7	12.6	104	19.7
Zn(II)	383	72.2	554	105
UO_2(VI)	806	152	1190	226

[a] These samples had been immersed in seawater for 40 d by the method described in Ref. 5.

than 90%, even at the space velocity, S.V., < 3 h^{-1}. On the other hand, the elutions of Fe(III), Cu(II), and UO_2(VI) are 6, 40, and 10%, respectively, and these values hardly change at S.V. < 6 h^{-1}. Therefore, if 16.5 L/L$_p$ of an 0.1 *M* HCl solution is passed through at S.V. < 3 h^{-1}, 90% of uranium is separated satisfactorily from Mg(II), Ca(II), Ni(II), and Zn(II).

A second elution with 0.5-1.0 *M* HCl was made with 0.1 *M* HCl at S.V. = 3 h^{-1}. The extent of elution of Fe(III), Cu(II), and UO_2(VI) are shown against the S.V. values in Table 3. These metal ions were eluted simultaneously in all cases; therefore, by the present method, uranium could not be separated from these two metal ions.

TABLE 2
Elution of Metal Ions from Amidoxime Polymer[a] with 0.1 *M* HCl

		Elution[b] (%)						
Run	S.V. (h^{-1})	Mg(II)	Ca(II)	Ni(II)	Zn(II)	Fe(III)	Cu(II)	UO_2(VI)
1	0.96	101	99	99	100	6.1	41	11
2	3.12	100	99	98	98	6.2	38	10
3	5.64	105	98	85	95	6.0	43	12

[a] Polymer Sample A (20 mL$_p$) was employed.

[b] The values were obtained from elution with 16.5 L/L$_p$ of 0.1 *M* HCl by a column method on a small scale.

TABLE 3
Elution of Metal Ions from Amidoxime Polymer[a] with 0.5/1.0 *M* HCl Following the First Elution[b] with 0.1 *M* HCl

Run	HCl (*M*)	S.V. (h^{-1})	Elution[c] (%) Fe(III)	Cu(II)	UO_2(VI)	U_m[d] (mg/L)
4	0.5	0.75	86	102	91	80
5	0.5	3.0	69	94	82	50
6	0.5	6.0	67	102	84	44
7	1.0	1.0	99	105	97	120
8	1.0	3.0	80	100	95	96
9	1.0	6.0	75	99	86	80

[a] Polymer Sample A (20 mL_p) was employed.

[b] The first elution was carried out by employing 16.5 L/L_p of 0.1 *M* HCl at S.V. = 3.0 h^{-1} in every case.

[c] These values are referred to the extent of elution at an E.V. value of 10.0 L/L_p.

[d] These values are the maximum concentrations of uranium in the fractions of eluate.

In the case of 0.5 *M* HCl, Cu(II) elutes completely at every value of S.V. whereas the extent of elution of Fe(III) and UO_2(VI) decreases with increasing values of S.V. When a 0.5 *M* HCl solution is passed through at S.V. < 1 h^{-1}, the extent of elution of UO_2(VI) is more than 90% at E.V. value of 10 L/L_p, and more than 80% of Fe(III) is eluted. Similarly, when S.V. < 3 h^{-1} in the case of 1.0 *M* HCl, more than 90% of UO_2(VI) can be eluted, while the extent of elution of Fe(III) goes up to more than 80%. Cu(II) elutes completely at all S.V. values.

It is concluded from these results that, if elution with 0.5 *M* HCl at S.V. < 1 h^{-1} or with 1.0 *M* HCl at S.V. < 3 h^{-1} is performed after a first elution of 16.5 L/L_p with 0.1 *M* HCl at S.V. < 3 h^{-1}, an eluate of enriched uranium separated from the metal ions other than Fe(III) and Cu(II) is obtained. More than 80% of the uranium taken up on the amidoxime polymer can be recovered into this eluate with an E.V. value of 10 L/L_p.

Separative Elution of Uranium by the Column Method on a Large Scale

The elution of uranium from the amidoxime polymer in a large system, as shown in Fig. 1, was examined to obtain information for a practical elution process. The experimental conditions were arranged as shown in Table 4 on the basis of the results obtained above. The following

TABLE 4
Experimental Conditions of Elution by Large-Scale Columns

Run	Sample		S.V.[a] (h^{-1})			Dead volume (L)
	No.	Volume (L_p)	0.1 *M* HCl	0.5 *M* HCl	1.0 *M* HCl	
10	B	9.1	2.0	0.98	—	19.4
11	A	20.6	2.0	3.2	—	15.1
12	A	20.8	2.0	—	1.24	15.0

[a] The first elution was done with 16.5 L/L_p of 0.1 *M* HCl, and the second was carried out with 16.0 L/L_p of 0.5 or 1.0 *M* HCl.

procedures were carried out successively: (a) washing with water, (b) elution with 0.1 *M* HCl, (c) elution with 0.5–1.0 *M* HCl, (d) recovery of eluate by inserting water in the same volume as the dead volume, and (e) washing with water. The water used in these large-scale experiments was an undistilled city water.

An example (Run 10) of the results is shown in Figs. 2–5. Washing of the amidoxime polymer with a large amount of seawater continued until the concentrations of Mg(II) and Ca(II) were minimal. This requirement

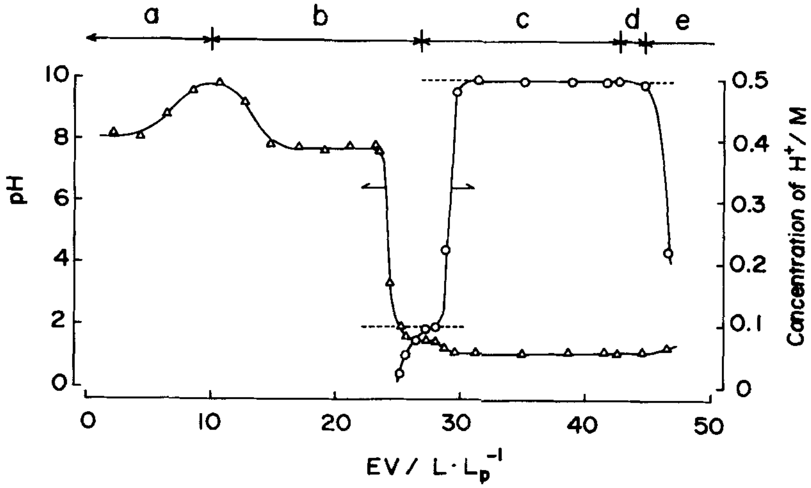

FIG. 2. Changes of pH and acid concentration of eluate (Run 10). The broken lines represent the initial concentrations of HCl solutions. Polymer Sample: B. Procedure: Washing with water (a), elutions with 0.1 *M* (b) and 0.5 *M* HCl (c), recovery of eluate by intrusion of water (d), and washing with water (e).

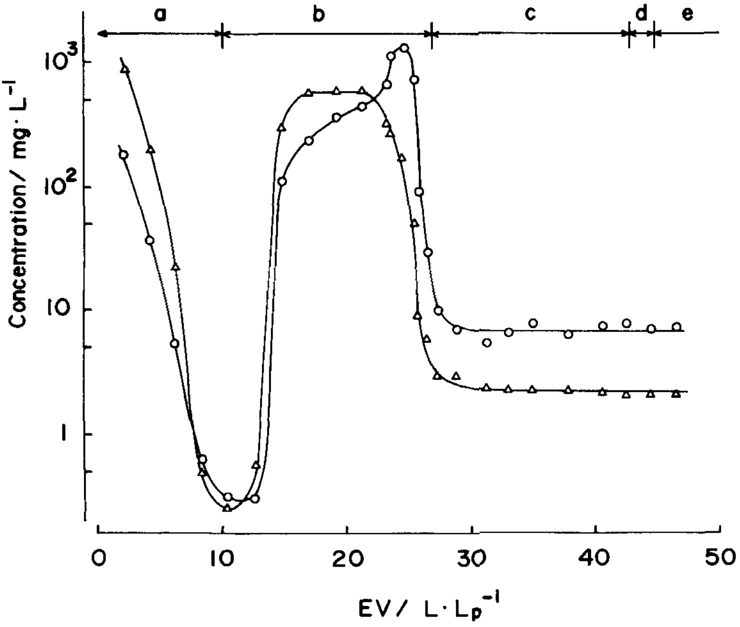

FIG. 3. Changes of the concentrations of Mg(II) (△) and Ca(II) (○) in the eluate (Run 10). Polymer sample and procedures as in Fig. 2.

was satisfied by washing with water of 10 L/L$_p$ in all cases, as shown in Fig. 3. Mg(II) and Ca(II) adsorbed on the polymer sample were eluted almost completely by treatment with 0.1 *M* HCl of 16.5 L/L$_p$ at S.V. = 2 h^{-1}, provided that the dead volume is considered in Fig. 3. The constant concentrations of Mg(II) and Ca(II) in the elution with 0.5 *M* HCl are higher than their minimal values in the washing. The former values of Mg(II) and Ca(II) were almost equal to their concentrations in the city water employed in the present experiments. This suggests that Mg(II) and Ca(II) are taken up on the polymer sample in the washing process. In fact, the elution amounts of these metal ions in the elution with 0.1 *M* HCl are larger than those values expected from the previous results obtained by using distilled water (*5*).

Ni(II) and Zn(II) are also eluted almost completely with 0.1 *M* HCl, as shown in Fig. 4, if the dead volume is taken into account. On the other hand, as is obvious from Figs. 4 and 5, Fe(III), Cu(II), and UO_2(VI) are hardly eluted; however, these metal ions are eluted predominantly and simultaneously in the second elution with 0.5 *M* HCl. Cu(II) is eluted

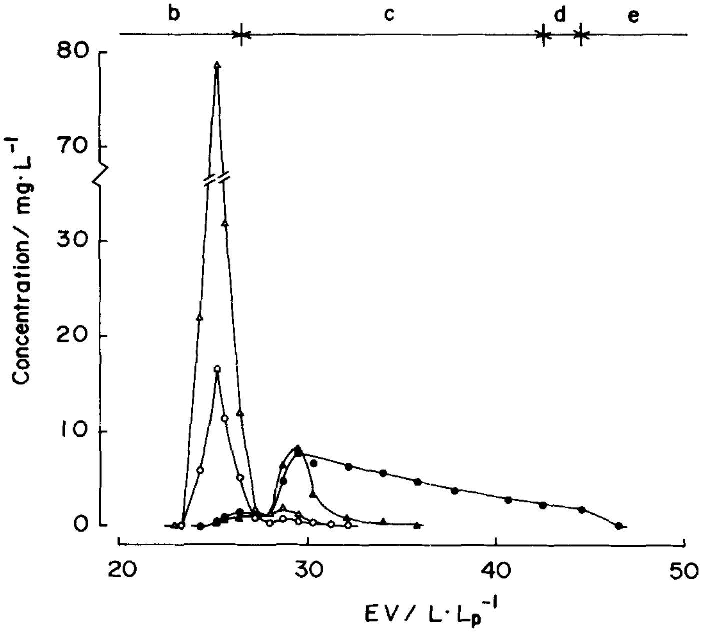

FIG. 4. Elution curves of Ni(II) (O), Zn(II) (△), Fe(III) (●), and Cu(II) (▲) (Run 10). Polymer sample and procedures as in Fig. 2.

readily, but Fe(III) is eluted slowly, with a long tailing. Therefore, the eluate of enriched uranium is contaminated by Cu(II) and Fe(III). Similar results were obtained in Runs 11 and 12.

The extent of elution of uranium is shown in Fig. 5 and Table 5. In all cases these values are close to those obtained by elution with a small-scale column. This shows that the efficiency of uranium elution is hardly affected by the scale of the elution system employed or by using undistilled city water instead of distilled water.

Changes of pH and the concentration of hydrogen ions in the eluate are shown in Fig. 2. The pH value of the eluate changes considerably from the small-scale case (5). It was found from the results of hydrogen ion concentration that acid consumption occurs predominantly in elution with 0.1 *M* HCl. Furthermore, the acidic eluate is satisfactorily recovered by the insertion of water with a volume corresponding to the dead volume. From these results the amount of acid consumption was calculated to be ~1.4 mol/L_p, as listed in Table 5.

In the present study the optimum flow rates of acidic eluents were

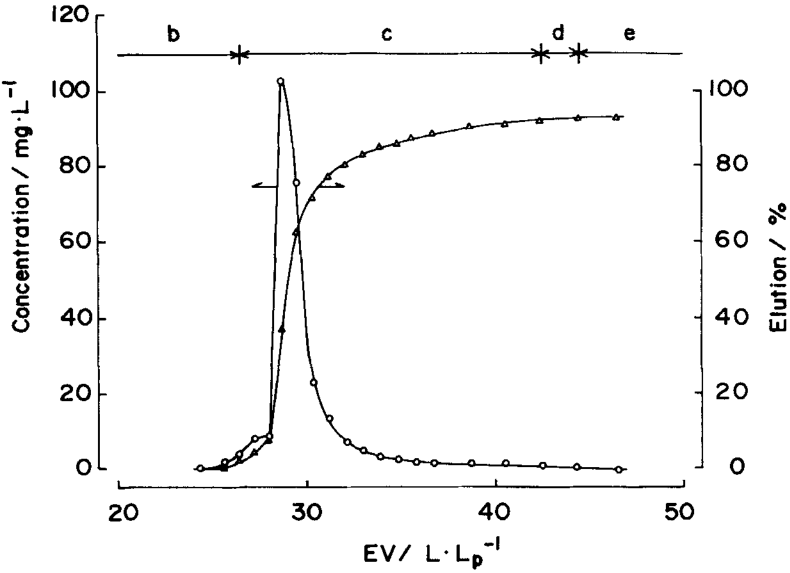

FIG. 5. Elution curve and elution extent of uranium (Run 10). Polymer sample and procedures as in Fig. 2.

determined in order to perform effectively the separative elution of uranium from the amidoxime polymer by a column method. On the basis of the results obtained, our large column system was equivalent to a small column system.

In this elution method, hydrogen ions of 1.4 mol/L_p are consumed. The eluate of enriched uranium is contaminated with Fe(III) and Cu(II);

TABLE 5
Extent of Elution of Uranium and Acid Consumption in a Large-Scale Elution Process

Run	Initial content of uranium (g)	Uranium eluted[a]		Acid consumption (mol/L_p)
		g	%	
10	2.06	1.84	89.4 (91.0)	1.40
11	3.18	2.41	76.0 (81.0)	1.38
12	3.18	2.78	87.4 (95.0)	1.43

[a] These values are the extent of elution at 10 L/L_p of 0.5/1.0 *M* HCl. The values in parentheses are estimated from a similar, small-scale elution.

however, it has been demonstrated that this contamination does not seriously interfere with the effective concentration of uranium from this eluate when a chelating resin with glycine-*N*,*N*-bis(methylene phosphonic acid) groups is used (*6*). Furthermore, as reported in a previous paper (*5*), this elution treatment with HCl solutions hardly affects the adsorptivity of amidoxime polymer to uranium in seawater. It is, therefore, concluded that the present elution method of uranium from the amidoxime polymer is promising in the recovery of uranium from seawater.

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Received by editor October 21, 1986