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A New Type of Amidoxime-Group-Containing Adsorbent for the Recovery of Uranium from Seawater

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Abstract

A new type of adsorbent containing amidoxime groups for the recovery of uranium from seawater was synthesized by the radiation-induced graft polymerization of acrylonitrile onto polymeric fiber followed by amidoximation with hydroxylamine. When amidoxime groups were introduced superficially on the fiber, the amount of uranium adsorbed by the amidoxime groups was higher than that with the amidoxime groups introduced homogeneously in the fiber. The introduction of the poly(acrylic acid) chain and the increase in temperature and flow rate in the adsorption process were effective in increasing the amount of adsorbed uranium. Although alkali metals and alkaline earth metals were found in the adsorbent, the concentration factors for these metals were less than $1/10^3$ of that for uranium. The present adsorbent had a high stability to various treatments such as contact with alkali and seawater.

INTRODUCTION

Separation of uranium from seawater has been studied with various kinds of inorganic (*1–5*) and organic adsorbents (*6–15*). Among them, amidoxime-group-containing polymeric adsorbents are noted because of the high loading of uranium and the rapid adsorption rate. Recently, a fibrous adsorbent containing amidoxime groups synthesized through the amidoximation of a commercially available acrylic synthetic fiber with hydroxylamine has been used. It has been reported that the fibrous adsorbent has much higher adsorption ability for uranium when compared with a corresponding bead-type adsorbent (*16*).

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The fibrous adsorbent, however, has poor mechanical stability when it is contacted with alkali. This is supposed to be due to the hydrolysis of residual cyano groups in the polymer chain, which brings about the swelling of the whole fiber and a decrease in mechanical strength. Therefore, in order to synthesize a more stable fibrous adsorbent, a controlled amount of amidoxime groups should be introduced in the prescribed part of the fibrous material without changing the original mechanical strength. Radiation-induced grafting is a convenient method for such a purpose.

When a polymeric substrate is irradiated with ^{60}Co γ-rays or electron beam, about 10^{19} radicals are produced in 1 gram of polymer. The graft polymerization of a monomer is initiated by using these radicals when the monomer is introduced to the irradiated substrate. The number and the length of graft chains are easily controlled by irradiation and polymerization conditions. For example, the number of graft chains has roughly a linear relationship with the irradiation dose. The chain length is affected by the reaction time, the temperature, the presence of chain transfer agents in a monomer solution, etc.

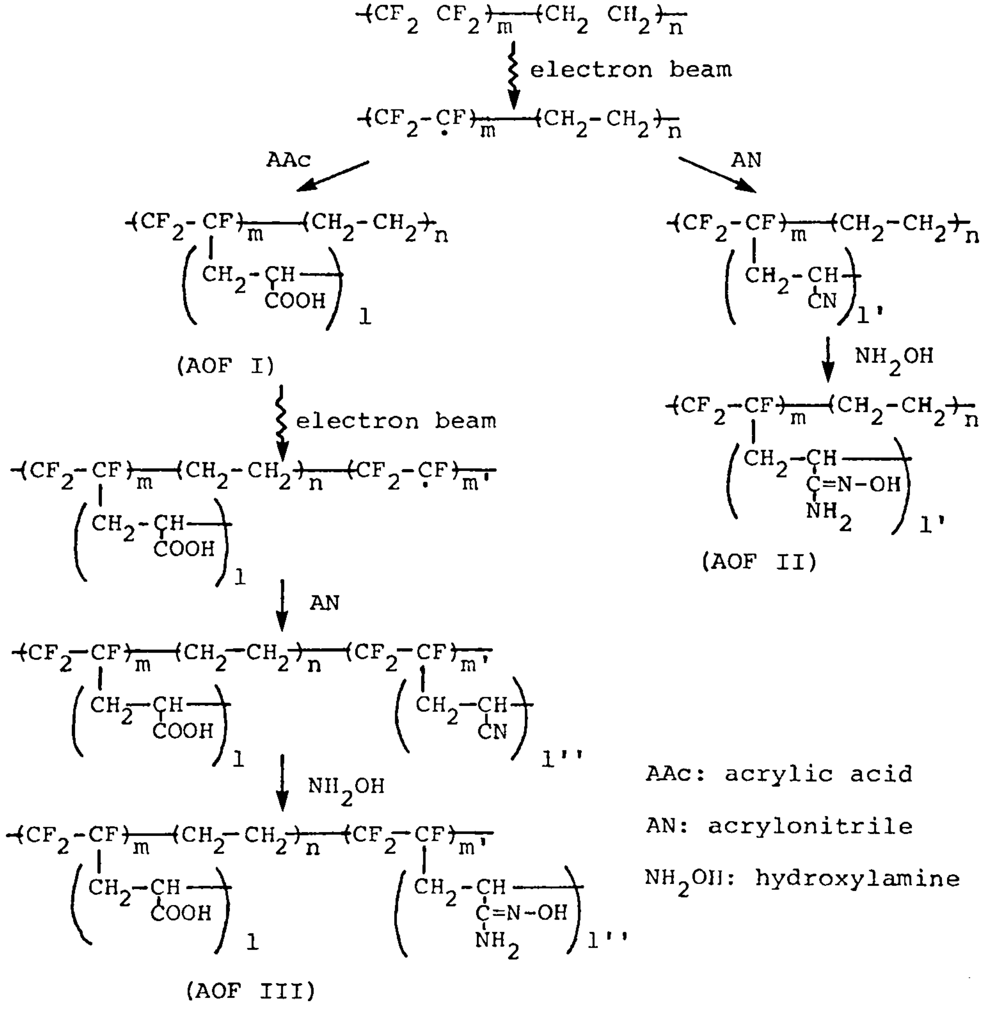
When acrylonitrile is grafted onto fiber followed by amidoximation, a fibrous adsorbent is obtained. This adsorbent has the prescribed number and the length of amidoxime-group-containing graft chains which are connected with the trunk polymer fiber only at their chain ends. It is said that about one graft chain is connected with one trunk polymer on the average (*17*). In other words, the chemical modification of a trunk polymer by grafting is restricted to a very tiny region of the trunk polymer. Therefore, the chemical structures which were previously possessed by the trunk polymer are well maintained even after grafting.

It is another advantage of the radiation-induced grafting method that the graft chains can be introduced to any part of the substrate—for example, only in the surface region, the inner part, or in the entire substrate. According to the distribution of graft chains containing functional groups, the ability to adsorb metals is expected to differ.

In the present paper, several types of fibrous adsorbents containing amidoxime groups were synthesized by changing the grafting condition of acrylonitrile onto tetrafluoroethylene–ethylene copolymer fiber and were applied to the recovery of uranium from seawater.

EXPERIMENTAL

Fibrous adsorbents containing amidoxime groups (AOF) were prepared by the routes shown in Scheme 1.



SCHEME 1. Synthesis of AOF by radiation-induced grafting.

Tetrafluoroethylene–ethylene copolymer fiber (40 μm ϕ, 15 mm length) was irradiated with a Radiation Dynamics electron accelerator, Dynamitron, model IEA 3000-25-2, under nitrogen atmosphere at room temperature. The irradiation dose was estimated as 10 Mrd (100 kGy). The irradiated fiber was introduced in a glass ampule containing purified monomer under nitrogen atmosphere. The graft polymerization was carried out at 25°C. After grafting, the homopolymer as well as the unreacted monomer were extracted with solvents: *N,N*-dimethylformamide for acrylonitrile homopolymers and water for acrylic acid homopolymers. When both acrylic acid and acrylonitrile were introduced to the fiber, acrylic acid was grafted as the first step, then the grafted fiber was irradiated again followed by the introduction of acrylonitrile as the second step of grafting (*18*). The cyano groups in the grafted fiber were converted to amidoxime groups through the reaction with hydroxylamine (3% methanol/water 1:1 solution) at pH = 7. The conversion was determined by elemental analysis. The details were reported in a previous paper (*19*).

The distribution of amidoxime groups in the cross section of the amidoximated fiber was measured by means of a JEOL electron probe x-ray microanalyzer, model JXA 733.

The adsorption of uranium from seawater with AOF was carried out by the following four processes:

1. Batch process: AOF was mixed with seawater in a vessel under vigorous agitation at 25 ± 1°C for the prescribed period.
2. Semibatch process I: The seawater in the batch vessel was intermittently exchanged for fresh seawater.
3. Semibatch process II: Seawater was supplied continuously to the stirred vessel.
4. Fixed-bed process: AOF was packed in a column (10 mm ϕ, 10 cm length) and seawater was continuously supplied.

The desorption of uranium adsorbed in 0.1 g of AOF was accomplished by contacting the fiber with 25 mL of sulfuric acid for 1 h at room temperature. The amount of uranium complexed with arsenazo III was measured optically (*20*) at 665 nm by means of a Shimadzu spectrophotometer, model UV-100-02. Metals other than uranium were determined by means of a Jarrell-Ash atomic absorption and flame emission spectrophotometer, model AA-8200.

RESULTS AND DISCUSSION

Preparation of Adsorbents

As mentioned above, one of the advantages of the grafting method for synthesizing adsorbents is that any amount of functional groups can be introduced to the trunk polymer fiber by selecting proper irradiation and

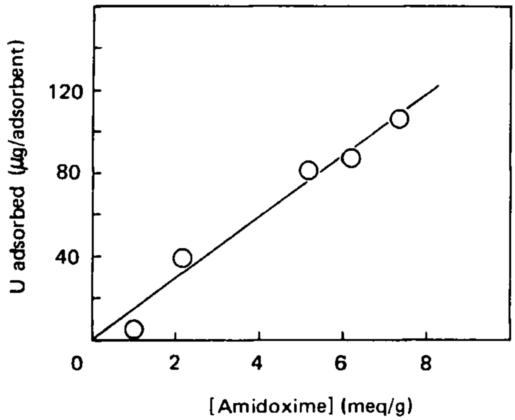


FIG. 1. Effect of concentration of amidoxime groups in AOF on the adsorption of uranium from seawater: AOF 0.1 g, seawater 10 L, in the semibatch process I at 25°C.

grafting conditions. Several kinds of fibrous adsorbents containing amidoxime groups up to 6.5 meq/g were synthesized by changing the reaction time. Figure 1 shows the results when these AOF were used for uranium adsorption from seawater in semibatch process I. As 2 L of seawater was exchanged with fresh seawater for 5 d, the total amount of supplied seawater was 10 L. The amount of adsorbed uranium increased in proportion to the increase in the concentration of amidoxime groups in AOF. Such relationships have been observed in various amidoxime-group-containing bead-type adsorbents (*9*).

Although the results in Fig. 1 show that the adsorption of uranium is facilitated by increasing the amount of amidoxime groups in the fiber, it should be pointed out that the amidoxime groups used for adsorption of uranium from seawater is only a small portion of the total amidoxime groups introduced in AOF. The molar ratio of the adsorbed uranium to amidoxime groups is of the order of 10^{-4}. Even if four amidoxime groups are necessary to make a chelate complex with one uranyl ion (*21*), the number of the amidoxime groups used is estimated as ~1/2500 of the total amidoxime groups. In other words, the present adsorbents shown in Fig. 1 can, in theory, adsorb 0.5–1.5 mmol uranium per 1 g adsorbent. This value is reasonable when compared with the previous work by Schwochau et al. (*21*).

Two types of AOF, AOF-L and AOF-V, each containing ~5 meq of amidoxime groups per 1 g of fiber, were synthesized by liquid-phase grafting and vapor-phase grafting of AN, respectively. As shown in Fig. 2, the distribution of amidoxime groups in the cross section of AOF-L

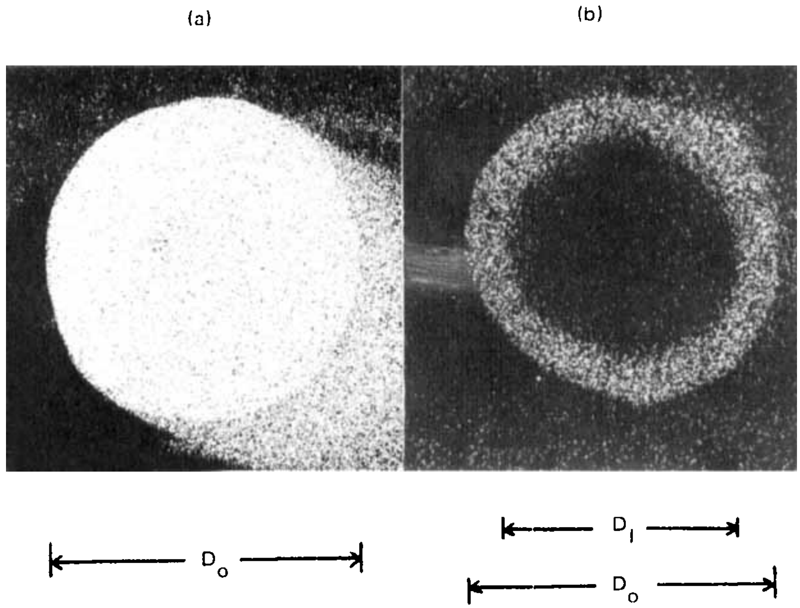


FIG. 2. Distribution patterns of amidoxime groups in the cross section of (a) AOF-V and (b) AOF-L. D_O and D_I are the outer and inner diameters, respectively.

observed by means of EPMA is homogeneous. On the other hand, in AOF-V the distribution is heterogeneous—mostly restricted to the layer within 10 μm from the surface. Because uranium in seawater is adsorbed in the thin surface layer of the adsorbent (*21*), only the amidoxime groups existing in the surface layer are supposed to be effective for adsorbing uranium.

The concentration of amidoxime groups in the thin surface layer of AOF-L was compared with that of AOF-V. The ratio between the two amounts is given as

$$F_1 \frac{S_O - S_I}{S_O} \Big/ F_2 = (F_1/F_2)\left(\frac{D_O^2 - D_I^2}{D_O^2}\right) \tag{1}$$

where F_1 and F_2 are the concentrations of amidoxime groups for AOF-L (5.1 meq/g) and AOF-V (5.0 meq/g), respectively, and D_O and D_I are the outer and inner diameters of cross section, respectively, as shown in Fig. 2. S_O and S_I are the corresponding areas. By introducing $D_O = 80$ μm, $D_I = 60$ μm, $F_1 = 5.1$ meq/g, and $F_2 = 5.0$ meq/g, the ratio was obtained as 0.45. This result indicates that the concentration of amidoxime groups in a unit surface layer of AOF-V is twice as large as that of AOF-L. According

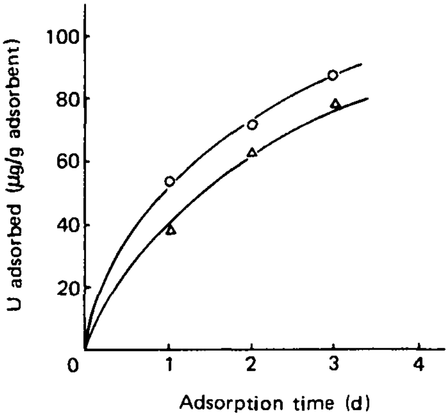


FIG. 3. Adsorption of uranium from seawater with (O) AOF-V and (Δ) AOF-L in the semibatch process I.

to the results in Fig. 1, therefore, the adsorption of uranium with AOF-V is expected to be twice as much as that with AOF-L. However, Fig. 3 shows that the adsorption of uranium with AOF-V is slightly higher than that with AOF-L. This is a rather unexpected result because we observed that the adsorption of copper ions from a buffer solution at pH = 6 with AOF-V was about twice as much as that with AOF-L (*22*). In the case of adsorbing uranium from seawater, the functional groups existing on the surface layer are occupied by various kinds of metal ions other than uranium and are quickly covered with organic substances such as seaweeds. Therefore, there are fewer residual functional groups which work for adsorbing uranium compared with those functional groups existing inside an adsorbent like AOF-L. In the latter case, the surface layer may work as a filter for these obstacle substances. The result in Fig. 3 indicates that an adsorbent which is effective in a pure solution is not always effective in seawater. Therefore, the following experiments were carried out with the homogeneous adsorbent AOF-L.

Figure 4(a) shows the amount of uranium adsorbed from 2 L of seawater with 0.1 of three types of adsorbents, AOF-I, II, and III, which were made by liquid-phase grafting. The compositions of the adsorbents are shown in Table 1. AOF-I, containing only carboxyl groups, did not adsorb uranium at all. Referring to the report that poly(acrylic acid) can make a chelate complex with uranyl ions under acidic condition (*23*), the present result may be partly due to the insufficient pH value of seawater for chelate formation between carboxyl groups and uranyl ions. At pH = 8,

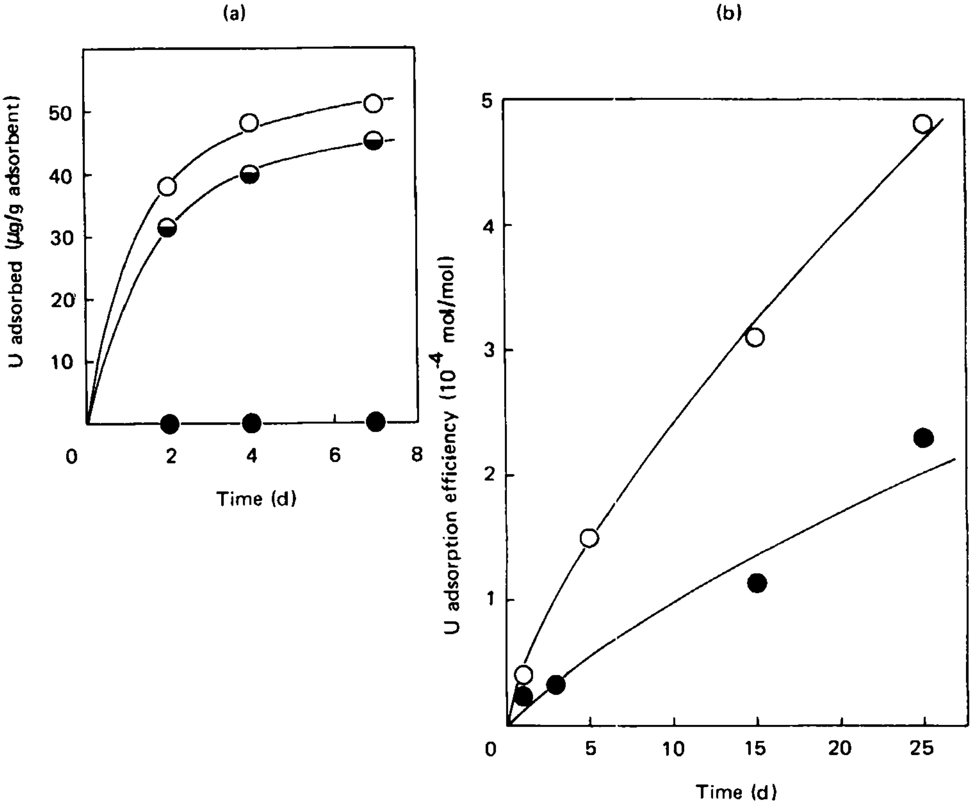


FIG. 4. Amounts of uranium adsorbed in (a) the batch process with (●) AOF-I, (◒) AOF-II, and (○) AOF-III, and in (b) the semibatch process I with (●) AOF-II and (○) AOF-III.

TABLE 1
Composition of Adsorbents AOF

Adsorbent	Concentration of functional groups (mmol/g)	
	Carboxyl	Amidoxime
AOF-I	5.2	0
AOF-II	0	5.1
AOF-III	1.9	3.4

poly(acrylic acid) dissociates into carboxylate anion, which may be undesirable for chelate formation.

When AOF-II and III are compared, AOF-III adsorbed more uranium in spite of the fact that the amount of amidoxime groups in AOF-III is less than in AOF-II. Therefore, the higher adsorption with AOF-III is supposed to be due to carboxyl groups. The effect of carboxyl groups on uranium adsorption was more clearly indicated when the molar ratio of adsorbed uranium to amidoxime groups was plotted against the adsorption period as shown in Fig. 4(b). AOF-III adsorbed twice as much uranium as did AOF-II. The effect of carboxyl groups on uranium adsorption with AOF is explained as follows: As already pointed out (*14*), uranyl tricarbonate, which is the major form of uranyl ion in seawater at pH = 8, is converted to bicarbonate when the pH value is lowered. Therefore, it is probable that poly(acrylic acid) graft chains locally decrease the pH of seawater sorbed in the adsorbent, which promotes the conversion from tricarbonate to bicarbonate. This conversion may be accompanied by a new chelate formation with uranyl bicarbonate and an amidoxime group in the vacant site. In other words, the presence of carboxyl groups is thought to have a synergistic effect on chelate formation between amidoxime groups and uranyl ions.

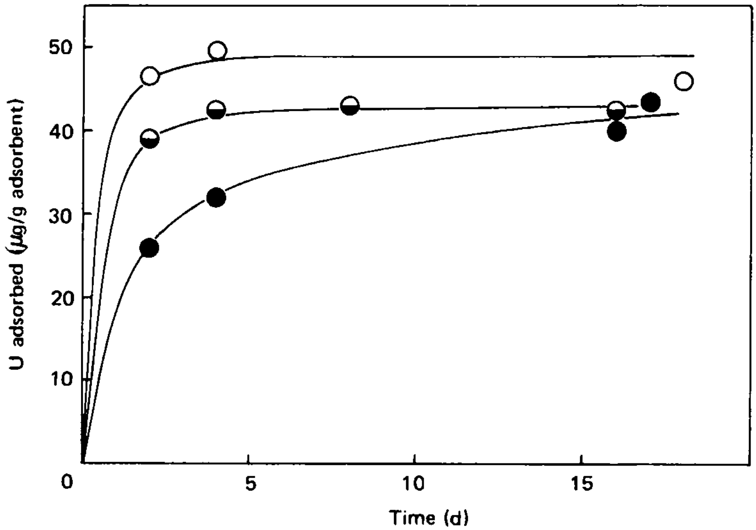


FIG. 5. Effect of temperature of seawater on adsorption of uranium with AOF in the batch process: (●) 15°C, (◒) 25°C, and (○) 35°C.

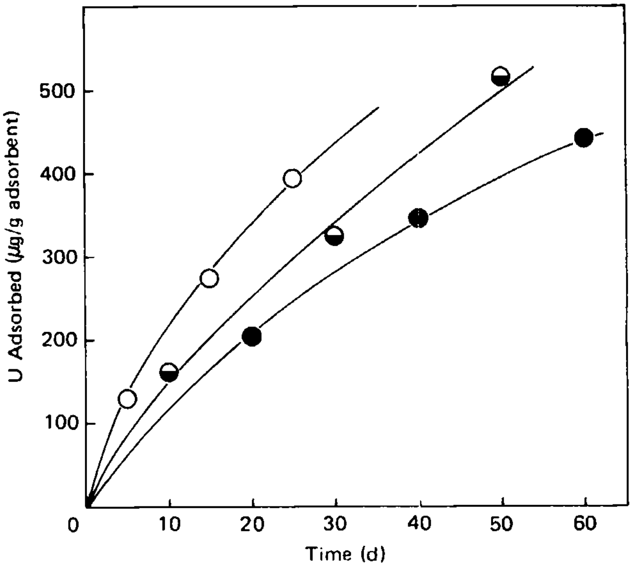


FIG. 6. Effect of exchange rate of 2 L of seawater on adsorption of uranium with AOF-III in the semibatch process I: (●) every 1 d, (◒) 2 d, and (○) 4 d.

Adsorption Method

The adsorption of uranium from seawater with AOF was carried out at 15 to 35°C. Although the equilibrium amount of adsorbed uranium did not change, the initial rate of adsorption was increased by increasing the temperature as shown in Fig. 5. From Arrhenius plots, the activation energy for adsorption was estimated as ~8.8 kcal/mol.

The results in Fig. 5 indicate that a higher temperature is preferable for the recovery of uranium from seawater with AOF. Especially when the adsorption–desorption cycle is carried out at short intervals, such a large initial rate is desirable.

As shown in Fig. 4(a), the amount of adsorbed uranium levels off after 7 day's adsorption in the batch process. About 0.1 g of AOF-III recovered more than 80% of the uranium contained in 2 L of seawater. The saturation of adsorption is, therefore, supposed to be due to the depletion of uranium in seawater contained in the batch vessel. In order to clarify this assumption, seawater was exchanged with fresh seawater every 1, 2, and 4 days in semibatch process I. Figure 6 shows the amount of adsorbed

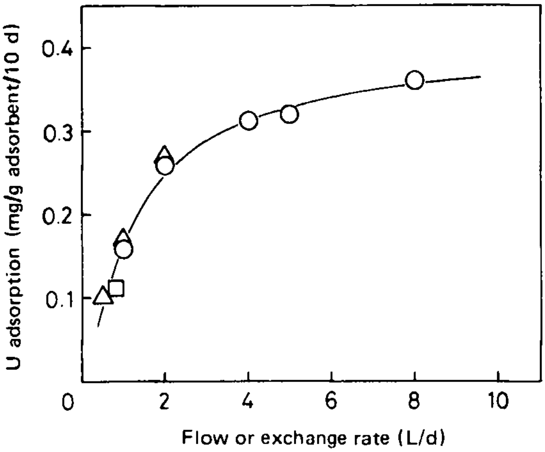


FIG. 7. Effect of flow rate and exchange rate of seawater on adsorption of uranium with AOF-III in (○) semibatch process I, (△) semibatch process II, and (□) fixed-bed process.

uranium thus obtained. When the results in Fig. 6 are compared with those in Fig. 4(a), it is clear that uranium adsorption is facilitated by exchanging seawater. The adsorbed uranium was at most 50% of the total uranium in seawater, even if the exchange rate was small. This result indicates that the depletion of uranium was fairly avoided by this exchange procedure.

Uranium adsorption did not increase in proportion to the exchange rate of seawater. Doubling the exchange rate brought about only a 20 to 30% increase in uranium adsorption. This adsorption behavior was observed when the flow rate was increased in semibatch process II and the fixed-bed process. As shown in Fig. 7, the increase in uranium adsorption levels off when the flow rate of seawater in semibatch process II and the fixed-bed process increases. It is interesting that the amount of adsorbed uranium obtained in semibatch process I is virtually the same as in semibatch process II and the fixed-bed process. This is probably due to the slow feed of seawater. For example, 10 L/d of flow, adopted in the present experiment, corresponds to only 8.8 cm/min of line velocity, which means that at least 2 s is necessary for one drop (~0.2 mL) of seawater to get out of the column. Therefore, it is supposed that the flow rate in the continuous processes is slow enough to assure a sufficient contact of AOF with seawater as observed in the batch process with vigorous agitation.

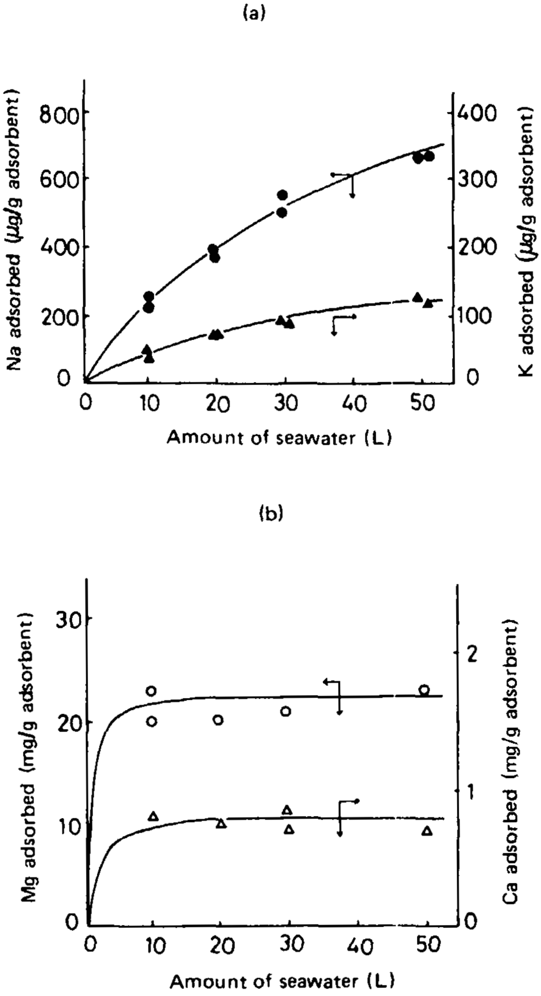


FIG. 8. Amounts of (a) alkali metals ((●) Na and (Δ) K) and (b) alkaline earth metals ((O) Mg and (Δ) Ca) adsorbed in AOF-III at different periods.

Characteristics of AOF

It has been reported that alkaline earth metals disturb the recovery of uranium from seawater (*24*). The smaller uptake of these metals is desirable as adsorbents for uranium. Although alkali metal ions and alkaline earth metal ions were reported to have small affinity for amidoxime groups (*10*),

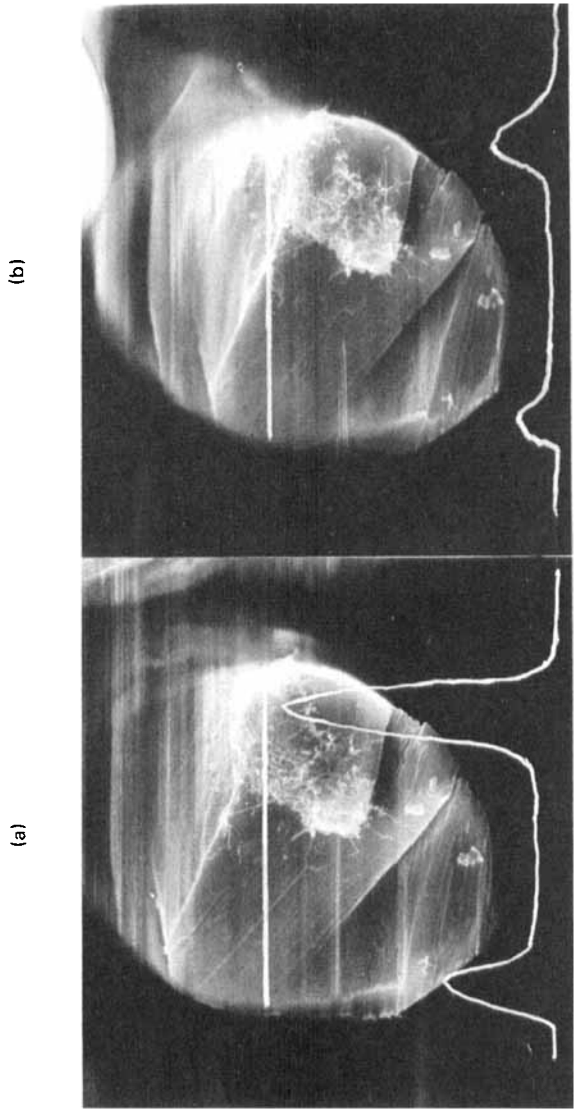


FIG. 9. Distribution of (a) Mg and (b) Ca in the cross section of AOF-III when contacted with seawater for 25 d.

TABLE 2
Natural Abundance of Various Metal Ions in Seawater, and Concentration Factors (CF) Based on Adsorption with AOF

Metal ion	Abundance in seawater (g/L)	CF
U	3×10^{-6}	1.3×10^{4}
Zn	5×10^{-6}	7.0×10^{5}
Ni	7×10^{-6}	2.0×10^{3}
Ca	0.41	29
Mg	1.3	6.3
Na	10.8	0.34
K	0.39	0.13

a considerable amount of these metals was found in AOF after contact with seawater. Figure 8 shows the amounts of (a) alkali metals and (b) alkaline earth metals in AOF-III at different adsorption periods in the fixed-bed process. The amount of such alkali metals as sodium and potassium gradually increases with an increase in the adsorption period (amount of seawater). The amount of alkaline earth metals, on the other hand, levels off quite soon, as shown in Fig. 8(b). From the distribution pattern of Mg and Ca in AOF as shown in Fig. 9, it is clear that these alkaline earths locate only in the surface region of the adsorbent even if AOF are contacted with seawater for a long period.

The equilibrium adsorption of Mg was ~2 mg, which is at least 10 times that of uranium. However, this large amount is due to the large content of Mg in seawater. Table 2 shows the natural abundances of various metal ions in seawater, and the concentration factors (CF) indicated are the ratios of the concentration in the adsorbent to that in seawater. It is clear that CF for uranium and some transition metals is over 10^4. On the other hand, CF for alkalis and alkaline earths is less than 10^2. These results indicate that amidoxime groups in AOF have a high selectivity for heavy metal ions.

The adsorbent AOF made by the radiation-induced grafting method has some characteristic polymer structures when compared with the corresponding adsorbents made from commercially available acrylic synthetic fiber. First, the graft chains which contain amidoxime groups are connected with the trunk polymer fiber only at the chain ends. Therefore, the mechanical properties of the trunk polymer itself is mostly unchanged, even after grafting. Second, swelling occurs only in the amorphous region of the trunk polymer because grafting is restricted to this region (*17*). This heterogeneous swelling behavior brings about a small dimensional change of the adsorbent when it is contacted with various solutions such as alkali,

TABLE 3
Change in Diameter of AOF by Contact with Various Liquids

Liquid	Diameter (μm)
Original AOF	66
Alkali[a]	70
Seawater[b]	72

[a] 2.5% KOH solution, 10 min at 80°C.
[b] 24 h at 30°C.

acid, and seawater. As shown in Table 3, the increase in diameter of AOF by contact with these liquids is less than 10% on the whole. This dimensional stability is very important when the adsorbent is used repeatedly through the cycle: pretreatment with alkali—contact with seawater—acid desorption. A preliminary study showed that the decrease in adsorption of uranium and the dimensional change of AOF are both negligible up to cycle five. Further details will be presented in future publications.

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