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Recovery of Uranium from Seawater by Immobilized Tannin

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Abstract

Tannin compounds having multiple adjacent hydroxy groups have an extremely high affinity for uranium. To prevent the leaching of tannins into water and to improve the adsorbing characteristics of these compounds, we tried to immobilize tannins. The immobilized tannin has the most favorable features for uranium recovery; high selective adsorption ability to uranium, rapid adsorption rate, and applicability in both column and batch systems. The immobilized tannin can recover uranium from natural seawater with high efficiency. About 2530 μg uranium is adsorbed per gram of this adsorbent within 22 h. Depending on the concentration in seawater, an enrichment of up to 766,000-fold within the adsorbent is possible. Almost all uranium adsorbed is easily desorbed with a very dilute acid. Thus, the immobilized tannin can be used repeatedly in the adsorption-desorption process.

INTRODUCTION

In an effort to develop efficient adsorbents for the recovery and removal of uranium that may be present in seawater, industrial effluents, mine wastewater, and other waste sources, we have previously examined the uptake of uranium by a variety of biomass and related model compounds representing attractive functional groups for uranium (*1-6*). Our previous studies have shown that some biopigments having multiple hydroxy groups that might be useful for binding uranium, such as alizarin (1,2-dihydroxyanthraquinone), quercetin (3,3′,4′,5,7-pentahydroxyflavonol), and morin (2′,3,4′,5,7-pentahydroxylflavonol), can ac-

cumulate large amounts of uranium from aqueous systems (*1, 6, 7*). On the basis of these data, we presume that the uranyl ion is coordinated by the adjacent hydroxy groups existing in the biopigments.

Consequently, in this paper we extend our investigation of uranium recovery from seawater to tannins having multiple adjacent hydroxy groups. Our approach is based on the ability of tannins to chelate and retain uranium in seawater. Tannin compounds are ubiquitous and inexpensive natural products, but when they are used as adsorbing agents for the recovery of uranium, they have the disadvantage that they are quite easily leached by water. Therefore, in order to prevent the leaching of tannins into seawater and to improve the adsorbing characteristics of these compounds, we have tried to immobilize tannin compounds by coupling them with such water-insoluble matrices as Bemberg rayon fiber, cellulose powder, and crosslinked polyvinyl alcohol (PVA).

Watanabe et al. reported that an immobilized tannin can be used as a protein adsorbent for various applications, such as recovery, separation, and purification of proteins. They also attempted to remove traces of iron from water for brewing with an immobilized tannin (*8, 9*).

However, up to the present, none of the reports has clarified uranium recovery using an immobilized tannin. In the present study we found that an immobilized tannin has an extremely high ability to accumulate uranium. Accordingly, along with our fundamental research regarding uranium uptake using this adsorbent, some attempts were made to recover uranium from seawater.

MATERIALS AND METHODS

Materials

Chinese gallotannin (tannic acid) was obtained from Wako Pure Chemical Industries, Ltd.; chestnut, wattle, myrobalan, quebracho, and gambir tannins from Gokyo Industries Co. Ltd.; and cellulose powder CF1, CF11, and CC31 from Whatman Ltd. Cellulose powder Avicel, viscose rayon fiber, and Bemberg rayon fiber were kindly donated by Asahi Chemical Industries Co. Ltd. Both fibers were cut into small pieces (less than 2 mm in length) and used for the immobilization of tannin.

Immobilization of Gallotannin on Various Matrices

Several species of tannin were immobilized on various matrices by the procedures cited in the Results and Discussion section.

Adsorption Experiments

Adsorption experiments were conducted as previously described (*1*).

RESULTS AND DISCUSSION

Immobilization of Tannin

The tannin compounds were immobilized on cellulosic matrices and crosslinked PVA by the epichlorohydrin coupling procedure reported by Watanabe et al. (*8*). In order to enhance the uranium adsorbing ability of the product, some factors affecting adsorption capacity, such as kinds of matrix, conditions for epoxy activation of matrix, kinds of tannin, the interposition of spacer arm, and the coupling conditions of tannin with epoxy-activated matrix, were investigated in detail.

Kinds of Matrix

Various cellulosic matrices were activated with epichlorohydrin. To select the suitable matrix, the six species of cellulosic matrices shown in Table 1 were screened. Chinese gallotannin was coupled with the epoxy-activated matrices. It is evident from Table 1 that among the matrices tested, no significant differences are observed with regard to their adsorbing abilities for uranium.

TABLE 1
Adsorption of Uranium by Chinese Gallotannin Immobilized on Various Cellulosic Matrices[a]

Matrix			U adsorbed (mg/g adsorbent)
Cellulose powder:	Whatman	CF1	92.1
		CF11	91.5
		CC31	90.2
	Avicel		91.1
Viscose rayon fiber			97.0
Bemberg rayon fiber			97.9

[a]Three milligrams of adsorbents were suspended in 100 mL of seawater enriched with 10 ppm of uranium for 1 h at 30°C.

Kinds of Tannin

The hydrolyzable and condensed tannins are two groups of tannins widely distributed in the vegetable kingdom. The six species of tannin belonging to these two groups were tested for their ability to accumulate uranium. In general, high adsorbing abilities for uranium were found in Chinese gallo, chestnut, and myrobalan tannins belonging to the hydrolyzable tannin group compared to gambir, quebracho, and wattle tannins belonging to the condensed tannin group (Table 2).

Therefore, in the following experiments, Chinese gallotannin, which is readily available as a reagent and is cheap, was immobilized on a suitable matrix.

Effect of Spacer Arm

In affinity chromatography the interposition of spacer arms between matrices and ligands is known to enhance the absorption of proteins including enzymes. According to the text published by Pharmacia Fine Chemicals (*10*), it is often observed that adsorbents prepared by coupling small ligands directly to matrices can exhibit low capacities due to steric interference between the matrix and substances binding to the ligand. Accordingly, in these cases a spacer arm is interposed between matrix and ligand to facilitate effective binding (*10, 11*).

The purpose of this experiment was to determine whether or not the interposition of a spacer arm (hexamethylenediamine) between the epoxy-activated matrix and the tannin ligand increases the uptake of uranium by the immobilized tannin.

As shown in Table 3, the accumulating ability of the adsorbent for

TABLE 2
Adsorption of Uranium by Various Tannins Immobilized on Bemberg Rayon Fiber[a]

Tannin	U adsorbed (mg/g adsorbent)
Chinese gallotannin	38.1
Chestnut tannin	43.4
Myrobalan tannin	34.5
Gambir tannin	7.2
Quebracho tannin	17.1
Wattle tannin	27.0

[a]Ten milligrams of adsorbents were suspended in 100 mL of seawater enriched with 10 ppm of uranium for 1 h at 30°C.

TABLE 3
Effect of the Spacer Arm Interposition on the Uranium Adsorbing Ability of the Adsorbent[a]

Spacer arm	U adsorbed (mg/g adsorbent)
Without	70
With	112

[a]Adsorption conditions are described in the footnote to Table 1.

uranium was strongly increased by the interposition of a spacer arm. This effect is mainly attributable to the complementary relationships between matrix and tannin ligand, although other factors might be involved.

Optimal Conditions for the Immobilization of Tannin

The optimal conditions for the immobilization of Chinese gallotannin by the epichlorohydrin procedure, such as initial concentrations of NaOH and epichlorohydrin, reaction time, temperature, and coupling conditions of tannin with epoxy-activated matrix, were examined systematically.

After many attempts, we realized the results summarized in Fig. 1. The presumed structure of the resulting immobilized gallotannin is shown in Fig. 2. From Fig. 2 it seems reasonable to assume that this adsorbent has multiple hydroxy groups, which are attractive functional groups for uranium uptake, and it has the most favorable steric structure for uranium binding.

Selective Adsorption of Metal Ions

To determine which heavy metal ion can be most readily adsorbed by the immobilized tannin, we examined the selective adsorption of heavy metal ions by four species of adsorbent from a solution containing 4×10^{-5} *M* of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and UO_2^{2+} at pH 5.

As shown in Table 4, the relative order of magnitude of heavy metal ions adsorbed by the adsorbents is $UO_2^{2+} \gg Cu^{2+} \gg$ others. It is obvious from Table 4 that the immobilized tannin is more selective to uranyl ion than are all the bivalent cations tested.

The next step in our study was to examine the selective accumulation between uranium and thorium. A comparative study of the selective

Cellulose (1 g)
Suspended in the mixture (3 *N* NaOH, 60 mL; epichlorohydrin, 60 mL; and a drop of Span 85)
Shaken for 2 h at 50°C
Washed thoroughly with deionized water

Epoxy-activated cellulose
Suspended in 50 mL of 2% hexamethylenediamine (pH 11)
Shaken for 2 h at 60°C
Washed thoroughly with deionized water

Aminohexylcellulose
Suspended in the mixture (3 *N* NaOH, 60 mL; epichlorohydrin, 60 mL; and a drop of Span 85)
Shaken for 2 h at 50°C
Washed thoroughly with deionized water

Epoxy-activated cellulose
Suspended in 80 mL of 3% Chinese gallotannin
Add the least amount of $NaBH_4$, N_2 passed through
Shaken overnight at 40°C
Washed thoroughly with 0.01 *N* HCl and deionized water

Tannin immobilized on cellulose

FIG. 1. Recommended method for immobilization of tannin by the epichlorohydrin coupling procedure.

TABLE 4
Selective Adsorption of Heavy Metal Ions by the Immobilized Tannin[a]

Matrix	Spacer arm	Metal adsorption ratio[b]						
		Ni	Cu	Zn	Cd	U		
Bemberg Rayon fiber	Without	4.5	6.4	5.6	30.5	7.7	8.4	89.8
	With	3.1	4.8	5.3	28.3	7.9	6.6	94.9
Cellulose powder	Without	7.3	8.5	8.3	32.1	8.9	7.6	89.1
	With	3.4	6.8	6.7	31.4	4.6	6.8	90.5

[a]Twenty milligrams of adsorbents were suspended in 100 mL of the solution (pH 5) containing 4×10^{-5} *M* of heavy metal ions for 1 h at 30°C.
[b]((Initial metal concentration − residual metal concentration in the solution)/initial metal concentration in the solution) × 100.

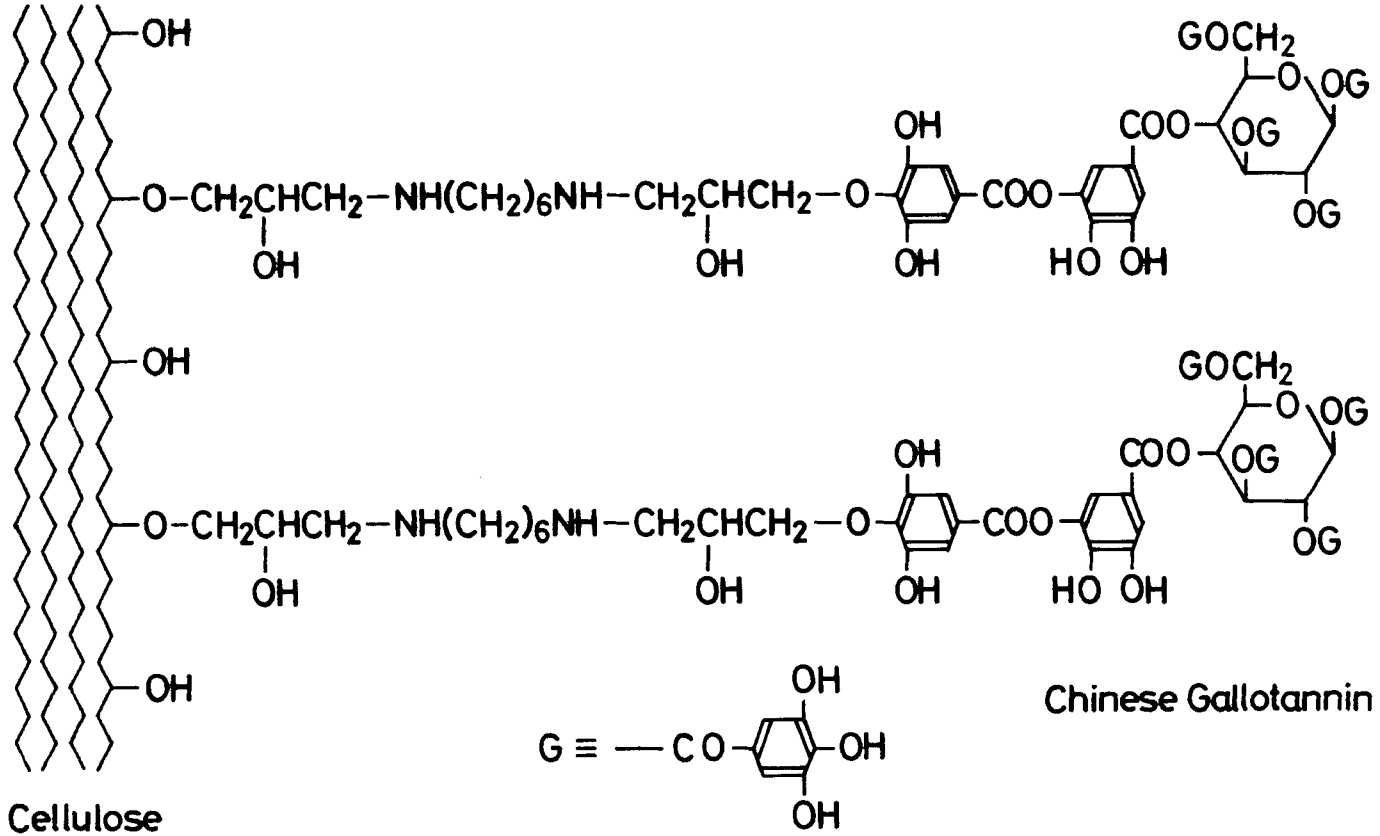

FIG. 2. Presumed structure of immobilized Chinese gallotannin on cellulosic matrix.

accumulation between these two metals by the immobilized tannin holds both academic and practical interest because both uranium and thorium are chemically similar nuclear fuels.

The present experiment was therefore planned to determine whether or not selective accumulation by the immobilized tannin occurred among three ions: UO_2^{2+}, Th^{4+}, and Cu^{2+}. From Table 5 it can be seen that all adsorbents take up far larger amounts of uranyl and thorium ions than copper ions. Regarding the selective adsorption between uranium and thorium, it was observed that the adsorbents which are interposed with hexamethylenediamine as a spacer arm accumulate somewhat larger amounts of thorium than uranium, whereas the adsorbents without a spacer arm accumulate equal amounts of these two metals.

Of the four adsorbents tested at pH 4, the adsorbents which are interposed with hexamethylenediamine as a spacer arm accumulate far larger amounts of uranium and thorium compared with those without spacer arms. As described above, with regard to the uptake of uranium and thorium at pH 4, the effect of spacer arm interposition is clearly shown (Table 5). At pH 5, however, we could not recognize the effect of spacer arm interposition on the uranium and thorium uptake (Table 4). This proved that there is an interesting difference between pH 4 and 5 regarding the effect of spacer arm interposition on the uptake of uranium and thorium.

Effect of pH on Uranium Adsorption

The adsorption of uranium has been studied with respect to solution pH, retention time, and adsorbent amount in order to determine the optimal conditions for uranium recovery.

TABLE 5
Selective Adsorption among Uranyl, Thorium, and Copper Ions by the Immobilized Tannin[a]

Matrix	Spacer arm	Metal adsorption ratio[b]		
		Cu	Th	U
Bemberg rayon fiber	Without	14.1	54.1	54.6
	With	19.8	97.4	90.1
Cellulose powder	Without	15.7	53.4	53.4
	With	20.4	96.5	88.1

[a]Twenty milligrams of adsorbents were suspended in 100 mL of the solution (pH 4) containing 4×10^{-5} *M* of heavy metal ions for 1 h at 30°C.
[b]See footnote *b* in Table 4.

The effect of pH on the adsorption of uranium by Chinese gallotannin immobilized on Bemberg rayon fiber was determined in the pH range from 3 to 7. As shown in Fig. 3, maximum uranium uptake is observed at around pH 6, below and above which uptake falls off rapidly. Thus the uptake of uranium by an immobilized tannin was markedly affected by the pH of the solution, which is similar to the result obtained with alizarin (*1*).

We also examined the uptake of thorium by the immobilized tannin at pH 3 and 4. The upper limit for the thorium solution is set by precipitation of thorium which commences at ca. pH 4. As a result, it was recognized that the adsorbent takes up larger amounts of thorium at pH 4 than at pH 3. As shown in Fig. 3, this adsorbent can accumulate a somewhat larger amount of thorium than uranium at pH 4. This result was also confirmed by the experiment cited in Table 5.

Time Course of Uranium Adsorption

As described in the above sections, the immobilized tannin has an extremely high ability to accumulate uranium from aqueous systems. On the basis of the results obtained above, an attempt was made to recover

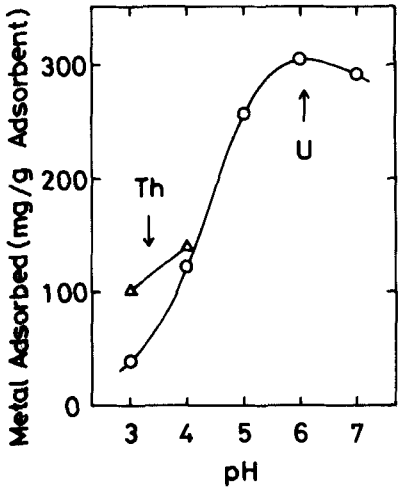

FIG. 3. Effect of pH on the adsorption of uranium by the immobilized tannin. Six milligrams of the adsorbent were suspended in 200 mL of the solution containing 10 ppm of uranium for 30 min at 30°C. The pH of the solution was controlled by the pH controller for the time required. The adsorption of thorium by the immobilized tannin was also examined at pH 3 and 4 under the same conditions described above.

uranium from natural seawater using the immobilized tannin. Some factors affecting uranium recovery by the immobilized tannin were investigated.

First, the time course of uranium recovery from natural seawater was determined by using the tannin immobilized on Bemberg rayon fiber. As shown in Fig. 4, the adsorption equilibrium was attained within 10 h, which indicates that the uptake of uranium is rapid and efficient. This rapid uptake of uranium by the immobilized tannin is similar to the rate of uptake observed with the immobilized 1,2-dihydroxyanthraquinone (alizarin) (*1*).

Effect of the Amount of Adsorbent on Uranium Adsorption

As shown in Fig. 5, the amounts of uranium adsorbed by the immobilized tannin (mg U/g adsorbent) decreases as the amounts of the adsorbent increased, whereas the amounts of adsorbent increased the total amount of uranium adsorbed by the adsorbent increased. Twenty milligrams of the adsorbent can recover uranium almost quantitatively from seawater.

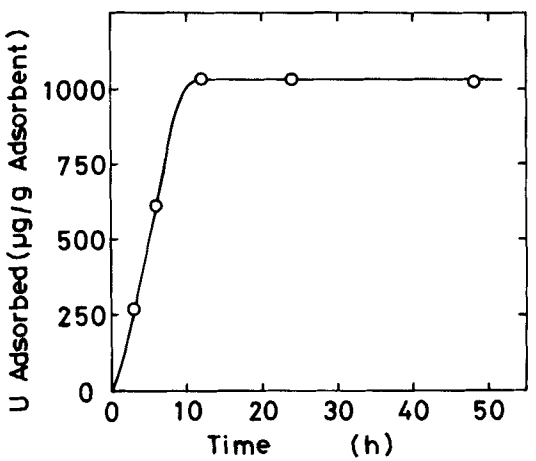

FIG. 4. Time course of uranium recovery from natural seawater by the immobilized tannin. Twelve milligrams of the adsorbent were suspended in 5 L of natural seawater sampled at the coast of Miyazaki at 30°C.

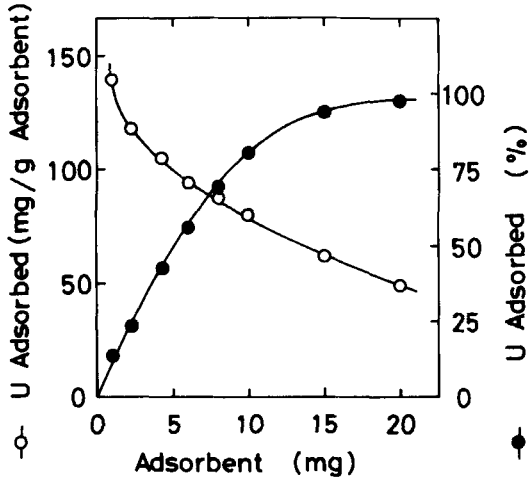

FIG. 5. Effect of the amount of adsorbent on the adsorption of uranium by immobilized tannin. Desired amounts of the adsorbent were suspended in 100 mL of seawater enriched with 10 ppm of uranium for 1 h at 30°C.

Accumulation of Various Ions from Seawater

The present experiment was carried out to determine which elements accumulate in the immobilized tannin from seawater. The tannin immobilized on crosslinked PVA (16.5 mg dry matter, 0.25–0.5 mm granule radius) was suspended in 2.5 L of natural seawater with constant shaking for 24 h. As a result, about 75% of the uranium existing in seawater was recovered by the adsorbent under the present conditions.

Next, the adsorbent was analyzed qualitatively with an energy dispersive x-ray fluorescence spectrometer developed by Rigakudenki Co. Ltd. Japan. The following 19 species of elements were found in the adsorbent by means of this nondestructive technique: Mg, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Sr, Zr, Nb, and U.

Attention has recently been focused on such rare metals as zirconium, niobium, vanadium, and titanium in relation to resource recovery. The recovery of these useful rare metals from seawater seems to be a worthwhile subject to investigate. Further experiments will be made in the future.

Uranium Adsorption Capacity of the Adsorbent

To determine the maximum capacity of the immobilized tannin to adsorb uranium from natural seawater, equilibrium experiments have

been conducted by constantly shaking a desired amount of the tannin immobilized on Bemberg rayon fiber in 10 L of seawater for 22 h.

The maximum capacity for uranium uptake can be estimate from Fig. 6 by extrapolation to be a uranium concentration of natural seawater of 3.3 ppb. About 2530 μg U is absorbed per gram of the adsorbent within 22 h. Depending on the concentration in seawater, an enrichment up to 766,000-fold within the adsorbent is possible.

The experimental results determined in the present work clearly indicate that the uptake of uranium from seawater by the immobilized tannin is rapid and efficient. The uranium in natural seawater is present mainly as the stable complex ion $UO_2(CO_3)_3^{4-}$(*12*). The present studies show that the immobilized tannin presents a high affinity for the complex anion described above, and that it may be used as an adsorbent for uranium recovery for seawater.

Recovery of Uranium from Seawater in a Column System

On the basis of the results described above, an attempt was made to recover uranium from natural seawater using the tannin immobilized on crosslinked PVA in a column system.

The adsorbent can recover uranium almost quantitatively from natural

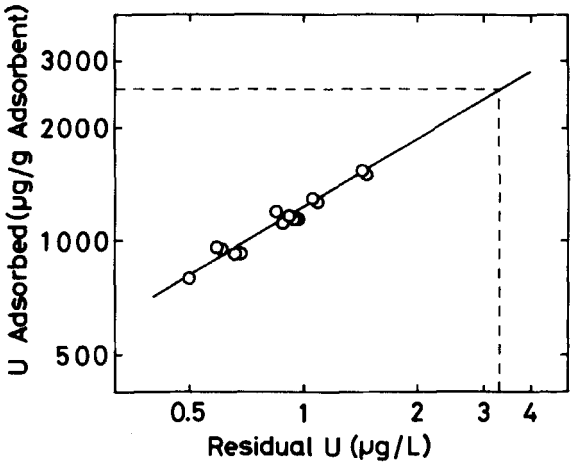

FIG. 6. Uranium adsorption equilibrium of the immobilized tannin in natural seawater. The equilibrium adsorption tests were conducted by suspending the adsorbents (20–40 mg) in 10 L of natural seawater for 22 h at 30°C.

seawater in a column system under the experimental conditions cited in Table 6. As described above, the tannin immobilized on crosslinked PVA has the most favorable features for uranium recovery: high adsorption ability, good mechanical properties, and applicability in a column system.

Repetition Test of Uranium Adsorption-Desorption Cycle

To obtain basic information on the recovery of uranium by the immobilized tannin from seawater, Chinese gallotannin immobilized on crosslinked PVA was studied through two adsoprtion-desorption cycles in a batch system.

In a preliminary test it was recognized that almost all the uranium adsorbed onto the adsorbent can be desorbed by washing with 0.01–1 *N* HCl, so we used 0.01 *N* HCl as the desorbent.

As described above, the uranium retained on the immobilized tannin can be quantitatively and easily eluted with a very dilute acid. As shown in Table 7, almost quantitative recovery of the uranium from seawater can be achieved by the adsorbent, and almost all uranium adsorbed was

TABLE 6
Recovery of Uranium from Natural Seawater by the Immobilized Tannin in a Column System[a]

Uranium (μg)	Recovered (%)
8.11	96.4

[a]Natural seawater (2.55 L) was adsorbed on a column (diameter, 8 mm) of the adsorbent (dry weight, 99.0 mg) at space velocity 40 h^{-1}. The concentration of uranium in natural seawater sampled at the coast of Miyazaki was found to be 3.3 ppb.

TABLE 7
Repetition Test of Uranium Adsorption-Desorption by the Immobilized Tannin[a]

Times of repetition	U adsorbed (%)	U desorbed (%)
1	97.0	100.0
2	98.0	94.0

[a]Fifty milligrams of the adsorbent were suspended in 2.5 L of natural seawater for 24 h at 25°C. After washing with water, the uranium adsorbed on the adsorbent was desorbed with 0.01 *N* HCl.

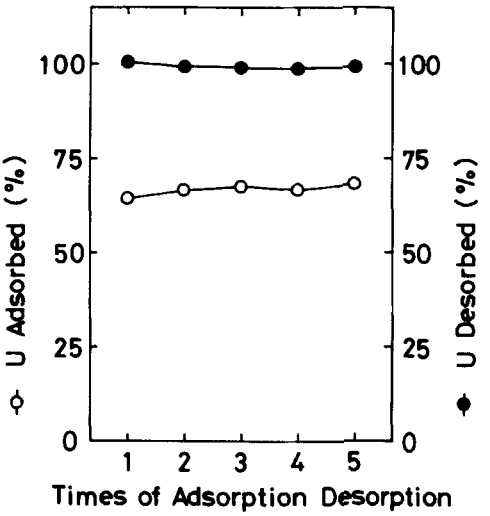

FIG. 7. Repitition test of uranium adsorption-desorption by the immobilized tannin. Twenty milligrams of the adsorbent were suspended in 100 mL of seawater enriched with 10 ppm of uranium for 1 h at 30°C. After washing with water, the uranium adsorbed on the adsorbent was desorbed with 0.01 *N* HCl.

desorbed with 0.01 *N* HCl. This result was also confirmed by the experiment using seawater enriched with 10 ppm of uranium (Fig. 7). Thus, the immobilized tannin can be used repeatedly in an adsorption-desorption process.

As stated above, the immobilized tannin seems to be an excellent adsorbent for uranium recovery from seawater. Along with the present basic research, further developmental studies are being directed toward uranium recovery on a practical scale.

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REFERENCES

1. T. Sakaguchi and A. Nakajima, *Sep. Sci. Technol., 21,* 519 (1986).
2. T. Horikoshi, A. Nakajima, and T. Sakaguchi, *Eur. J. Appl. Microbiol. Biotechnol., 12,* 90 (1981).
3. T. Sakaguchi, T. Horikoshi, and A. Nakajima, *Agric. Biol. Chem., 45,* 2191 (1981).

4. A. Nakajima, T. Horikoshi, and T. Sakaguchi, *Eur. J. Appl. Microbiol. Biotechnol., 16,* 88 (1982).
5. A. Nakajima and T. Sakaguchi, *J. Chem. Tech. Biotechnol., 36,* 281 (1986).
6. T. Sakaguchi, A. Nakajima, and T. Horikoshi, *J. Agric. Chem. Soc. Jpn., 53,* 211 (1979).
7. Unpublished.
8. T. Watanabe, Y. Matsuo, T. Mori, R. Sano, T. Tosa, and I. Chibata, *J. Solid-Phase Biochem., 3,* 161 (1978).
9. I. Chibata, T. Tosa, T. Mori, T. Watanabe, and N. Sakata, *Enzyme Microbiol. Technol., 8,* 130 (1986).
10. Pharmacia Fine Chemicals, *Affinity Chromatography,* 1983, p. 8.
11. P. Ocarra, S. Barry, and T. Griffin, *Biochem. Soc. Trans., 1,* 289 (1973).
12. N. Ogata, N. Inoue, and H. Kakihana, *J. At. Energy Soc. Jpn., 13,* 560 (1971).

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