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Accumulation of Uranium by Immobilized Persimmon Tannin

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ABSTRACT

We have discovered that the extracted juice of unripe astringent persimmon fruit, designated as "kakishibu" or "shibuol," has an extremely high affinity for uranium. To develop efficient adsorbents for uranium, we tried to immobilize kakishibu (persimmon tannin) with various aldehydes and mineral acids. Persimmon tannin immobilized with glutaraldehyde can accumulate 1.71 g (14 mEq U) of uranium per gram of the adsorbent. The uranium accumulating capacity of this adsorbent is several times greater than that of commercially available chelating resins (2–3 mEq/g). Immobilized persimmon tannin has the most favorable features for uranium recovery; high selective adsorption ability, rapid adsorption rate, and applicability in both column and batch systems. The uranium retained on immobilized persimmon tannin can be quantitatively and easily eluted with a very dilute acid, and the adsorbent can thus be easily recycled in the adsorption–desorption process. Immobilized persimmon tannin also has a high affinity for thorium.

INTRODUCTION

The recovery of nuclear elements, such as uranium and thorium, from aqueous systems has recently become the center of wide interest in exploiting undeveloped energy resources. The removal of radioactive elements from contaminated sources also seems to be a worthwhile subject to investigate in terms of environmental control. Accordingly, attention has recently been paid to these problems in various countries.

In an effort to develop efficient adsorbents for the recovery of uranium that may be present in seawater, industrial effluent, and mine water, we have previously investigated the accumulation of uranium by a variety of biomass and related model compounds representing attractive functional groups for uranium (1–11). In one of our studies we discovered that the extracted juice of unripe astringent persimmon (*Diospyros lotus* L.) fruit, designated as "kakishibu" or "shibuol," has an extremely high affinity for uranium.

Kakishibu, which is a wine red to dark brown colored liquor, is widely produced in Japan, China, and neighboring countries. Since older times in Japan, kakishibu has been used as a dye for paper, cloth, and fishing net because it forms a sturdy water-insoluble thin layer on exposure to air (12). Furthermore, as kakishibu contains large amounts of tannin compounds, it is most extensively used as a clarificant for Japanese rice wine ("sake"). In the brewing process there are substances in "sake" that cause turbidity, thereby deteriorating its quality. The tannin compounds easily coagulate with the protein, causing the turbidity (12–15).

However, up to the present, there have been no reports on uranium recovery and removal using the persimmon fruit juice "kakishibu." We report here that kakishibu (persimmon tannin), immobilized with various aldehyde compounds such as formaldehyde, acetoaldehyde, and glutaraldehyde, presents an extremely high affinity for uranium and thorium.

MATERIALS AND METHODS

Materials

Commercially available kakishibu (the extracted juice of unripe persimmon fruit) was used throughout this study. The content of tannin in kakishibu was determined to be 4.0% by the Folin–Denis' method (16, 17).

In this paper, kakishibu is hereinafter called persimmon tannin.

Immobilization of Persimmon Tannin

Unless otherwise stated, the immobilization of persimmon tannin was conducted as follows: One part of 25% glutaraldehyde solution was mixed with four parts of persimmon tannin. After 16 hours a pale pink homogeneous gel was obtained. The gel was crushed into small particles (less than 60 mesh), washed thoroughly with deionized water, and then used for adsorption experiments.

Adsorption Experiments

Desired amounts of the adsorbents were suspended in 100 mL of the solution containing a definite amount of uranium for 1 hour at 30°C. Uranium was supplied as $UO_2(NO_3)_2$. The pH of the solution was adjusted to the desired value with 0.1 N HCl or 0.1 N NaOH solution. After adsorption, the adsorbent was filtered off and the residual uranium in the filtrate was determined. The ppm levels of uranium were determined by spectrophotometry using Arsenazo III (18) or an inductively coupled plasma quantometer (Shimadzu ICPQ-100); the ppb levels were determined by fluorometry using $NaKCO_3$–NaF flux (19, 20).

Infrared Absorption Measurements

Infrared absorption spectra were measured by the KBr method using an IR absorption spectrometer (Hitachi 170-30).

RESULTS AND DISCUSSION

Uranium Accumulating Ability of Persimmon Tannin Immobilized with Various Aldehydes and Mineral Acids

As commercially available persimmon tannin is an aqueous liquor, it is not suitable to use as an adsorbing agent for the recovery of uranium in an intact liquid state. Therefore, to improve handling and the adsorbing characteristics of persimmon tannin, we tried to immobilize persimmon tannin with the various aldehyde compounds shown in Table 1. The liquid

TABLE 1
Uranium Accumulating Ability of Persimmon Tannin Immobilized with Various Aldehydes[a]

Aldehyde	Solvent	U adsorbed (%)
Acetoaldehyde	Water	86.5
Benzaldehyde	Ethanol	86.2
Crotonaldehyde	Water	84.3
Formaldehyde	Water	84.6
Furfural	Ethanol	85.7
Glutaraldehyde	Water	82.7
Glyoxal	Water	86.6
Glyoxilic acid	Water	89.3
p-Nitrobenzaldehyde	Water	81.6
Protocatechualdehyde	Acetic acid	85.0
Salicylaldehyde	Water	85.9
Terephthalaldehyde	Ethanol	81.6
trans-Cinnamaldehyde	Acetic acid	76.9
Vanilin	Acetic acid	83.8

[a] Each aldehyde (0.005 mol) was dissolved in 2 mL solvent (water, ethanol, or acetic acid) and mixed with 8 mL persimmon tannin. The gel obtained was homogenized and then washed thoroughly with deionized water. Each adsorbent (2 mg dry weight basis) was suspended in 100 mL of the solution (pH 6) containing 20 ppm uranium for 1 hour at 30°C.

persimmon tannin was treated with aldehyde compounds to polymerize the tannin and thus insolubilize the colored gels. As shown in Table 1, almost all of the immobilized persimmon tannin has an extremely high ability to accumulate uranium.

We also tried to immobilize persimmon tannin with the various mineral acids shown in Table 2. The resulting gels also have a high ability to accumulate uranium. However, they are intractable in a column system because they cause plugging. Henceforth, in the following experiments, persimmon tannin immobilized with glutaraldehyde was used as an adsorbent.

Selective Adsorption of Heavy Metals

To determine which heavy metal ion can be most readily adsorbed by immobilized persimmon tannin, we examined the selective adsorption of heavy metal ions 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 (Table 3). The relative order of magnitude of heavy metal ions adsorbed on the adsorbent appeared to be $UO_2^{2+} \gg Cu^{2+} >$ others, which shows that the adsorbent has a high ability to adsorb uranium selectively from aqueous systems. In our previous study, similar results were obtained with immobilized Chinese gallotannin (10, 11).

According to the hard and soft acids and bases (HSAB) principle first proposed by Pearson (21), uranyl ion belongs to the hard acids while

TABLE 2
Uranium Accumulating Ability of Persimmon Tannin Immobilized with Various Mineral Acids[a]

Acid	Concentration	U adsorbed (%)
HCl	3 N	89.9
	6 N	87.0
$HClO_4$	20%	89.4
	40%	95.1
HNO_3	4 N	89.4
	6 N	89.3
H_2SO_4	3 N	94.2
	6 N	86.3
	10 N	90.4

[a] Five milliliters of persimmon tannin was added to 100 mL of each acid solution. The gel obtained was filtered off and washed thoroughly with deionized water. Adsorption conditions for uranium are described in the footnote to Table 1.

TABLE 3
Selective Accumulation of Heavy Metal Ions by Immobilized Persimmon Tannin[a]

Metal adsorbed (mg/g adsorbent)						
Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	UO_2^{2+}
0.0	0.0	3.4	23.6	0.0	1.5	439.3

[a] Two milligrams of the adsorbent (dry weight basis) was suspended in 100 mL of the solution (pH 5) containing 4×10^{-5} M of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and UO_2^{2+}. Each metal ion was presented as its nitrate.

copper(II) and other ions tested belong to the boundary or soft acids. Consequently, hydroxy group belonging to the hard base can couple with uranyl ion most favorably. Thus, our results on selective adsorption can be explained on the basis of the HSAB Principle (21).

Separation of Uranyl and Copper(II) Ions by Immobilized Persimmon Tannin

On the basis of the results obtained above, the separation of uranyl and copper(II) ions, which are the most accumulative two ions of the seven ions tested, using immobilized persimmon tannin was attempted in a column system. As shown in Fig. 1, uranyl and copper(II) ions retained on the adsorbent are easily separated from each other with very dilute HCl.

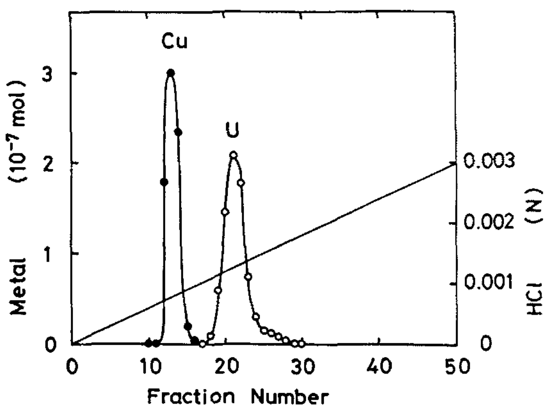


FIG. 1 Chromatographic separation of uranyl and copper(II) ions by immobilized persimmon tannin. Uranyl and copper(II) ions (each ion, 1.7×10^{-6} mol) were adsorbed on the column (bed volume, 4 mL) of the adsorbent. After adsorption, the column was washed with 10 mL of deionized water, and then the retained ions were eluted with a linear gradient of HCl from 0 to 0.003 N. The eluate was fractionated every 2 mL.

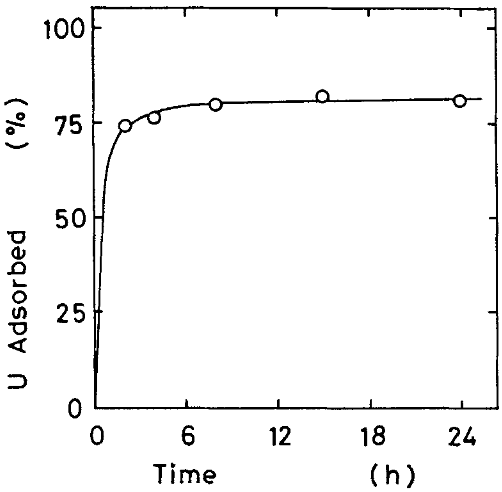


FIG. 2 Time course of uranium adsorption by immobilized persimmon tannin. Two milligrams of the adsorbent were suspended in 300 mL of the solution (pH 6) containing 10 ppm of uranium at 30°C.

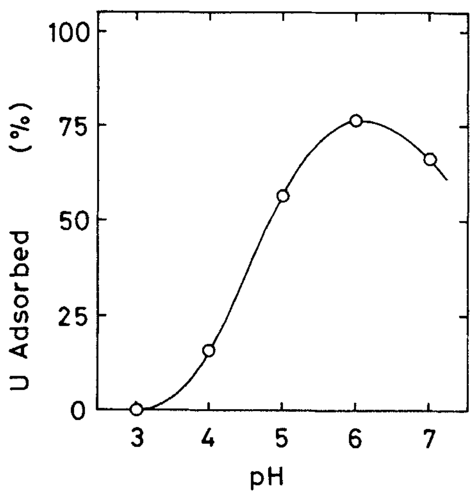


FIG. 3 Effect of pH on uranium adsorption by immobilized persimmon tannin. Two milligrams of the adsorbent were suspended in 300 mL of the solution containing 10 ppm of uranium for 2 hours at 30°C. The pH of the solution was adjusted with 0.1 N HCl or 0.1 N NaOH.

Basic Features of Uranium Adsorption by Immobilized Persimmon Tannin

To search for appropriate conditions for the recovery of uranium from aqueous systems, some factors affecting uranium adsorption by immobilized persimmon tannin were studied in detail.

Kinetics of Uranium Adsorption

As shown in Fig. 2, the amount of uranium adsorbed on the adsorbent increased very rapidly during the half hour following addition and reached a plateau within 2 hours, which indicates that the adsorption of uranium by immobilized persimmon tannin is very rapid and efficient.

Effect of pH on Uranium Adsorption

As shown in Fig. 3, maximum uranium uptake is observed at pH 6, below and above which uptake falls off rapidly.

Effect of External Uranium Concentration on Uranium Adsorption

As shown in Fig. 4, the amount of uranium adsorbed by the adsorbent (mg uranium/g adsorbent) increased as the external uranium concentration increased.

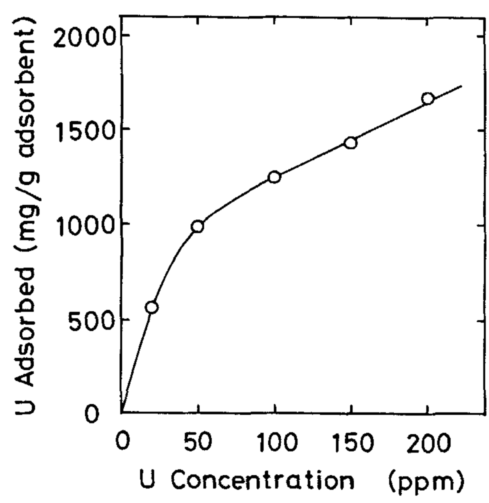


FIG. 4 Effect of external uranium concentration on uranium adsorption by immobilized persimmon tannin. Two milligrams of the adsorbent were suspended in 100 mL of the uranium solution (pH 6) for 16 hours at 30°C.

The relationship between the concentration of residual uranium in the solution and the amount of uranium adsorbed is shown in Fig. 5. It is obvious from this figure that the adsorption of uranium by the adsorbent obeys the following Freundlich isotherm: $C = KC_s^{1/n}$, where C indicates the amount of uranium adsorbed (mg U/g adsorbent), C_s is the residual uranium in the solution (ppm), and K and n (>1) are constants which depend on the adsorbent and temperature. The values of K and n were estimated to be 290 and 2.91, respectively.

Effect of Various Anions on Uranium Adsorption

As described above, uranium uptake by the adsorbent is little affected by any coexisting cations. The next step in our study was to determine whether or not various anions would interfere with the uptake of uranium by the adsorbent.

As shown in Fig. 6, bicarbonate, nitrate, sulfate, thiosulfate, and silicate ions scarcely affect uranium uptake by the adsorbent at pH 5, whereas the presence of fluoride ion in the uranium solution had a tendency to retard uranium uptake.

The inhibiting effect of fluoride ion on the uranium uptake is shown in Fig. 7. The adsorption of uranium by the adsorbent was markedly affected by sodium fluoride, as shown in this figure. It may be concluded from these results that the depression of uranium uptake is due to the formation of the competing fluoride complexes UO_2F^+ and UO_2F_2, as shown in

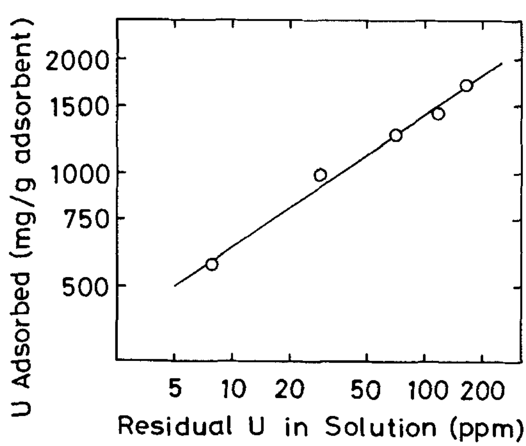


FIG. 5 Equilibrium isotherm of uranium adsorption by immobilized persimmon tannin. The experimental conditions are described in the legend to Fig. 4.

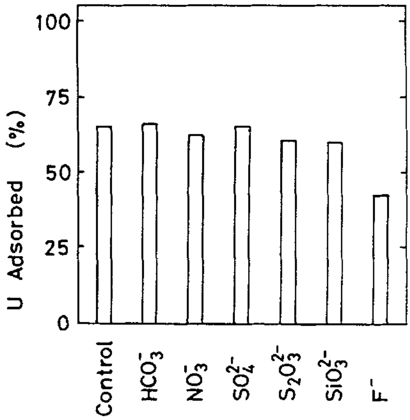


FIG. 6 Effect of various anions on uranium adsorption by immobilized persimmon tannin. Each anion (4×10^{-5} M) was added as its sodium salt to the solution containing 10 ppm of uranium. Two milligrams of the adsorbent were suspended for 1 hour at 30°C in 100 mL of the solution (pH 5) mentioned above.

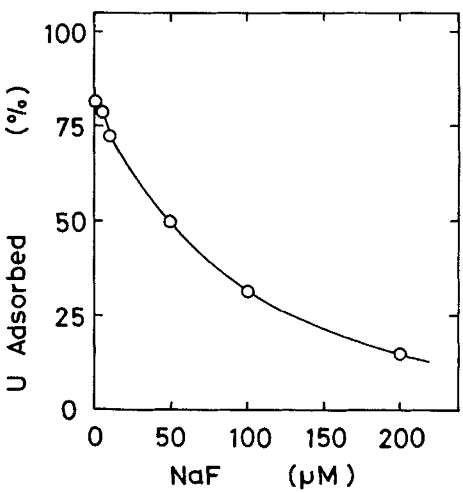


FIG. 7 Effect of fluoride ion on uranium adsorption by immobilized persimmon tannin. Two milligrams of the adsorbent were suspended in 100 mL of the uranium solution (pH 5, 10 ppm U) containing 0–200 μM of sodium fluoride for 1 hour at 30°C.

Table 4. The adsorbent apparently cannot take up such stable uranyl fluoride complexes.

On the other hand, uranium accumulation by the adsorbent was hardly affected by the coexistence of sodium carbonate at pH 5 (Figs. 6 and 8). However, it was affected markedly at pH 8, as shown in Fig. 8. As we previously reported (2, 10), uranium exists mainly as cations such as UO_2^{2+} and UO_2OH^+ in carbonate solution at pH 5, while at pH 8 it exists mainly as complex anions such as $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$. The adsorbent cannot take up these stable uranium complex anions at pH 8.

Maximum Capacity of Immobilized Persimmon Tannin to Accumulate Uranium

The maximum capacity of immobilized persimmon tannin to accumulate uranium was estimated from measurements in a column system. The uranium solution [pH 5.8, 1480 mL, 50 ppm U as $UO_2(NO_3)_2$] was passed through a column (diameter, 3 mm; bed volume, 0.4 mL) packed with immobilized persimmon tannin (18.6 mg dry weight basis) at a space velocity of 90 h^{-1}. As a result, 1.71 g uranium (14 mEq U) was adsorbed per gram of the adsorbent. The uranium accumulating capacity of this

TABLE 4

Chemical Species of Uranyl Ion in a Solution Containing Sodium Fluoride at pH 5[a]

Chemical species	Concentration of sodium fluoride ($\times 10^{-4}$ M)					
	0	0.05	0.1	0.5	1.0	2.0
$[UO_2^{2+}]$	35.46	34.45	33.45	26.06	18.79	10.30
$[UO_2OH^+]$	35.46	34.45	33.45	26.06	18.79	10.30
$[UO_2(OH)_2]$	2.23	2.17	2.11	1.65	1.18	0.65
$[UO_2(OH)_3^-]$	0.28	0.27	0.26	0.20	0.14	0.08
$[(UO_2)_2(OH)_2^{2+}]$	11.58	10.93	10.31	6.25	3.25	0.97
$[(UO_2)_3(OH)_4^{2+}]$	0.37	0.34	0.31	0.14	0.05	0.0
$[(UO_2)_3(OH)_5^+]$	14.56	13.35	12.22	5.77	2.16	0.35
$[(UO_2)_4(OH)_6^{2+}]$	0.0	0.0	0.0	0.0	0.0	0.0
$[(UO_2)_4(OH)_7^+]$	0.0	0.0	0.0	0.0	0.0	0.0
$[UO_2F^+]$	0.0	3.95	7.72	31.41	47.73	56.56
$[UO_2F_2]$	0.0	0.02	0.11	2.38	7.65	19.59
$[UO_2F_3^-]$	0.0	0.0	0.0	0.03	0.20	1.15
$[UO_2F_4^{2-}]$	0.0	0.0	0.0	0.0	0.0	0.0

[a] These values were calculated using Sillen's table (23).

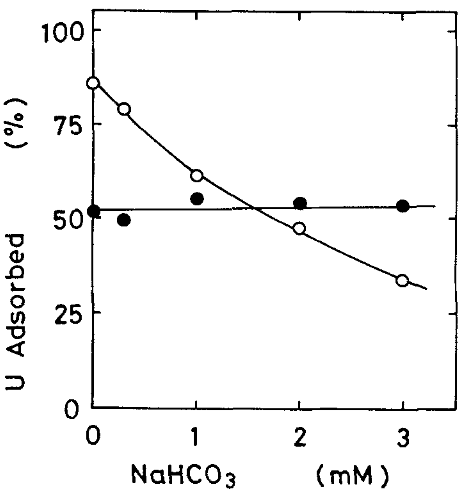


FIG. 8 Effect of carbonate ion on uranium adsorption by immobilized persimmon tannin. Two milligrams of the adsorbent were suspended for 1 hour at 30°C in 100 mL of the uranium solution [pH 5 (●), pH 8 (○), 10 ppm U] containing 0–3 μM of sodium hydrogen carbonate.

adsorbent is several times that of commercially available chelating resins (2–3 mEq/g).

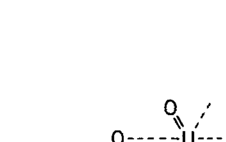
As described above, we found that immobilized persimmon tannin has an extremely high ability to accumulate uranium. It seems reasonable to assume that the high affinity to uranium of immobilized persimmon tannin is due to the following: Persimmon tannin has multiple adjacent hydroxy groups, such as catechol and pyrogallol groups, which are attractive functional groups for uranium uptake, and the uranyl ion is coordinated by these polyhydroxyphenyl groups. Previously, we have shown that some biosubstances having multiple adjacent hydroxy groups, such as 1,2-dihydroxyanthraquinone (8), quercetin and morin (9), and Chinese gallotannin (10), can accumulate large amounts of uranium. Furthermore, Hancock and Martell suggested that the negatively charged oxygen donors existing in a compound such as catecholate are attractive ligands for uranium uptake (22). It may be considered from these facts that adjacent hydroxy groups are the most attractive groups for uranium uptake. Immobilized persimmon tannin has a favorable steric structure for uranium binding. In addition, this adsorbent is extremely hydrophilic.

Matsuo et al. reported that persimmon tannin consists of catechin, catechin-3-gallate, gallocatechin, and gallocatechin-3-gallate at the ratio of

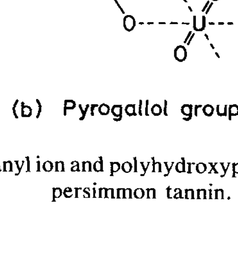
1:1:2:2 (14), which means that persimmon tannin has seven pyrogallol groups and two catechol groups in a molecular unit (MW = 2248). If we assume that each pyrogallol group combines with two uranyl ions and that each catechol group combines with one uranyl ion, as shown in Fig. 9, the number of ligands in a molecular unit of persimmon tannin is 16. Therefore, the chelate-forming capacity of persimmon tannin for uranium is estimated to be 7.1×10^{-3} mol/g. Thus, 1 g immobilized persimmon tannin should adsorb 1.7 g uranium. This theoretical value is in fair agreement with the experimental value obtained.

Chemical State of Uranium Adsorbed on Immobilized Persimmon Tannin

To investigate the chemical state of uranium adsorbed on immobilized persimmon tannin, the infrared (IR) spectra were measured. The IR spectra of immobilized persimmon tannin before and after adsorption of uranium are shown in Fig. 10. The IR spectrum of the immobilized persimmon tannin adsorbed uranyl ion has an absorption peak of the stretch vibration of O=U=O (910 cm^{-1}). These results indicate that the uranium adsorbed



(a) Catechol group



(b) Pyrogallol group

FIG. 9 Chelation between uranyl ion and polyhydroxyphenyl group existing in immobilized persimmon tannin.

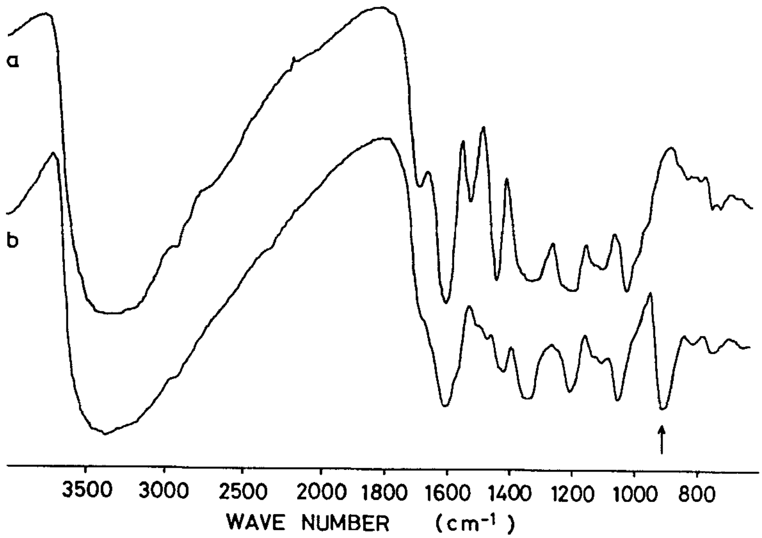


FIG. 10 Infrared spectra of immobilized persimmon tannin, before (a) and after (b) the adsorption of uranium. Two milligrams of the adsorbent were suspended in 100 mL of the solution (pH 6) containing 10 ppm of uranium for 1 hour at 30°C. The arrow shows the absorption peak of the stretching vibration of O═U═O.

on immobilized persimmon tannin exists in the form of the UO_2^{2+} ion species.

Repetition Test of Uranium Adsorption–Desorption Cycle

As mentioned above, immobilized persimmon tannin has an extremely high ability to accumulate uranium in both batch and column systems. To obtain basic information on the recovery of uranium using immobilized persimmon tannin, a repetition test of the uranium adsorption–desorption cycle was carried out.

In a preliminary test it was recognized that the uranium retained on the adsorbent can be quantitatively and easily desorbed by washing with dilute (0.003–0.01 N) HCl solution (Table 5), so we used 0.01 N HCl solution as the desorbent in the following experiment.

As shown in Fig. 11, the ability of the adsorbent to accumulate uranium did not decrease after 10 repetitions of the adsorption–desorption cycles in a column system. Thus, immobilized persimmon tannin has excellent handling characteristics and can be used repeatedly in the adsorption–desorption cycle.

TABLE 5
Desorption of Uranium Adsorbed on Immobilized Persimmon Tannin[a]

Eluate	U desorbed (%)
0.001 N HCl	96.0
0.003 N	100.0
0.01 N	100.0

[a] Ten milligrams of the adsorbent were suspended in 100 mL of the solution (pH 6) containing 10 ppm of uranium for 1 h at 30°C. Uranium adsorbed on the adsorbent was desorbed with 20 mL of each eluate.

Thorium Accumulation by Immobilized Persimmon Tannin

We have also found that this adsorbent has a high affinity for thorium as well as for uranium. As shown in Fig. 12, the adsorbent (18.4 mg dry weight basis) can recover thorium almost quantitatively from a solution containing 9.3 ppm thorium [pH 3, 100 mL, thorium as $Th(NO_3)_4$] during 1 hour.

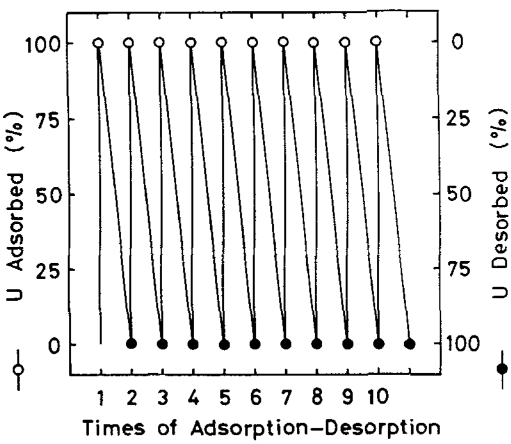


FIG. 11 Repetition test of uranium adsorption (○)–desorption (●) by immobilized persimmon tannin. Thirty milliliters of the solution (pH 6) containing 10 ppm of uranium were adsorbed on a column (diameter, 7 mm; bed volume, 0.4 mL) of the adsorbent. The retained uranium was desorbed with 20 mL of 0.01 N HCl.

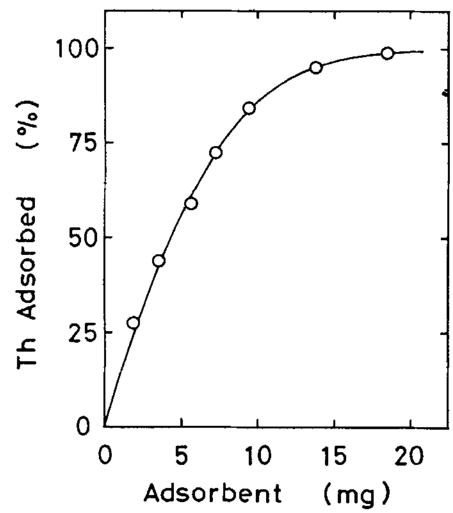


FIG. 12 Effect of the amount of adsorbent on thorium adsorption by immobilized persimmon tannin. The desired amounts of the adsorbents were suspended in 100 mL of the solution (pH 3) containing 9.28 ppm of thorium for 1 hour at 30°C.

Table 6 indicates the selective adsorption between uranium and thorium at pH 3.5, which shows that immobilized persimmon tannin accumulates thorium far more readily than uranium at this pH value.

The thorium retained on the adsorbent can be quantitatively and easily desorbed by washing with dilute HCl or H_2SO_4 solution (Table 7). As shown in Fig. 13, immobilized persimmon tannin can be used repeatedly in the thorium adsorption–desorption cycle.

In summary, it has been demonstrated that immobilized persimmon tannin is useful for the recovery and removal of uranium and thorium

TABLE 6
Selective Adsorption of Uranium and Thorium by Immobilized Persimmon Tannin[a]

U adsorbed (%)	Th adsorbed (%)
25.5	93.1

[a] Ten milligrams of the adsorbent were suspended in 100 mL of the solution (pH 3.5) containing 4×10^{-5} M of uranium and thorium for 1 hour at 30°C.

TABLE 7
Desorption of Thorium Retained on Immobilized Persimmon Tannin[a]

Eluate	Th desorbed (%)
0.001 N HCl	75.5
0.003 N HCl	95.1
0.01 N HCl	98.2
0.5 N HCl	98.5
0.1 N H_2SO_4	97.6
0.5 N H_2SO_4	97.7
0.1 M Na_2CO_3	0
0.5 M Na_2CO_3	0

[a] Eighteen milligrams of the adsorbent were suspended in 100 mL of the solution (pH 3.5) containing 10 ppm of thorium for 1 hour at 30°C. Thorium adsorbed on the adsorbent was desorbed with 20 mL of each eluate.

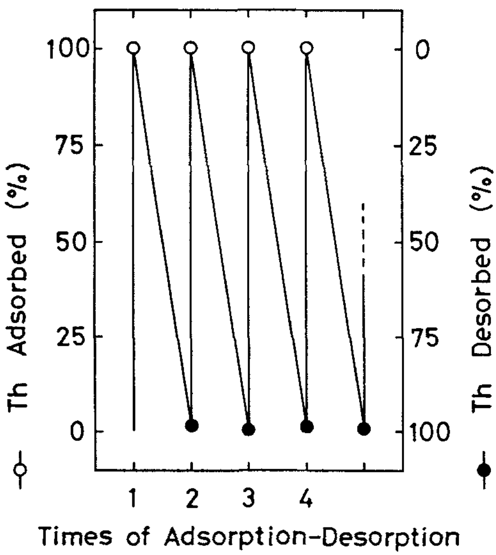


FIG. 13 Repetition test of thorium adsorption (○)–desorption (●) by immobilized persimmon tannin. Fifty milliliters of the solution (pH 3.5) containing 10 ppm of thorium were adsorbed on a column (diameter, 8 mm; bed volume, 2.5 mL) of the adsorbent. The retained thorium was desorbed with 25 mL of 0.1 N HCl.

from aqueous systems. The uranium retained on immobilized persimmon tannin can be quantitatively and easily eluted with a very dilute acid, and the adsorbent can thus be easily recycled in the adsorption–desorption process.

On the basis of these results, further studies will be undertaken to devise a practical approach to recover the nuclear elements that may be present in nuclear fuel refining and manufacturing wastewater, mine wastewater, and other water resources.

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