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Recovery of Uranium by Immobilized Polyhydroxyanthraquinone

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Abstract

Nine species of polyhydroxyanthraquinone and two of polyhydroxynaphthoquinone were screened to determine which have the greatest ability to accumulate uranium. 1,2-Dihydroxyanthraquinone and 3-amino-1,2-dihydroxyanthraquinone have extremely high accumulation abilities. To improve the adsorbing characteristics of these compounds, we tried to immobilize these compounds by coupling with diazotized aminopolystyrene. The immobilized 1,2-dihydroxyanthraquinone 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. This adsorbent can recover uranium almost quantitatively from natural seawater. Almost all uranium adsorbed is desorbed with a solution of 1 *N* HCl. Thus, immobilized 1,2-dihydroxyanthraquinone can be used repeatedly in the adsorption–desorption process.

INTRODUCTION

In recent years the recovery of uranium from aqueous systems, notably seawater, has become the center of wide interest because a shortage of uranium is expected by the end of the century. Accordingly, various attempts have been made by many researchers to establish an effective method of uranium recovery from seawater (*1*). On the other hand, attention has been focused on the removal of uranium that may be present in industrial effluents, mine wastewater, and other waste sources in relation to the pollution of the natural environment (*2*).

We have hitherto investigated systematically the uranium accumulation from aqueous systems by using various microorganisms (*3–7*) and

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biological substances (*8–10*). Our previous studies have shown that *Chlorella regularis* (*3*), one of the freshwater green microalgae, and *Streptomyces viridochromogenes* (*7*), one of the actinomycetes group of microorganisms, have the ability to absorb large amounts of uranium from aqueous systems. Synthesizing these experimental results, we suggested that the uptake of uranium into these microbial cells is not directly mediated by any metabolic process, but almost completely dependent upon physicochemical adsorption on the cell components.

In one of our studies (*8*), various biological substances, such as chitin, chitosan, alginate, and pectinate, were screened to determine their abilities to accumulate uranium. As a result, extremely high abilities to accumulate uranium were found in polycarboxylic acids, phosphorylated polyscaccharides, and polyphenol compounds. Analyzing these results systematically, we presume that carboxyl, phosphoryl, and hydroxyl groups existing in the biological substances play a very important role in uranium binding.

Consequently, in this paper, to screen polyphenol compounds which have the abilities to accumulate large amounts of uranium from seawater, we extend our investigation of uranium uptake to polyhydroxyanthraquinone compounds. As a result, we found that polyhydroxyanthraquinones, such as 1,2-dihydroxyanthraquinone and 1,2,7-trihydroxyanthraquinone, have a high adsorbing power for uranium. Furthermore, to improve the adsorbing characteristics of polyhydroxyanthraquinone compounds having high adsorbing abilities for uranium, we have tried to immobilize these compounds by coupling them with diazotized aminopolystyrene. In this paper, we discuss in detail the basic features of uranium accumulation by immobilized 1,2-dihydroxyanthraquinone.

MATERIALS AND METHODS

Materials

1,2-Dihydroxyanthraquinone was obtained from Yoneyama Chemicals Co. Ltd., 1,4-dihydroxyanthraquinone and 1,5-dihydroxyanthraquinone from Tokyo Kasei Co. Ltd., 1,8-dihydroxyanthraquinone and 1,2,4-trihydroxyanthraquinone from Wako Pure Chemicals Ind. Ltd., 1,2,7-trihydroxyanthraquinone from ICN Pharmaceuticals Inc., 5-hydroxynaphthoquinone and 1-amino-4-hydroxyanthraquinone from Aldrich Chemicals Co. Inc., 5,8-dihydroxynaphthoquinone from Fluka AG Chemische Fabrik, and 1,2,5,8-tetrahydroxyanthraquinone from Nakarai Chemicals Co. Ltd. 3-Amino-1,2-dihydroxyanthraquinone was prepared from 1,2-dihydroxyanthraquinone by the dichlorobenzene procedure (*11*).

Immobilization of 1,2-Dihydroxyanthraquinone

Polystyrene (molecular weight 70,000–100,000) was nitrated with fuming HNO_3 to the extent of approximately one nitro group per aromatic ring, and then nitropolystyrene was reduced to aminopolystyrene by $Na_2S_2O_4$ in NaOH solution at 90–100°C (*12*). The aminopolystyrene was diazotized by $NaNO_2$ in 4 *N* HCl and was coupled with 1,2-dihydroxyanthraquinone in 1 *N* NaOH solution at 0°C. The resulting adsorbents were washed thoroughly with 1 *N* NaOH solution, 1 *N* HCl, followed by deionized water. The adsorbents so obtained had a dark red color and 1.5×10^{-3} mol of quinone per gram. The degree of substitution was found to be 0.285.

1,2,7-Trihydroxyanthraquinone has also been used as a coupling component with the same diazonium polymer.

Adsorption Experiments

Adsorption of Uranium from Seawater

Desired amounts of adsorbents were suspended in 100 mL seawater supplemented with 10 ppm uranium as $UO_2(NO_3)_2$. The pH of the seawater was adjusted to the desired value with 0.1 *N* HCl and 0.1 *N* NaOH solution. In the experiment on pH effect, the pH of the seawater was controlled by pH controller for the time required. Unless otherwise stated, the adsorption experiments were conducted by stirring continuously at 30°C at a pH value of 8.0 for 1 h. After adsorption, the adsorbents were filtered off and the residual uranium in the filterate was determined by spectrophotometry using Arsenazo III (*13*).

Selective Adsorption of Heavy Metal Ions

Twenty-six milligrams of the adsorbent were suspended in 100 mL of the solution (pH 5) containing equivalent concentrations of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and UO_2^{2+}. Each cation was given as its nitrate in the concentration of 4×10^{-5} *M*. After 30 min stirring at 30°C, the adsorbents were filtered off and the residual metal ions, except uranyl ion, in the filtrate were determined by atomic absorption spectroscopy with an Hitachi 180-70A. Uranyl ion was determined as described above.

Recovery of Uranium from Natural Seawater

Column System. Four liters of natural seawater sampled at the coast of Miyazaki were adsorbed on a column (diameter 10 mm, bed volume 2.5 mL) of the adsorbent (dry weight 220 mg) at space velocity (S.V.) 23–24 h^{-1}. The uranium adsorbed on the adsorbent was determined by neutron activation analysis. The detailed procedure of this method was described in the preceding papers (*6, 8, 9*).

Batch System. One and a half grams of the adsorbent were suspended in 5 L natural seawater for 24 to 72 h at 30°C. After adsorption, the adsorbents were filtered off and the residual uranium in the filtrate was determined by spectrophotometry using Arsenazo III (*14*).

Recovery of Uranium from Uranium Refining Wastewater

One liter of uranium-refining wastewater sampled at the Ningyo-toge Station of the Power Reactor and Nuclear Fuel Development Corporation was adsorbed on a column (diameter 10 mm, bed volume 2.5 mL) of the adsorbent (dry weight 200 mg) at S.V. 60 h^{-1}. The uranium concentration of the wastewater was found to be 13.6 ppb. The uranium adsorbed on the adsorbent was determined by neutron activation analysis.

RESULTS AND DISCUSSION

Adsorbing Abilities of Polyhydroxyquinone Compounds to Uranium from Seawater

The present experiment was carried out to screen polyhydroxyquinone compounds which have high abilities to adsorb uranium from seawater. Nine species of polyhydroxyanthraquinone compounds and two species of polyhydroxynaphthoquinone, shown in Fig. 1 and Table 1, were

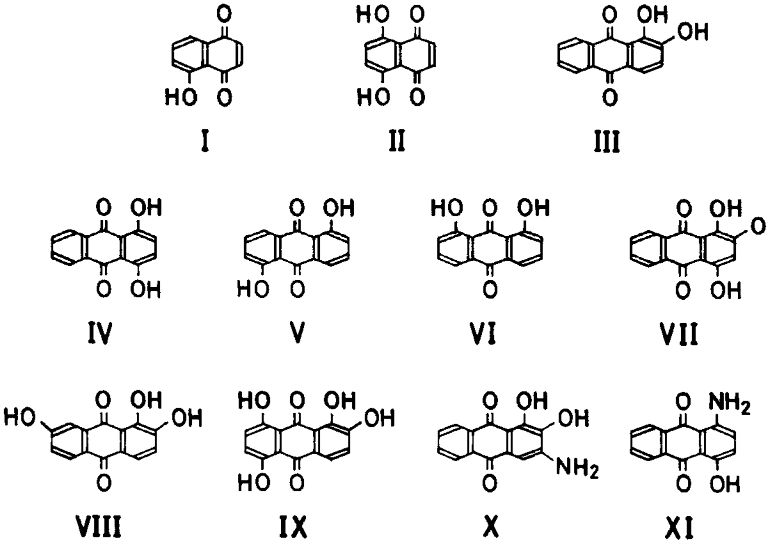


FIG. 1. Chemical structures of polyhydroxyanthraquinones and polyhydroxynaphthoquinones used in uranium adsorption.

TABLE 1

Adsorption of Uranium from Seawater by Polyhydroxyquinones[a]

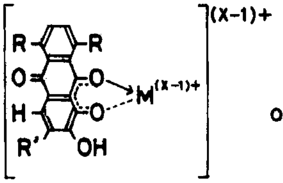
Quinones	U adsorbed (%)
5-Hydroxynaphthoquinone (I)	0.7
5,8-Dihydroxynaphthoquinone (II)	1.7
1,2-Dihydroxyanthraquinone (III)	99.4
1,4-Dihydroxyanthraquinone (IV)	0.8
1,5-Dihydroxyanthraquinone (V)	2.9
1,8-Dihydroxyanthraquinone (VI)	0.9
1,2,4-Trihydroxyanthraquinone (VII)	56.3
1,2,7-Trihydroxyanthraquinone (VIII)	98.4
1,2,5,8-Tetrahydroxyanthraquinone (IX)	31.5
3-Amino-1,2-dihydroxyanthraquinone (X)	98.5
1-Amino-4-hydroxyanthraquinone (XI)	1.6

[a] Fifty milligrams of quinones were suspended in 100 mL seawater supplemented with 10 ppm uranium (pH 8) for 1 h at 30°C.

suspended in 100 mL seawater supplemented with 10 ppm uranium for 1 h.

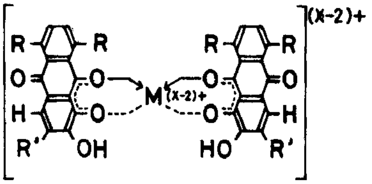
Of the compounds tested, extremely high adsorbing abilities were found in 1,2-dihydroxyanthraquinone (III, alizarin), 1,2,7-trihydroxyanthraquinone (VIII, anthrapurpurin), and 3-amino-1,2-dihydroxyanthraquinone (X, alizarin maroon) (Table 1). However, 1,2,4-trihydroxyanthraquinone (VII, purpurin) and 1,2,5,8-tetrahydroxyanthraquinone (IX, quinalizarin), two members of compounds analogous to alizarin (III), had relatively low abilities to adsorb uranium, while others, 1,4-dihydroxyanthraquinone (IV, quinizarin), 1,5-dihydroxyanthraquinone (V, anthrarufin), 1,8-dihydroxyanthraquinone (VI, chrysazin), 1-amino-4-hydroxyanthraquinone (XI), and all species of naphthoquinones tested (I, II), hardly adsorbed uranium from seawater. Of particular interest in regard to this discussion is the adsorbing ability of different polyhydroxyanthraquinone compounds in the adsorption of uranium. As mentioned above, the adsorbing power for uranium differs markedly with different species of the polyhydroxyquinone compound group. Compounds having the ability to adsorb uranium, such as III, VII, VIII, IX, and X, have two adjacent hydroxy groups in their molecule, while compounds having low adsorbing ability, such as IV, V, VI, and XI, do not have these hydroxy groups (Fig. 1).

From the above results and the chemical structures of the compounds tested, it is presumed that the uranyl ion is coordinated by the adjacent hydroxy groups existing in polyhydroxyanthraquinone compounds. Idriss et al. (*15*) supposed the model for complexes of uranium and polyhydroxyanthraquinone to be



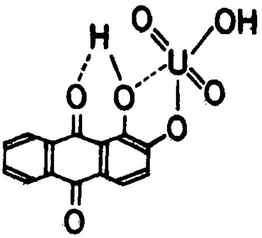
1:1 complex

or



1:2 complex

($R = H$ or $NHCH_3C_6H_4SO_3H$, $R' = H$ or NH_2). The proton in the 1-hydroxy group combines with the neighboring carbonyl oxygen through the hydrogen bond, and this hydroxy group does not easily dissociate. On the other hand, the 2-hydroxy group can easily dissociate (pK_a of 1-hydroxy and 2-hydroxy groups of the 1,2-dihydroxyanthraquinone-3-sulfonate complex are 10.72 and 5.39 (*16*)), and the dissociated oxyanion of the 2-hydroxy group must be a very important ligand for the uranyl ion:



These investigations showed that the two adjacent hydroxy groups play a very important role in uranium adsorption by these adsorbents.

Adsorption of Uranium by Immobilized Polyhydroxyanthraquinones

As described in the above section, some compounds of polyhydroxyanthraquinone with 1,2-dihydroxy groups, such as 1,2-dihydroxyanthraquinone (III) and 3-amino-1,2-dihydroxyanthraquinone (X), have excellent high abilities to adsorb uranium. These compounds are commonly available as synthetic dyes and inexpensive products, but when they are used as uranium adsorbents, they have the disadvantage that they are gradually leached by seawater over a long period. Furthermore, these compounds are not suitable for use in a column system because they cause plugging. To overcome these deficiencies, these quinone compounds were immobilized. We obtained an adsorbent by coupling 1,2-dihydroxyanthraquinone with diazotized aminopoly-

TABLE 2
Adsorption of Uranium from Seawater by Immobilized Polyhydroxyanthraquinones[a]

	Dry weight (mg)	U adsorbed	
		%	mg/g adsorbent
1,2-Dihydroxyanthraquinone	18.1	74.9	43.5
1,2,7-Trihydroxyanthraquinone	22.3	83.8	40.0

[a] About 20 mg of adsorbents were suspended in 100 mL seawater (pH 8) supplemented with 10 ppm uranium for 1 h at 30°C.

styrene. Additionally, 1,2,7-trihydroxyanthraquinone has been used as a coupling component with the same diazonium polymer. As shown in Table 2, after immobilization 1,2-dihydroxyanthraquinone and 1,2,7-trihydroxyanthraquinone still have a high adsorbing power for uranium.

To search for appropriate conditions for the recovery of uranium from aqueous systems, the basic features of uranium adsorption by immobilized 1,2-dihydroxyanthraquinone were studied in detail in the following experiments.

Selective Adsorption of Metal Ions by Immobilized 1,2-Dihydroxyanthraquinone

To determine which heavy metal ion can be most readily adsorbed by the immobilized 1,2-dihydroxyanthraquinone, we examined the selective adsorption of heavy metal ions by the 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 3, the relative order of magnitude of metal ions adsorbed by the immobilized 1,2-dihydroxyanthraquinone appeared to be $UO_2^{2+} > Cu^{2+} \gg Ni^{2+} > Cd^{2+}, Co^{2+}, Zn^{2+} > Mn^{2+}$. These results show that the adsorbent takes up far larger amounts of uranyl and copper ions than other metal ions. It is apparent from these results that the immobilized 1,2-dihydroxyanthraquinone has a high ability to adsorb uranium selectively from aqueous systems.

TABLE 3
Selective Adsorption of Heavy Metal Ions by the Immobilized 1,2-Dihydroxyanthraquinone[a]

			Metal adsorption ratio[b]			
Mn	Co	Ni	Cu	Zn	Cd	U
10.3	16.1	22.2	84.9	15.1	17.1	93.6

[a] The adsorbent (26.2 mg dry basis) was suspended in 100 mL of the solution (pH 5) containing 4 × 10^{-5} *M* of heavy metal ions for 30 min at 30°C.

[b] ((Initial metal concentration − residual metal concentration in the solution)/initial metal concentration in the solution) × 100.

Basic Features of the Adsorption of Uranium from Seawater by Immobilized 1,2-Dihydroxyanthraquinone

As described in the above section, the immobilized 1,2-dihydroxyanthraquinone has an extremely high ability to accumulate uranium. In preceding papers we found that the accumulation of uranium by various microorganisms (*3, 6, 7*) and biological substances (*9, 10*) is markedly affected by such factors as retention time, biomass amount, reaction pH, and co-existing ions. Consequently, some factors affecting uranium adsorption from seawater by immobilized 1,2-dihydroxyanthraquinone were investigated in detail.

Effect of pH on Uranium Adsorption

The effect of pH on the adsorption of uranium by the adsorbent is shown in Fig. 2. The amounts of uranium adsorbed are highest at around pH 6 and decrease below and above pH 6. At pH 8, which is almost the pH of natural seawater, 1 g of the adsorbent can still adsorb 26 mg uranium, 60% of the uranium adsorbed on the adsorbent at pH 6.

Thus, the adsorption of uranium by the immobilized 1,2-dihydroxyanthraquinone is markedly affected by the pH of seawater, but its adsorbing ability is still relatively high in the pH region of natural seawater.

Effect of the Amount of Adsorbent on Uranium Adsorption

As shown in Fig. 3, the amount of uranium adsorbed on the adsorbent (mg uranium/g adsorbent) decreased as the amount of the adsorbent increased, whereas the total amount of uranium adsorbed increased. Forty milligrams of adsorbent can almost quantitatively adsorb uranium existing in seawater.

Effect of Carbonate Ion on Uranium Adsorption

As reported previously, *Chlorella* cells (*3*), actinomycetes cells (*7*), and phosphorylated polysaccharides (*10*) can take up a great quantity of uranium from uranium solution. However, it was shown that in the presence of carbonate ions the uranium solution had a tendency to retard

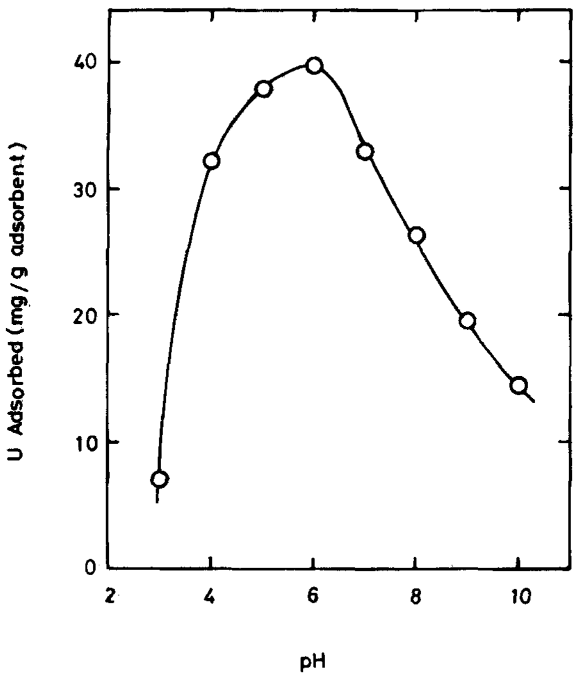


FIG. 2. Effect of pH on the adsorption of uranium from seawater by immobilized 1,2-dihydroxyanthraquinone. Thirty milligrams of the adsorbent were suspended in 100 mL seawater supplemented with 10 ppm uranium for 1 h at 30°C. The pH of the seawater was kept stationary with 0.1 *N* HCl and 0.1 *N* NaOH solutions.

uranium uptake because of the stable complex ion $UO_2(CO_3)_3^{4-}$ formation. The purpose of the present experiment was to determine whether or not carbonate ion in seawater interferes with the adsorption of uranium by immobilized 1,2-dihydroxyanthraquinone.

As shown in Fig. 4, the adsorption of uranium by the adsorbent was hardly affected by sodium hydrogen carbonate in the concentration range from 0 to 3 m*M*. Since the carbonate concentration in natural seawater is usually 2.34 m*M*, carbonate ion at this level has no effect on the uranium uptake by immobilized 1,2-dihydroxyanthraquinone. From these results it is evident that the adsorption of uranium by immobilized 1,2-dihydroxyanthraquinone is hardly affected by carbonate ion.

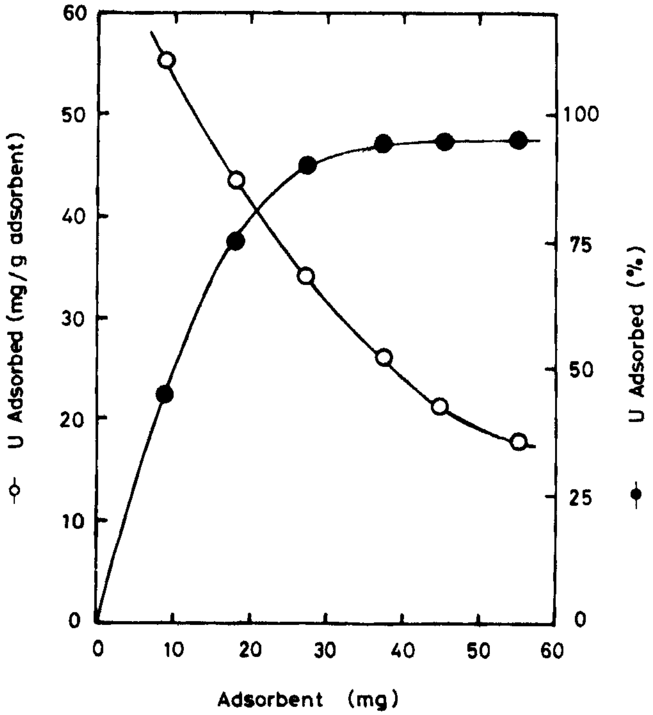


FIG. 3. Effect of the amount of adsorbent on the adsorption of uranium from seawater. Desired amounts of the adsorbent were suspended in seawater for 1 h. Other experimental conditions were the same as described in Fig. 2.

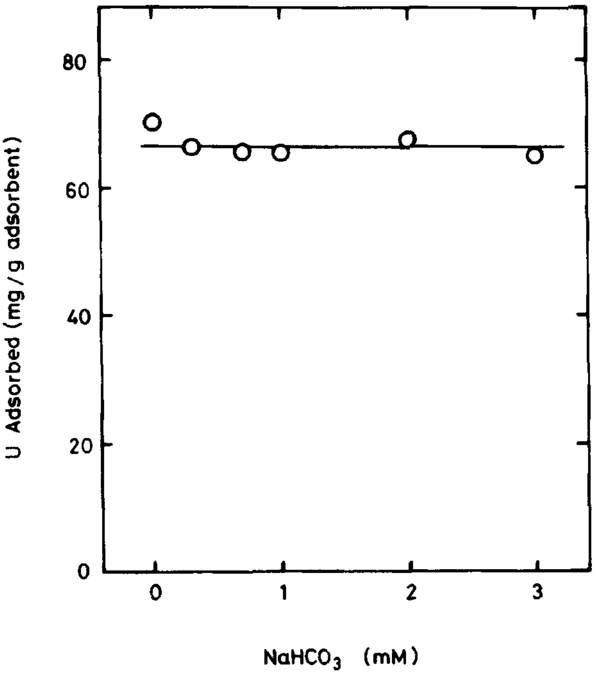


FIG. 4. Effect of carbonate ion on the adsorption of uranium by immobilized 1,2-dihydroxyanthraquinone. Fifteen milligrams of the adsorbent were suspended in 100 mL of a solution (pH 8) containing 10 ppm uranium and the desired amounts of sodium hydrogencarbonate for 1 h at 30°C.

Time Course of Uranium Adsorption

It is apparent from Fig. 5 that the amounts of uranium adsorbed on the adsorbent increase very rapidly during the first hour following the addition of uranium and reach a plateau within 4 h.

Desorption of Uranium Adsorbed by Immobilized 1,2-Dihydroxyanthraquinone

As mentioned above, immobilized, 1,2-dihydroxyanthraquinone can adsorb large amounts of uranium from seawater. In order to obtain basic information on the recovery of uranium from seawater by the adsorbent, we determined the optimal eluate for uranium desorption.

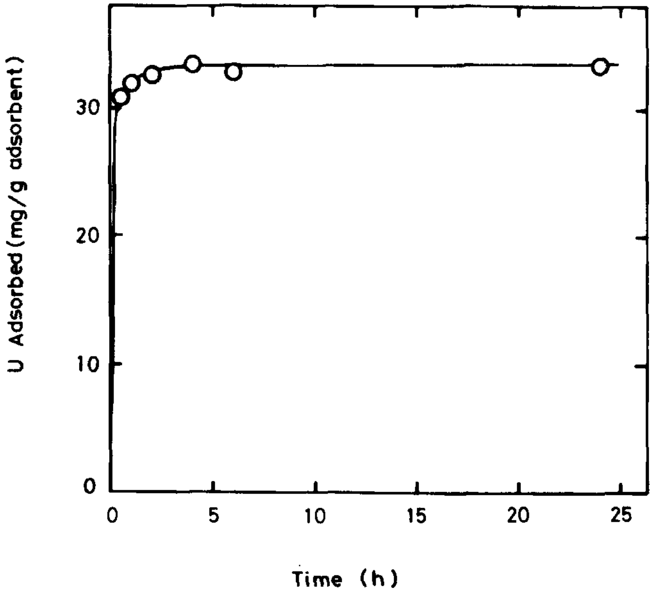


FIG. 5. Time course of the adsorption of uranium from seawater by immobilized 1,2-dihydroxyanthraquinone. Thirty milligrams of the adsorbent were suspended in 100 mL seawater (pH 8) supplemented with 10 ppm uranium at 30°C.

TABLE 4

Desorption of Uranium Adsorbed by the Immobilized 1,2-Dihydroxyanthraquinone[a]

Eluate	U adsorbed (%)
0.01 *M* $(NH_4)_2CO_3$	4.1
0.1 *M* $(NH_4)_2CO_3$	62.1
0.01 *M* Na_2CO_3	13.1
0.1 *M* Na_2CO_3	71.3
1 *M* Na_2CO_3	94.3
0.01 *N* HCl	22.0
0.1 *N* HCl	84.8
1 *N* HCl	100.0

[a] Twenty-five milligrams of the adsorbent were suspended in 50 mL seawater (pH 8) supplemented with 10 ppm uranium for 1 h at 30°C. After adsorption, the uranium adsorbed was desorbed with 12.5 mL of each eluate by shaking for 1 h.

The adsorbent adsorbed uranium was washed with the various eluates shown in Table 4. As shown in Table 4, almost all the uranium adsorbed onto the adsorbent can be desorbed by washing with 1 *N* HCl.

Repetition Test of Uranium Adsorption-Desorption Cycle

Along with the results reported in the above sections, a repetition test of the uranium adsorption-desorption cycle by immobilized 1,2-dihydroxyanthraquinone was made with 1 *N* HCl as the desorbent in a column system. Figure 6 shows that the ability of the adsorbent to adsorb uranium from seawater did not decrease after 10 repetitions of the adsorption-desorption cycle. Thus, 1,2-dihydroxyanthraquinone is more

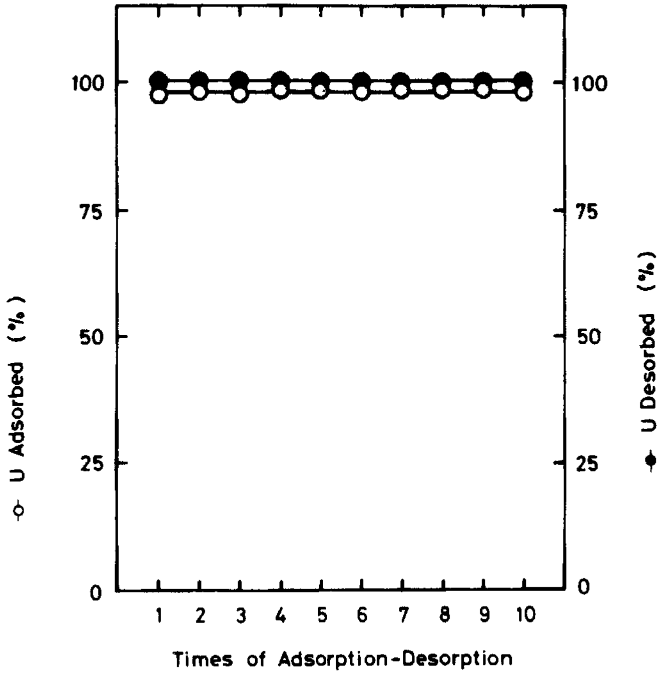


FIG. 6. Repetition test of uranium adsorption (○)-desorption (●) by immobilized 1,2-dihydroxyanthraquinone. Ten milliliters of seawater (pH 8) supplemented with 10 ppm uranium were adsorbed on a column (diameter 10 mm, bed volume 2.5 mL) of the adsorbent (dry weight 200 mg) at S.V. 34-40 h^{-1}. The uranium adsorbed was desorbed with 5 mL of 1 *N* HCl at S.V. 30-35 h^{-1}.

TABLE 5
Recovery of Uranium from Natural Seawater[a] by the Immobilized 1,2-Dihydroxyanthraquinone

System	U adsorbed (μg)	U recovery (%)
Column system[b]	11.2	93.3
Batch system:[c] 24 h	15.1	97.4
72 h	15.1	97.4

[a] The concentration of uranium in natural seawater sampled at the coast of Miyazaki was found to be 3.0 ppb.

[b] Column system: Four liters of natural seawater were adsorbed on a column (diameter 10 mm, bed volume 2.5 mL) of the adsorbent (dry weight 220 mg) at S.V. 23–24 h^{-1}.

[c] Batch system: One and a half grams of the adsorbent were suspended in 5 L natural seawater for 24 or 72 h at 30°C.

stable after immobilization in polystyrene. Furthermore, the immobilized adsorbent acquires better mechanical properties and can be used repeatedly in the adsorption–desorption cycle.

Recovery of Uranium from Natural Seawater by Immobilized 1,2-Dihydroxyanthraquinone

On the basis of the results described above, an attempt was made to recover uranium from natural seawater using the immobilized 1,2-dihydroxyanthraquinone. As shown in Table 5, an almost quantitative recovery of the uranium from natural seawater can be achieved by using this adsorbent.

TABLE 6
Recovery of Uranium from Uranium Refining Wastewater by the Immobilized 1,2-Dihydroxyanthraquinone[a]

U adsorbed (μg)	U recovered (%)
10.1	74.3

[a] One liter of the uranium refining wastewater sampled at the Ningyo-toge Station of the Power Reactor and Nuclear Fuel Development Corporation was adsorbed on a column (diameter 10 mm, bed volume 2.5 mL) of the adsorbent (dry weight 200 mg) at S.V. 60 h^{-1}. The uranium concentration of the wastewater was found to be 13.6 ppb.

These results show that immobilized 1,2-dihydroxyanthraquinone has an extremely high adsorbing power for uranium existing in natural seawater.

Recovery of Uranium from Uranium Refining Wastewater by Immobilized 1,2-Dihydroxyanthraquinone

As mentioned above, immobilized 1,2-dihydroxyanthraquinone has an excellent ability to recover uranium from natural seawater. To extend the application of this immobilized compound as an adsorbent, removal tests for uranium existing in uranium refining wastewater were carried out. Table 6 shows that the adsorbent can recover about 74% uranium from uranium refining wastewater containing 13.6 ppb uranium.

As described above, immobilized 1,2-dihydroxyanthraquinone has a high ability to recover uranium existing in seawater and industrial wastewater. On the basis of these results, further studies will be undertaken to devise a practical approach to remove and recover uranium from aqueous systems.

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