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Takahiro Hirotsu[a]; Shunsaku Katoh[a]; Kazuhiko Sugasaka[a]; Nobuharu Takai[b]; Manabu Seno[b]; Takaharu Itagaki[c]

[a] Government Industrial Research Institute, Takamatsu, Japan [b] Institute of Industrial Science the University of Tokyo, Minato-Ku, Tokyo, Japan [c] Central Research Laboratory Mitsubishi Chemical Industry, Ltd., Midori-Ku, Yokohama, Japan

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Selective Elution of Uranium from Amidoxime Polymer. I

TAKAHIRO HIROTSU,* SHUNSAKU KATOH, and
KAZUHIKO SUGASAKA

GOVERNMENT INDUSTRIAL RESEARCH INSTITUTE, SHIKOKU
2-3-3 HANANOMIYA-CHO, TAKAMATSU 761, JAPAN

NOBUHARU TAKAI and MANABU SENŌ

INSTITUTE OF INDUSTRIAL SCIENCE
THE UNIVERSITY OF TOKYO
MINATO-KU, TOKYO 106, JAPAN

TAKAHARU ITAGAKI

CENTRAL RESEARCH LABORATORY
MITSUBISHI CHEMICAL INDUSTRY, LTD.
MIDORI-KU, YOKOHAMA 227, JAPAN

Abstract

The separative elution of uranium from an amidoxime polymer was examined by the column method with hydrochloric acid solutions. The amidoxime polymer was immersed in seawater for 40 d for preparation of an uranium-loaded polymer sample for the elution experiments; the metal ions adsorbed were Mg(II), Ca(II), Fe(III), Ni(II), Cu(II), and Zn(II) as well as UO_2(VI). It was found from the pH dependence of elution extent by a batch method that the order of elution pH values is Fe(III) < UO_2(VI) < Cu(II) < Ni(II) < Zn(II) < Ca(II) < Mg(II). In the elution by a column method, Mg(II), Ca(II), Zn(II), and Ni(II) were eluted completely by 0.1 *M* HCl and the eluate of enriched uranium was obtained by a succeeding elution with 0.5 or 1 *M* HCl. This eluate contained Cu(II) and Fe(III), which could be removed in the succeeding step. The elution treatment with hydrochloric acid solutions hardly affected the adsorptivity for uranium in seawater. It was suggested that the elution of uranium with hydrochloric acid solutions from amidoxime polymers is satisfactorily applicable to uranium elution in the recovery of uranium from seawater with amidoxime polymers.

*To whom correspondence should be addressed.

INTRODUCTION

In a series of research papers (*1–3*), it has been confirmed that polymers bearing amidoxime groups exhibit high adsorptivity toward uranium (3 μg/L) in seawater and their characteristic property is predominantly due to the metal ion-complexing ability of the ligand. Moreover, it has been clarified that the adsorption rate of uranium depends significantly on the hydrophilic and porous properties of the polymer matrix (*4–6*). On the other hand, it is also important from the standpoint of the recovery of uranium in seawater with the adsorbent to elute uranium effectively on the adsorbent. The present report concerns uranium elution from the amidoxime polymer.

Information was sought on the following points: (a) the rate of uranium elution, (b) the extent of uranium elution, and (c) the method of separative elution of uranium (*7*). Furthermore, it is necessary to examine the influence of elution treatment on the adsorptive properties of the adsorbent because the adsorbent is usually employed repeatedly. But first, a suitable eluent has to be selected. A sodium carbonate–sodium hydrogen carbonate solution is one of the common eluents for some inorganic adsorbents (*7*). With this eluent, uranium is selectively eluted by the complex formation of tricarbonatouranate(VI) ion, $[UO_2(CO)_3)_3]^{4-}$ (*7*). However, the rate of uranium elution from amidoxime polymer with this eluent was found to be very low.

In a previous paper (*3*) it was reported that the amidoxime polymer exhibits binding abilities with metal ions in the following order: Mg(II) ≈ Ca(II) < Zn(II) < Co(II) < Ni(II) < Cu(II) < UO_2(VI), and that the adsorptivities decrease with decreasing pH values. These results suggest the possibility of separative elution of uranium from amidoxime polymer with an acidic eluent. In the present study the separative elution of uranium is examined by a column method, in particular for an amidoxime polymer sample which has been immersed in seawater for a prescribed period.

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 (*5*). The polymer was treated with 1

M NaOH solution at room temperature for 24 h (*8*) and washed thoroughly with water until the washings were neutral.

The polymer samples for elution experiments were obtained by the following method. Fifty and 10 L of the amidoxime polymer were loaded in fluidization Columns F-A and F-B, respectively, which were designed for adsorption of uranium from seawater (*9*). Seawater at ambient temperature (22–25°C) was passed upward through Columns F-A and F-B at constant flow rates of LV = 17 and 19 cm/min for 39 and 42 d, respectively, to prepare Polymer Samples A and B. Then the polymer samples were washed with pure water.

Elution of Metal Ions by the Batch Method

A solution (50 mL) containing prescribed quantities of 1 *M* HCl and 1 *M* NaOH was added to 0.25 g of Polymer Sample A in a 100-mL vessel, sealed, and maintained at 25°C. After elution equilibrium was reached, the pH of the solution phase and the concentrations of metal ions in the filtrate were determined in order to determine the pH dependence of elution.

Elution of Uranium by the Batch Method

A prescribed quantity of Polymer Sample B was immersed in 100 mL HCl solutions (0.1–2 *M*) in 200 mL vessels and sealed. The vessels were maintained at 25°C and, after elution equilibrium was reached, the pHs of the solution phases were measured. After filtration, the uranium concentration in the filtrate, $C_{U,s}$ (μg/mL), was determined. The residual amount of uranium in the polymer sample, $C_{U,p}$ (μg/g), was determined by the following method. After elution, the polymer sample was washed with pure water and refluxed with 1 *M* HCl solution. After filtration, the uranium concentration in the filtrate was determined in order to obtain the $C_{U,p}$ value. The distribution coefficient of uranium between the polymer and the solution phases, D_U, was calculated by

$$D_U = C_{U,p}/C_{U,s} \qquad (1)$$

The concentration of hydrogen ions in the solution phase, [H], was determined by the titration method.

Selective Elution of Uranium by the Column Method

Polymer Sample A (20 mL) was loaded in a column (inner diameter, 1 cm; height, 30 cm), and 0.1-1 *M* HCl solutions were passed downward at a constant flow rate with the aid of a peristapump (Atto model SJ-1215). The eluate was divided into 10 mL fractions by means of a fraction collector. The pH and metal ion concentrations of each fraction were measured.

Measurements

The pH values of solutions were measured with a Horiba model M-8s pH meter. The concentrations of uranium in 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.

RESULTS AND DISCUSSION

The amounts of metal ions adsorbed on Polymer Samples A and B are listed in Table 1, together with their concentration factors. It is evident from these results that the amidoxime polymer shows high adsorptivities for the first-row transition metal ions as well as for the uranyl(VI) ion.

TABLE 1
Amount of Metal Ions Adsorbed on Amidoxime Polymer Samples for Uranium Elution

Metal ion	Amount adsorbed (μg/g) Sample A	Amount adsorbed (μg/g) Sample B	Concentration in seawater[a] (μg/L)	Concentration factor[b] (L/g) Sample A	Concentration factor[b] (L/g) Sample B
Mg(II)	22×10^3	22×10^3	12.9×10^5	1.7×10^{-2}	1.7×10^{-2}
Ca(II)	22×10^3	24×10^3	4.12×10^5	5.3×10^{-2}	5.8×10^{-2}
Fe(III)	440	587	2	2.2×10^2	2.9×10^2
Ni(II)	150	142	1.7	8.8×10	8.4×10
Cu(II)	66.7	104	0.5	1.1×10^2	2.1×10^2
Zn(II)	383	554	4.9	7.8×10	1.1×10^2
UO_2(VI)	806	1190	3.2	2.5×10^2	3.7×10^2

[a] See Ref. *10*.

[b] The values are defined as $C_p \times C_s^{-1}$, where C_p and C_s are the amount of metal ion adsorbed and the concentration of metal ion in seawater, respectively.

The order of adsorptivity is consistent with previous result (*4*); this is satisfactorily interpreted by the metal ion-complexing property of the ligand (*1*). On the other hand, the amounts of Mg(II) and Ca(II) adsorbed are considerably larger than the result given in a previous paper (*4*). In the present experiment the amidoxime polymer was treated with 1 *M* NaOH to condition it for the adsorption of uranium in seawater. By this treatment the adsorption rate of uranium from seawater increases significantly and so do the adsorptivities for Mg(II) and Ca(II). It was reported that carboxylic acid groups are formed by the hydrolysis of unreacted nitrile groups on alkaline treatment of amidoxime polymer (*8*). It is therefore supposed that the higher adsorptivities of Mg(II) and Ca(II) are due to the formation of carboxylic acid groups (*11*).

From these results it was found that polymer samples thus prepared contain alkaline-earth and the first-row transition metal ions as well as uranyl(VI) ions. It is therefore desirable to elute uranyl(VI) ion separately from the other metal ions.

Elution Property of Uranium

The elution rates of uranium with hydrochloric acid solutions of different concentrations are shown in Fig. 1. The elution rate of uranium increases significantly with an increase in HCl concentration. In the case of elution with 1 *M* HCl, uranium is eluted almost quantitatively in 20 min. On the other hand, by the use of sodium hydrogen carbonate, the elution rate of uranium is much lower than with hydrochloric acid. In this case the elution of uranium proceeds through the complex formation of tricarbonatouranate(VI) ion (*7*); it is, therefore, supposed that the diffusion of this species in the polymer matrix determines the elution rate. The low elution rate makes use of the elution process by column operation difficult. Uranium elution by hydrochloric acid solutions is examined in detail in this study.

The dependence of the distribution coefficient of uranium, D_U, upon the concentration of hydrogen ions, [H], is shown in Fig. 2. This relation is expressed by

$$\log D_U = 0.416 - 1.004 \log [H] \qquad (2)$$

This relation shows that the extent of uranium elution increases with an increasing concentration of hydrogen ions, and that more than 90% of the uranium can be eluted by 0.5–1 *M* HCl. It is clear that uranium elution by

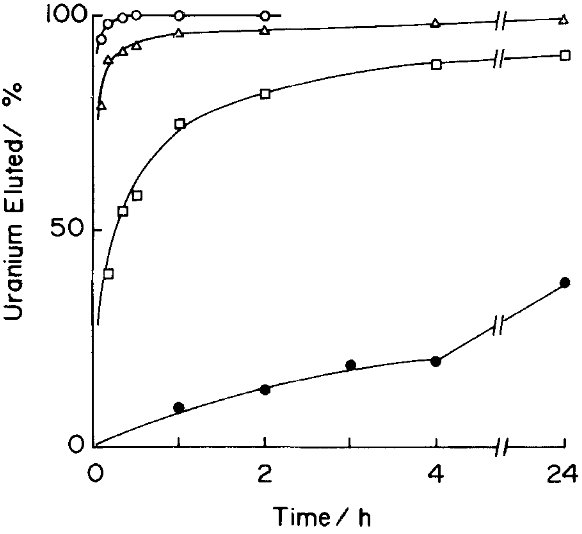

FIG. 1. Elution rate of uranium from amidoxime polymer at 25°C. Polymer: Sample B. Polymer/eluent ratio: 0.005 g/mL. Eluent: 1 *M* (○), 0.5 *M* (△), and 0.1 *M* HCl (□); 1 *M* $NaHCO_3$ (●).

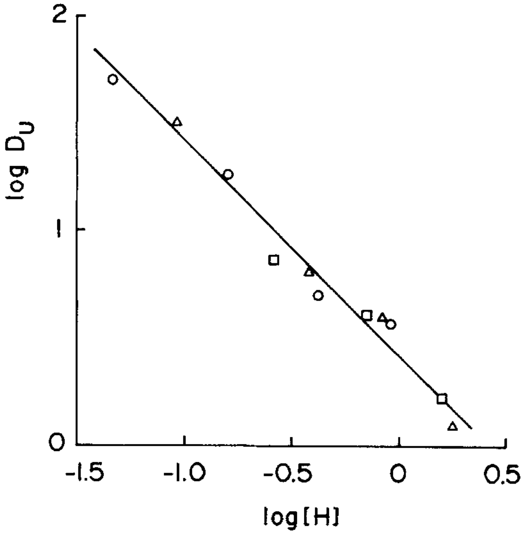

FIG. 2. Elution equilibrium of uranium from amidoxime polymer with HCl at 25°C. Polymer: Sample A. Polymer/eluent ratio: 0.01 (○), 0.1 (△), and 0.2 g/mL (□).

column operation is feasible through the use of HCl solutions as eluents.

Elution Properties of the Metal Ions

In order to predict the selective elution of uranium by separation from other metal ions, the elution properties of the metal ions were examined in relation to their pH dependence. The results are shown in Fig. 3. Both Mg(II) and Ca(II) are eluted at $pH < 4$, and Ni(II) and Zn(II) are eluted at $pH < 1.5$. On the other hand, Cu(II) and Fe(III) can be eluted at $pH < 1$; the curves of these two metal ions are very close to that of uranyl(VI).

The results show that the order of adsorptivities is Mg(II) < Ca(II) ≪ Zn(II) < Ni(II) ≪ Cu(II) < UO_2(VI); this order is consistent with the results described in a previous paper (*3*). It is suggested by Fig. 3 that uranium can be eluted separately from Mg(II), Ca(II), Zn(II), and Ni(II) by column operation. However, the elution pH values of Fe(III) and Cu(II) are very close to that of UO_2(VI). This implies that the separation of uranium from Fe(III) and Cu(II) is difficult by the present method,

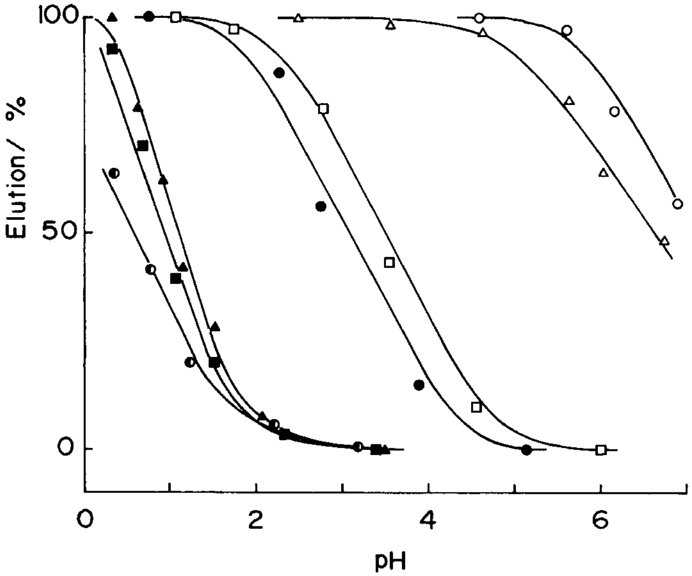

FIG. 3. pH dependence of elution extent at 25°C. Polymer: Sample B. Polymer/eluent ratio: 0.005 g/mL. Metal ions: Mg(II) (○), Ca(II) (△), Zn(II) (□), Ni(II) (●), Cu(II) (▲), UO_2(VI) (■), and Fe(III) (◐).

and that these metal ions contaminate the eluate containing enriched uranium.

Separative Elution of Uranium by the Column Method

On the basis of the results mentioned above, the elution of uranium by the column method was performed under various conditions. Elution with 0.1 *M* HCl is shown in Fig. 4. Mg(II) and Ca(II) were first eluted at

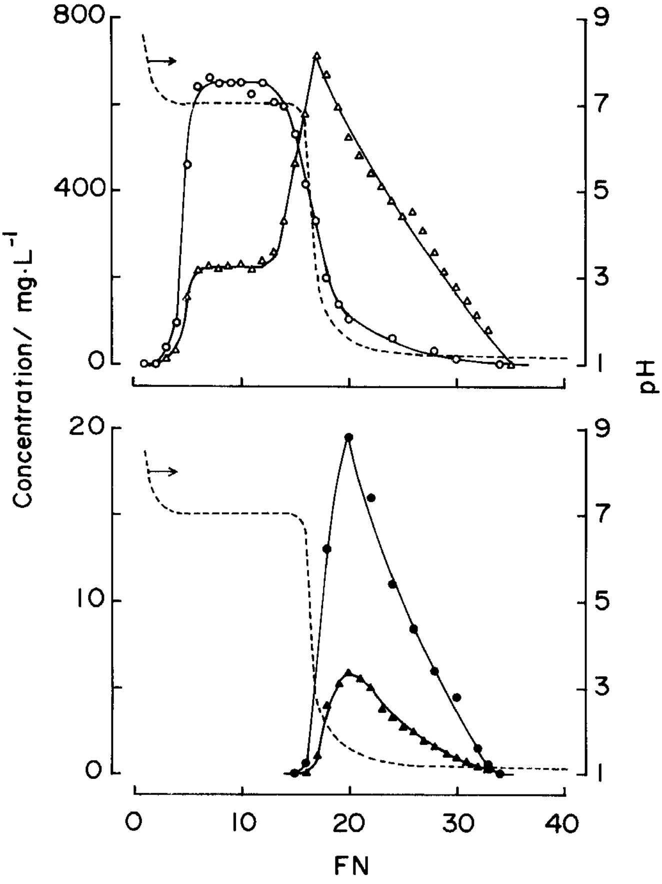

FIG. 4. Elution curves of metal ions with 0.1 *M* HCl at a space velocity of 3.0 h^{-1}. Polymer: Sample A (20 mL). Fraction volume: 10 mL. Metal ions: Mg(II) (○), Ca(II) (△), Zn(II) (●), and Ni(II) (▲).

pH = 7, and then Zn(II) and Ni(II) were eluted at pH < 5. These metal ions are completely eluted at FN = 33, as listed in Table 2.

The elution curves of Fe(III), Cu(II), and UO_2(VI) are shown in Fig. 5. These ions are only slightly eluted at FN $\leqslant$ 33 by 0.1 *M* HCl. The extent of elution of uranium is 10%, as shown in Table 2. These results clearly show that uranium can be almost completely separated from Mg(II), Ca(II), Zn(II), and Ni(II) by column operation with 0.1 *M* HCl.

Next, successive elutions with 0.5 or 1 *M* HCl were performed in order to recovery uranium. The results are shown in Fig. 5. In the case of 0.5 *M* HCl, uranium is eluted together with Fe(III) and Cu(II) and the maximum concentration of uranium, appearing at FN = 36, is 80 μg/mL. The extent of uranium elution at FN $\leqslant$ 53 is 90%. A similar result is obtained with 1 *M* HCl.

These results are summarized in Table 2. As expected, uranium is eluted separately from Mg(II), Ca(II), Zn(II), and Ni(II), but not separately from Cu(II) and Fe(III). When the fractions of FN = 34–53 are referred to an eluate of enriched uranium, more than 80% of the uranium adsorbed on the polymer is recovered in the eluate. As shown in Table 2, the extent of elution of Fe(III) is lower than that of Cu(II) and UO_2(VI). This is probably owing to the higher stability of $[Fe(LH)_2]^{3+}$ at low pH values, where LH refers to the neutral species of amidoxime ligand (*12*).

The effect of elution treatment on the adsorption properties of the amidoxime polymer was examined and the results are shown in Table 3. It is clear that elution treatment with hydrochloric acid solution barely affects the adsorptivity of uranium.

TABLE 2
Elution of Metal Ions from Amidoxime Polymer with HCl Solutions

Metal ion	Elution (%)		
	0.1 *M* HCl[a]	0.5 *M* HCl[b]	1 *M* HCl[b]
Mg(II)	102	—	—
Ca(II)	99	—	—
Zn(II)	99	—	—
Ni(II)	98	—	—
Fe(III)	7	75	86
Cu(II)	38	98	100
UO_2(VI)	12	90	95

[a] The values are the extent of elution at FN $\leqslant$ 33.

[b] The elution was started with 0.1 *M* HCl (FN $\leqslant$ 33) followed by 0.5 or 1.0 *M* HCl (FN = 34–53). The values refer to the extent of elution at FN $\leqslant$ 53.

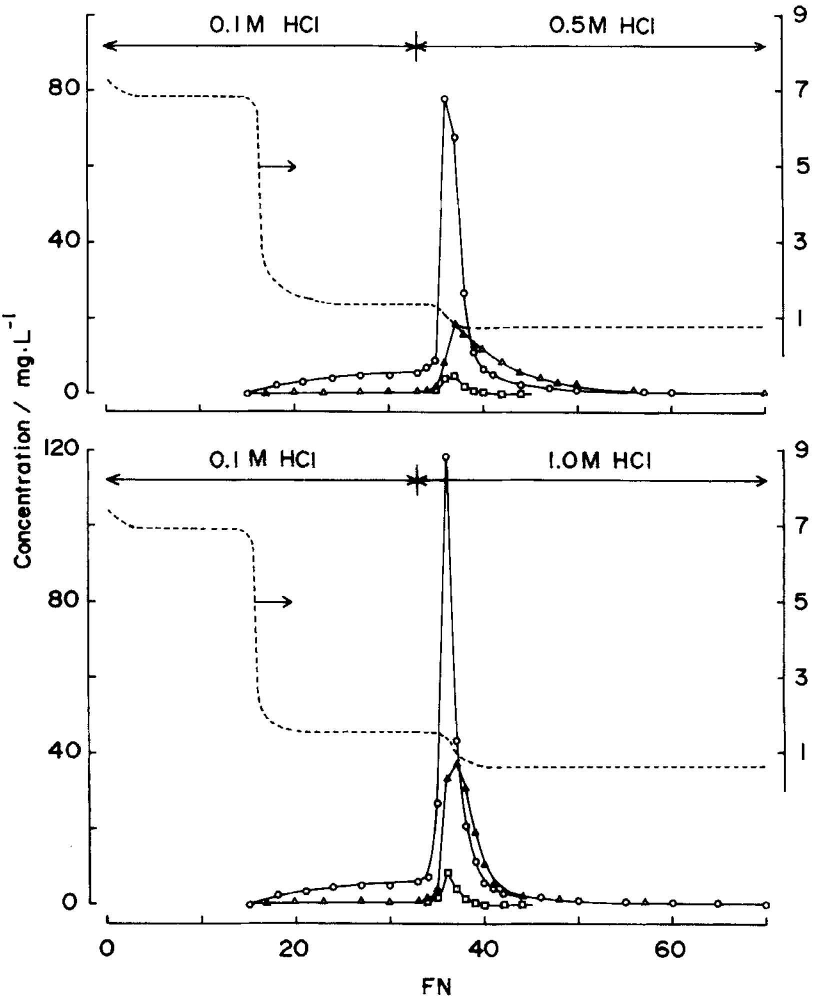

FIG. 5. Elution curves of metal ions with 0.1 *M* HCl–0.5 *M* or 1 *M* HCl. Polymer: Sample A (20 mL). Fraction volume: 10 mL. Space velocity: 3.0, 0.74, and 1.1 h^{-1} for the elutions with 0.1 *M*, 0.5 *M*, and 1.0 *M* HCl, respectively. Metal ions: UO_2(VI) (○), Fe(III) (△), and Cu(II) (□).

TABLE 3
Influence of Elution Treatment upon Adsorptivity of Uranium from Seawater on Amidoxime Polymer

Eluent	Uptake of H^{+} [a] (mmol/g)	Uptake of OH^{-} [a] (mmol/g)	Uptake of Cu(II)[a] (mmol/g)	Adsorption of UO_2(VI)[b] (μg/g)
—	2.03	3.95	2.84	300
0.1 *M* HCl–0.5 *M* HCl	1.95	4.00	2.90	310
0.1 *M* HCl–1.0 *M* HCl	1.98	3.90	2.95	305

[a] The experimental conditions are shown in Ref. *4*.
[b] The amidoxime polymer was immersed in seawater for 10 d under conditions similar to those described in Ref. *4*.

In the present study it was found that uranium is eluted separately from metal ions, except for Fe(III) and Cu(II), from amidoxime polymer with hydrochloric acid solutions. As reported previously, Fe(III) and Cu(II) are separated successfully from UO_2(VI) with a chelating resin having glycine-*N*,*N*-bis(methylene phosphonic acid) groups (*13*). It is therefore concluded that the elution method with hydrochloric acid solutions is applicable for the recovery of uranium in amidoxime polymers from seawater.

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