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Effect of Shape and Size of Amidoxime-Group-Containing Adsorbent on the Recovery of Uranium from Seawater

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Abstract

An amidoxime-group-containing adsorbent for the recovery of uranium from seawater was synthesized by radiation-induced graft polymerization of acrylonitrile onto polypropylene fiber of round and cross-shaped sections. The tensile strength and elongation of the synthesized adsorbent, both of which were one-half those of the raw material, were not affected by the shape of the fiber. The deterioration of the adsorption ability induced by immersing the adsorbent in HCl was negligible because of the short immersion time required for the desorption with HCl. The concentration factors for uranium and transition metals in 28 days were in the order of 10^5, while those for alkali metals and alkaline earth metals were in the order 10^{-1}–10^1. The recovery of uranium with the cross-shaped adsorbent was superior to that of the round-shaped one. XMA line profiles show that the distribution of uranium is much restricted to the surface layer when compared with that of alkaline earth metals. Diminishing the diameter or increasing the surface area was effective for increasing the adsorption of uranium.

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INTRODUCTION

Separation of uranium from seawater has been studied with various kinds of organic adsorbents (*1–10*). Among them, amidoxime-group-containing polymeric adsorbents are noted because of the high recovery of uranium and the large adsorption rate. In our previous studies (*11–14*) a new type of amidoxime-group-containing adsorbent was synthesized by radiation-induced graft polymerization of acrylonitrile (AN) onto polypropylene (PP) fiber, followed by amidoximation with hydroxylamine. The adsorbent obtained possesses not only a high adsorption ability for uranium from seawater but also sufficient mechanical and chemical stabilities because the initial strength of PP fiber was scarcely deteriorated by this synthesizing method.

In order to obtain a better adsorbent, however, an extensive study on the relation between the synthetic condition and the adsorption ability is necessary. It was found that some of the controlling factors on adsorption include the amount of functional group, its distribution inside the adsorbent, the presence of hydrophilic functional group, etc. (*12–14*). In the present study the effect of the shape and the size of the fibrous adsorbent on the recovery of uranium was studied.

EXPERIMENTAL

PP monofilaments of different sectional views, Fiber-O and Fiber-X, were made by extrusion from PP raw material (Mitsubishi Chemical, Novatec P). The melt flow index and the density of the fiber were ~4 g/10 min and 0.9 g/cm^3, respectively. The surface areas observed by a Yuasa Quantasorb surface area analyzer, model QS-6, were 0.30 m^2/g for Fiber-O and 0.33 m^2/g for Fiber-X. AN, acrylic acid (AAc), and hydroxylamine were commercially available GR grade.

Fiber of 1–2 cm length was irradiated with a Radiation Dynamics electron accelerator Dynamitron, model IEA 3000-25-2, in air at room temperature. The PP fiber irradiated with a dose of 200 kGy was contacted with AN at 25°C under N_2 flow to polymerize AN, followed by amidoximation of cyano groups of grafted chains by connecting the grafted fiber with a 3% hydroxylamine methanol/water (1:1 in volume ratio) solution at 80°C for ~5 h. In order to synthesize the adsorbents containing both amidoxime group and hydrophilic carboxyl group, the grafting of AAc was carried out before the grafting of AN. The amounts of carboxyl group and amidoxime group determined by elemental analysis (*11–14*) were maintained at ~1 meq/g-Ad and 8 meq/g-Ad, respectively.

Table 1 shows the characteristics of adsorbents obtained by this procedure.

The adsorbent was conditioned with 2.5% KOH solution at 80°C for 10 min. The adsorption of uranium from seawater was carried out both by a fixed-bed process and a batch process. In the fixed-bed process about 1 g of the adsorbent was installed in a column (diameter: 1.2 cm) where seawater was supplied at a flow rate of 100 mL/min at 25°C. In the batch process ~40 mg of the adsorbent and 2 L of seawater were agitated at 25°C for the prescribed periods. The adsorbed metal ions except uranium were analyzed with a Jarrell-Ash atomic absorption and flame emission spectrophotometer, model AA-8200. The amount of uranium was measured with an Aloka fluorimeter, model FMS-3.

The tensile strength and elongation were measured with a Toyo Bordwin Tensilon tensile tester, model UTM-II-20. The extension rate was 20 mm/min at room temperature. The measurement was carried out in both air and water. In the latter case, samples were preliminarily swollen with water for 1 day at room temperature.

The distribution of metals in the adsorbent was measured with a JEOL electron probe x-ray microanalyzer, model JXA 733.

RESULTS AND DISCUSSION

Chemical and Physical Properties

Table 2 shows the average changes in tensile strength and elongation of adsorbents of 10 observation values at each step for the synthesis. The

TABLE 1
Characteristics of Adsorbents

	Cross section				
Sample	Sectional view	Length of periphery (mm)	Area (mm^2)	[Carboxyl] (meq/g)	[Amidoxime] (meq/g)
AOF-O-1	Round	0.70	0.038	—	7.9
AOF-O-2				1.2	8.0
AOF-X-1	Cross-shaped	1.14	0.034	—	8.2
AOF-X-2				0.7	8.1

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TABLE 2
Change in Mechanical Properties of Adsorbent[a]

(i) Tensile Strength

Sample	Strength (g/d)			
	Initial	After irradiation	After grafting	After amidoximation
AOF-O	2.9	1.5 (1.9)	1.2 (1.1)	1.1 (0.9)
AOF-X	3.3	1.7 (1.7)	1.2 (1.1)	1.0 (0.8)

(ii) Elongation

Sample	Elongation (%)			
	Initial	After irradiation	After grafting	After amidoximation
AOF-O	160	10 (20)	97 (98)	52 (97)
AOF-X	98	16 (14)	90 (92)	40 (68)

[a] Values in parentheses were observed in water.

tensile strength and the elongation were diminished by irradiation to 50 and 10% of each initial value, respectively. These decreases were not affected by the presence of water during the measurement. Elongation was improved by the next grafting step, while tensile strength was not much changed. Amidoximation did not affect the tensile strength.

Elongation showed a characteristic change. Although elongation was low in air, it was much improved by immersing the adsorbent in water. This recovery of elongation may be related to the fact that the amidoximated fiber is partly hydrophilic (*11–14*). The water existing in the clustered hydrophilic grafted chains is supposed to be hydrogen bonded with the grafted chains (*15*). This weak bonding may work to absorb the stress which is given to the sample.

An advantage of organic adsorbents is that they are stable to acid treatment, which is necessary to desorb metals from the adsorbent (*11–14*). In the present study the adsorbent was prepared by the combination of a chemically stable PP fiber and poly(acrylonitrile). The only weak parts of the adsorbent in the acid treatment are probably the amidoxime groups which are converted from cyano groups in the poly(acrylonitrile) grafted chains. Figure 1 shows the residual ability to recover uranium from seawater when the adsorbent is treated with 1 *N* HCl for a prescribed period. The decrease in adsorption with an increase in

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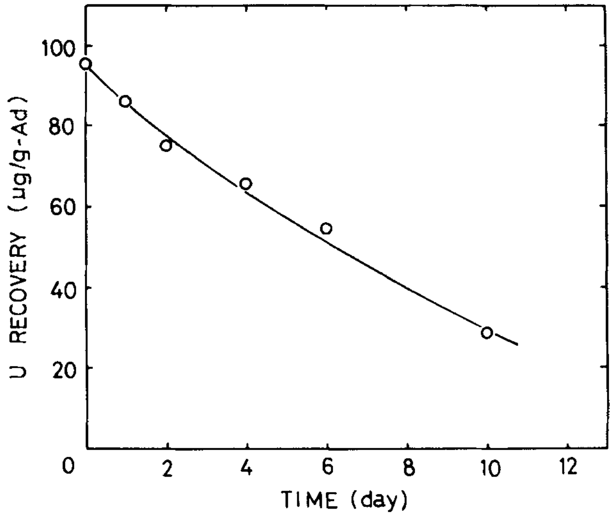

FIG. 1. Residual ability to recover uranium from seawater after the immersion of the adsorbent with 1 *N* HCl.

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immersion time in HCl is probably due to the degeneration of amidoxime groups brought about by HCl (*14*). However, the decrease is not very large when it is considered that almost one week of immersion is necessary to decrease the adsorption to one-half the initial value.

Figure 2 shows the relation between the amount of uranium desorbed and the time of immersion in 100 mL HCl of 1.2 g of the adsorbent which was used in the fixed-bed process for 28 days. At each sampling, 0.5 mL of HCl solution was taken out to measure the concentration of uranium in the solution. From the results in Fig. 2, the minimum immersion time to obtain equilibrium desorption is estimated to be ~20 min under the present condition. Therefore, the desorption time used in the following experiments was 30 min. The results in Figs. 1 and 2 show that the degeneration of amidoxime groups induced by HCl and the resultant decrease in the adsorption ability is negligibly small (~5% of the initial value) during this desorption period.

Adsorption Properties

The amidoxime group fixed in polymer substrates has been said to possess a high efficiency for adsorbing uranium from seawater (*1–14*).

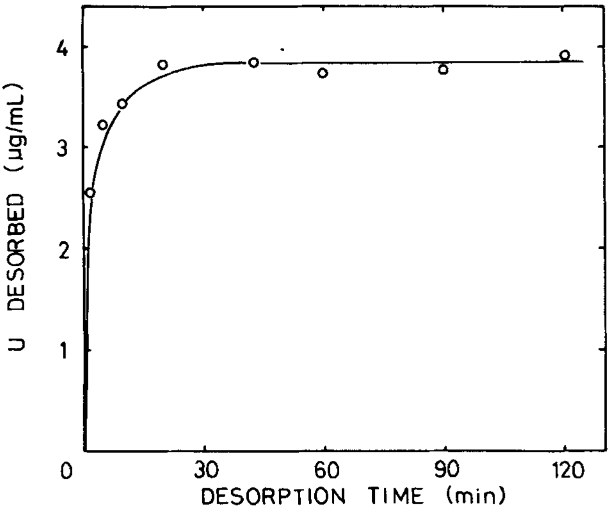

FIG. 2. Relation between the time to immerse the adsorbent in 1 *N* HCl and the amount of uranium desorbed.

However, this does not mean that only uranium is adsorbed. Actually, the amidoxime groups adsorbing uranium are estimated to be a very small portion of the total number of amidoxime groups in the adsorbent when it is considered, for example, that the ratio of the number of amidoxime groups in the adsorbent to that of uranium contained in seawater in the batch process under the present condition is ~10,000 to 1. A large number of amidoxime groups are expected to participate in the adsorption of other metals like Zn, Ni, Co, etc. Table 3 shows the initial concentration of various metals in seawater and the amount of these metals adsorbed onto the adsorbent in 28 days in the fixed-bed process. It is clear that the adsorbent has a high affinity to transition elements and uranium. The concentration factors (CF), which are calculated from the ratio of the adsorbed amount of metals to the initial concentration, are in the order of 10^5 for most transition metals and uranium. On the other hand, CF values for alkali metals and alkaline earth metals are between 0.1 and 20. These CF values agree with the previous results obtained by other organic adsorbents (*16*).

In order to study the effect of the shape of fibrous adsorbents on the recovery of uranium from seawater, adsorbents with round and cross-shaped sectional view were used in the batch process. Figure 3 shows that the amount of recovered uranium increases with an increase in the adsorption time. After a rapid increase in the initial period, the recovery

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TABLE 3
Adsorption of Various Metal Ions from Seawater with AOF[a]

Element	Concentration in seawater (mg/L)	Amount of adsorption (mg/g)	Concentration factor (CF)
Na	10,500	2.6	0.25
K	380	0.1	0.25
Mg	1,350	12.1	9.0
Ca	400	7.6	19.0
Zn	1×10^{-2}	8.9	8.9×10^{5}
Ni	2×10^{-3}	0.71	3.6×10^{5}
Co	1×10^{-4}	0.04	4.0×10^{5}
Cu	3×10^{-3}	0.62	2.0×10^{5}
Fe	1×10^{-2}	0.20	2.0×10^{4}
Mn	2×10^{-3}	<0.01	—
Cr	5×10^{-5}	<0.01	—
V	2×10^{-3}	1.0	5.0×10^{5}
U	3×10^{-3}	0.80	2.7×10^{5}

[a] In column process at 25°C; flow rate, 100 mL/min; period, 28 days.

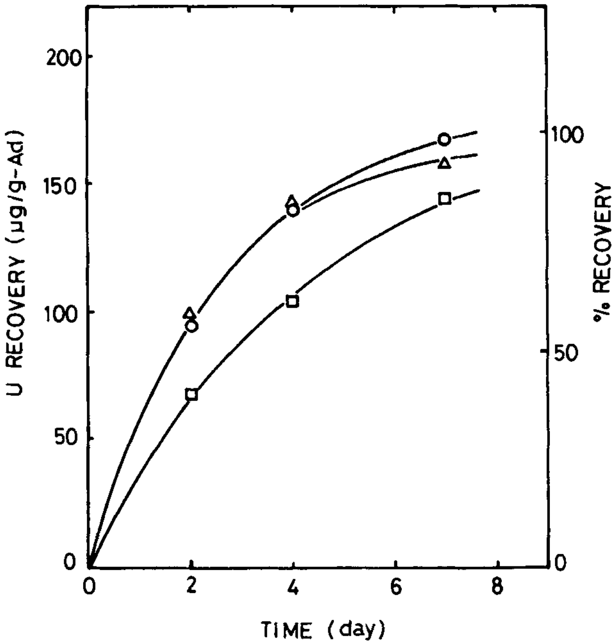

FIG. 3. Recovery of uranium with adsorbents (□) AOF-O-2, (○) AOF-X-1, and (△) AOF-X-2 in the batch process.

slows down gradually till it reaches 100% in 7 days in the case of AOF-X. In the same period the recovery with AOF-O was 90%. The rate of the recovery of uranium with AOF-X is apparently much higher than that with AOF-O. There is virtually no difference between AOF-X-1 and AOF-X-2.

When these adsorbents were used in the fixed-bed process, the amount of recovered uranium increased with the adsorption time as shown in Fig. 4. The increase in recovery is approximately linear in the case of AOF-X and rather concave upward in the case of AOF-O. The results in Fig. 4 indicate that recovery with AOF-X is much larger than that with AOF-O. On the other hand, the difference is small between AOF-X-1 and AOF-X-2, and between AOF-O-1 and AOF-O-2. Taking into account the results in Fig. 3, it is possible to conclude that the inclusion of a hydrophilic group into the adsdorbent is not necessary to the adsorbent. The hydrophilic character of the adsorbent introduced by amidoximation (*11–14*) is probably adequate to take up a sufficient amount of seawater inside the adsorbent.

Such a difference in receovery between AOF-O and AOF-X is reflected in the distribution pattern of adsorbed metals in the cross section of the adsorbents. Figure 5 shows line profiles of calcium adsorbed in the cross section of (a) AOF-O and (b) AOF-X at various adsorption times in the fixed-bed process. When the adsorption time is small, calcium is located

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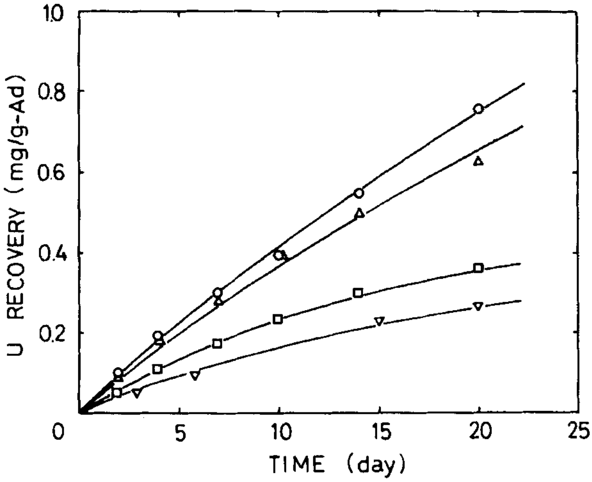

FIG. 4. Recovery of uranium with adsorbents (∇) AOF-O-1, (□) AOF-O-2, (O) AOF-X-1, and (△) AOF-X-2 in the column process.

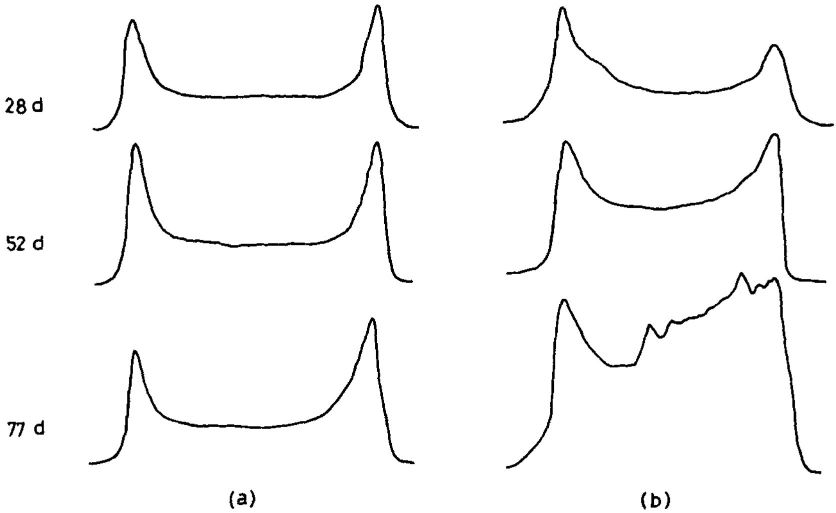

FIG. 5. Line profiles for calcium distributed in the cross section of (a) AOF-O and (b) AOF-X at various adsorption times.

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only in the surface layers of AOF-O and AOF-X. The line profile scarcely changes with an increase in adsorption time in the case of AOF-O, while a clear increase in the area under the distribution curve is observed in the case of AOF-X. The distribution curve observed in AOF-X after 77 days indicates that calcium exists not only in the surface layer but also in the core layer, although the distribution is still not homogeneous.

A difference in the distribution between AOF-O and AOF-X was also observed for uranium. As shown in Fig. 6, the presence of uranium in AOF-O was not apparent until the adsorption time was 77 days, while it was already observed by 52 days' adsorption in the case of AOF-X. For both AOF-O and AOF-X, uranium is localized only in the layer within ~40 μm from the surface. This distribution pattern did not change much even if the adsorption time was extended to more than 300 days. From a comparison of the distribution patterns between calcium and uranium, uranium seems to have more difficulty diffusing into the core layer of the adsorbent. This may be based on the fact that uranyl tricarbonate, which is the main species in seawater, has a large ionic radius (~10 Å) compared with the ionic radius of calcium (~1 Å).

The above-mentioned results on the recovery of uranium in Figs. 3 and 4 and the distribution patterns in Figs. 5 and 6 indicate that one of the reasons for the difference in the recovery of uranium between AOF-O

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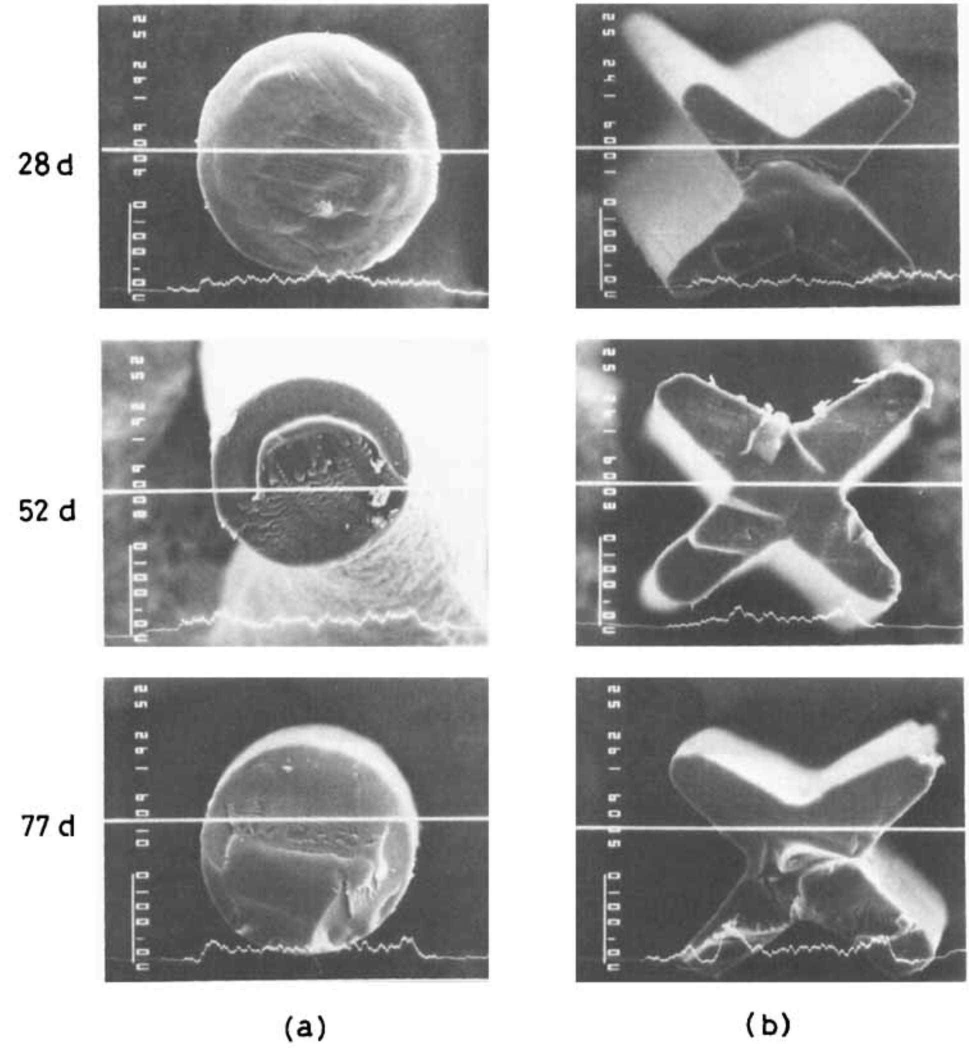

FIG. 6. Line profiles for uranium distributed in the cross section of (a) AOF-O and (b) AOF-X at various adsorption times.

and AOF-X is related to differences in the sections of the adsorbents. As shown in the Experimental part, the two adsorbents made from the same PP raw material contain almost the same amount of amidoxime groups. The area of the cross section is also similar, as shown in Table 1. The only difference is the length of the periphery of the cross section; the length of the periphery and the resultant surface area of AOF-X are 1.6 times those of AOF-O of the same volume. It is reasonable that AOF-X, with a larger surface area, shows better adsorption and a more homogeneous distribution of metals in the radius direction of the adsorbent when considered with the fact that the adsorption is controlled by the diffusion of ions through the surface of the adsorbents.

Based on these results, a new adsorbent, AOF-O-3, with a small diameter (40 μm), which is expected to provide a large surface area to the adsorbent at a certain volume of raw materials, was synthesized. Figure 7 shows a comparison in the recovery of uranium between AOF-O-3 and AOF-O-1. As expected, a great improvement in uranium recovery was achieved by using AOF-O-3. The amount of uranium in 140 days with AOF-O-3 was ~5 mg/g-Ad, which is almost 5 times that of AOF-O-1.

Figure 8 shows a comparison of uranium recovery by various

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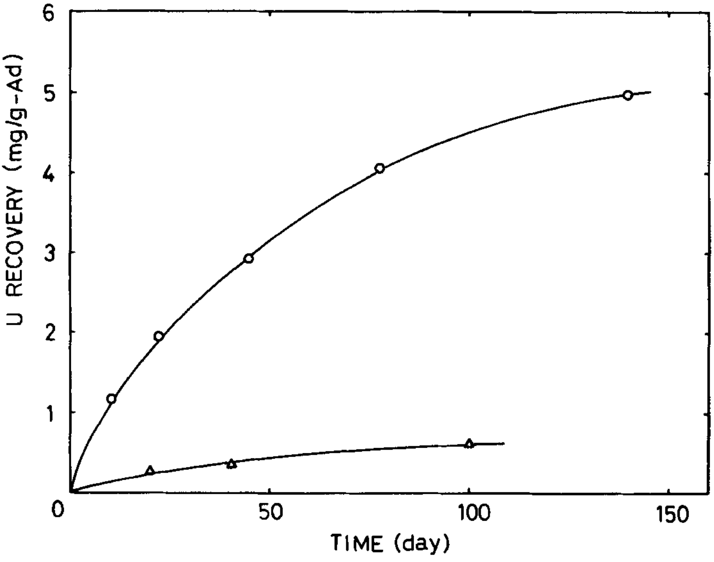

FIG. 7. Recovery of uranium with (Δ) AOF-O-1 and (O) AOF-O-3 in the fixed-bed process.

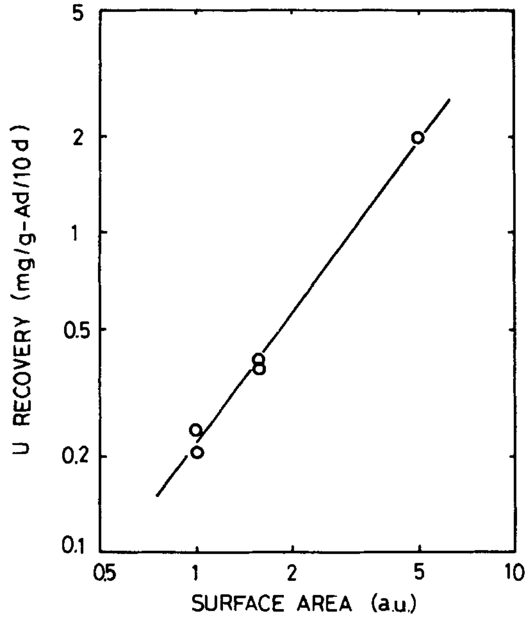

FIG. 8. Recovery of uranium with adsorbents of different surface areas at the same volume.

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adsorbents with different surface areas at constant fiber volume. The logarithmic increase in adsorption indicates the possibility of a further improvement of adsorption ability by using a fiber of a much smaller diameter or a porous fiber with a larger surface area. From these results it is concluded that the surface area of a fibrous adsorbent is of vital importance to its ability of recovering uranium from seawater.

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