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K. Sugasaka[a]; S. Katoh[a]; N. Takai[b]; H. Takahashi[b]; Y. Umezawa[c]
[a] GOVERNMENT INDUSTRIAL RESEARCH INSTITUTE, KAGAWA, JAPAN [b] INSTITUTE OF INDUSTRY AND SCIENCE, UNIVERSITY OF TOKYO, TOKYO, JAPAN [c] CENTRAL RESEARCH LABORATORY, MITSUBISHI CHEMICAL INDUSTRIES, LTD., MIDORIKU YOKOHAMA, KANAGAWA, JAPAN

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Recovery of Uranium from Seawater

K. SUGASAKA and S. KATOH

GOVERNMENT INDUSTRIAL RESEARCH INSTITUTE, SHIKOKU
2-3-3 HANANOMIYA-CHO, TAKAMATSU, KAGAWA, JAPAN 761

N. TAKAI and H. TAKAHASHI

INSTITUTE OF INDUSTRY AND SCIENCE, UNIVERSITY OF TOKYO
7-22-1 ROPPONGI, MINATOKU, TOKYO, JAPAN 106

Y. UMEZAWA

CENTRAL RESEARCH LABORATORY
MITSUBISHI CHEMICAL INDUSTRIES, LTD.
1000 KAMOSHIDA-CHO, MIDORIKU
YOKOHAMA, KANAGAWA, JAPAN 227

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ABSTRACT

Seawater contains various elements in solution. Deuterium, lithium, and uranium are the important ingredients for energy application at present and in the future. This paper deals with the recovery of uranium from seawater, with emphasis on the development of an adsorbent with high selectivity and rate of adsorption for uranium.

Polyacrylamidoxime chelating resins were synthesized from various co-polymers of acrylonitrile and cross-linking agents. The resulting resins with the chelating amidoxime group showed selective adsorption for uranium in seawater. The amount of uranium adsorbed from seawater at room temperature reached 3.2 mg/g resin after 180 days.

Polyacrylamidoxime fiber, which was prepared from polyacrylonitrile fiber and hydroxylamine, showed a high rate of adsorption for uranium. The polyacrylamidoxime fiber conditioned with 1 M HCl and 1 M NaOH adsorbed 4 mg U/g fiber from seawater in ten days.

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INTRODUCTION

The oceans contain various kinds of substances in solution. The time scale of oceanic circulation is assumed to be about 1000 years, and the oceans are well-stirred. Therefore, seawater is a homogeneous electrolytic solution which is kept at equilibrium. The concentration of electrolyte is about 0.6 M, with heavy metal ions at about 10^{-8} M.

The elements above 65 mg/L (e.g., Br) in seawater have been utilized in industry. In view of the anticipated demand for energy in Japan, there is a need to increase nuclear power generation in the near future, and nuclear fusion reactors may also need to be established. The minor constituents of seawater, especially uranium, are of interest since Japan has no ore resources.

At a concentration of 0.003 mg U/L, seawater contains 4×10^9 tons of uranium. Thus, seawater is a poor grade of, but inexhaustible resource for, uranium. Uranium is assumed to be present in seawater as uranyl tricarbonate ion, $UO_2(CO_3)_3^{4-}$ (1).

RECOVERY OF URANIUM FROM SEAWATER

The following problems are important in establishing a system to recover uranium from seawater. First, seawater is a moderately concentrated electrolytic solution and contains many kinds of substances. Only a few methods are applicable for the selective collection of uranium. Second, since the concentration of uranium in seawater is very low, large amounts of seawater must be handled. Therefore, the method of recovery of uranium must meet the following criteria: (1) the existing temperature and pH of the seawater must be accepted without change; (2) there must be effective contact between the collector and large amounts of seawater; (3) the collector must be recovered easily and completely after contact with the seawater; and (4) the collector must be insoluble in seawater.

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Many attempts to recover uranium from seawater have been reported in the literature, with the consensus that an adsorption method is the most applicable.

RECOVERY OF URANIUM BY ADSORPTION

One of the most important aspects in establishing the recovery process is the development of an adsorbent with high uranium selectivity and a high rate of uranium adsorption. The results of many investigations with inorganic adsorbents have indicated that hydrous titanium oxide and composite adsorbents consisting of hydrous titanium oxide with other materials such as activated carbon or hydrous iron oxide are useful adsorbents.

A flow diagram which was studied in our laboratory for the recovery of uranium from seawater is shown in Fig. 1. The uranium recovery was about 17% in the collection of 0.7 g of yellow cake. However, the rate of adsorption of the uranium on granulated hydrous titanium oxide or on titanium-activated carbon composite adsorbent (C-Ti-OH) was found to be only about 0.2 mg/g adsorbent in 10 days, showing the need to develop a new adsorbent with a higher adsorption rate.

RECOVERY OF URANIUM BY SYNTHETIC POLYMER

It has been reported that amidoxime compounds can be synthesized from nitriles and hydroxylamine (2) and that heavy metal ions are coordinated (3) with the amidoxime group. A metal-chelating resin with an amidoxime group was, therefore, synthesized (4,5) and applied to the separation and collection of metal ions from dilute solutions (6). Egawa et al. reported (7) that a metal-chelating amidoxime resin synthesized from acrylonitrile-divinylbenzene co-polymer and hydroxylamine shows selective adsorption of uranium from seawater. Continuation of this line of work is reported here.

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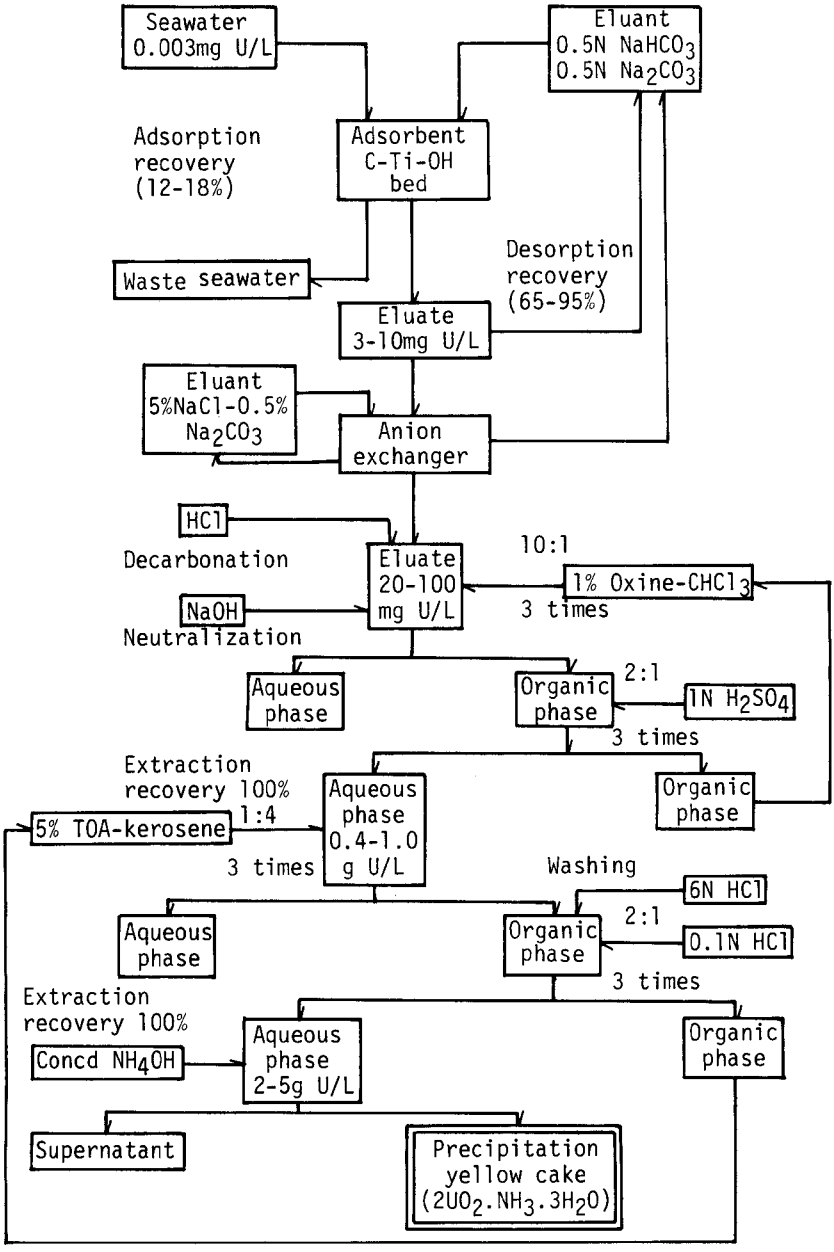

FIGURE 1. Flow diagram of system for uranium extraction from seawater with the fixed bed of titanium-activated composite adsorbent.

TABLE 1

Properties of AN-DVB-AO Resins

	No. 1	No. 2	No. 3	No. 4	No. 5
DVB/AN (%)	27	30	30	30	30
Cu^{2+} adsorbed (mM/g)	0.95	0.67	1.17	0.54	0.75
Anion exchange capacity (meq/g)	1.14	0.76	1.17	0.79	0.73
Swelling (mL/g)	2.64	3.54	3.39	3.79	3.77
Water content (%)	44.8	57.1	55.0	59.7	59.8
Surface area (m^2/g)	100	150	146	32	31
Pore volume (mL/g)	0.20	0.38	0.46	1.14	1.16
Pore radius (A)	90	100	140	1150	1100

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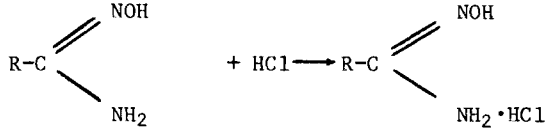
1. The Physicochemical Properties and Uranium Adsorptive Properties of Acrylonitrile-Divinylbenzene Co-Polymeric Amidoxime Resin (AN-DVB-AO Resin)

Synthesis and Physicochemical Properties of AN-DVB-AO Resin. AN-DVB co-polymers with different pore sizes and pore volumes were prepared by a literature method (5). The AN-DVB-AO resin was synthesized with AN-DVB co-polymer and hydroxylamine in methanol. The physicochemical properties of the resin are presented in Table 1. This resin consumes hydrochloric acid according to the following reaction:



The adsorptive capacity of AN-DVB-AO resin for Cu(II) ions correlates with the amount of hydrochloric acid consumed, which thus indicates the number of amidoxime groups in the resin.

Adsorptive Characteristics of AN-TEGDM-AO Resin for Uranium. The AN-TEGDM-AO resins with different degrees of cross-linking and amounts of the amidoxime group were synthesized, and their adsorptive properties were examined. Results are shown in Table 2 and Fig. 4.

TABLE 2

Properties of AN-TEGDM-AO Resins

Sample No.	TEGDM/AN (wt. %)	Water content (wt. %)	Swelling (cm^3/g resin)	Cu(II) adsorbed (mM/g resin)
3-1	20	67.5	5.31	1.67
3-2	30	65.2	4.26	1.98
3-3	40	60.5	3.98	2.09
3-4	50	54.9	3.45	1.65
3-5	60	53.7	3.18	1.92
3-6	40	54.7	3.52	0.31
3-7	40	55.5	3.57	0.58
3-8	40	58.1	3.81	1.27

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The rate of adsorption of uranium by the AN-TEGDM-AO resin from seawater showed a maximum value at 40-50% cross-linking.

With regard to the relation between pore structure and the degree of cross-linking of the AN-TEGDM-AO resin, the pore volume showed a maximum value at 30% cross-linking, whereas the specific surface area reached a maximum at 40%. These results suggest that the rate of adsorption of uranium is affeced by the pore structure of the resin; that is, the diffusion of uranium through the bulk of the resin is of importance in its adsorption from seawater. A linear relationship was observed between the rate of adsorption of uranium and the amount of amidoxime group, in analogy with the AN-DVB-AO resin, as shown in Fig. 5.

The pH Dependence of the Absorption of Copper(II) Ion and Uranyl Ion on the AN-DVB-AO Resin. As shown in Fig. 2, copper(II) and uranyl ions were not adsorbed on the resin from acidic solution below pH 2. However, when the pH of the solution increased to over 3, the copper(II) and uranyl ions were adsorbed. These results suggest that uranium adsorbed on the resin from seawater can be desorbed by acid solutions.

Uranium Adsorption on the AN-DVB-AO Resin from Seawater. The recovery of uranium from seawater by the resin was carried out by

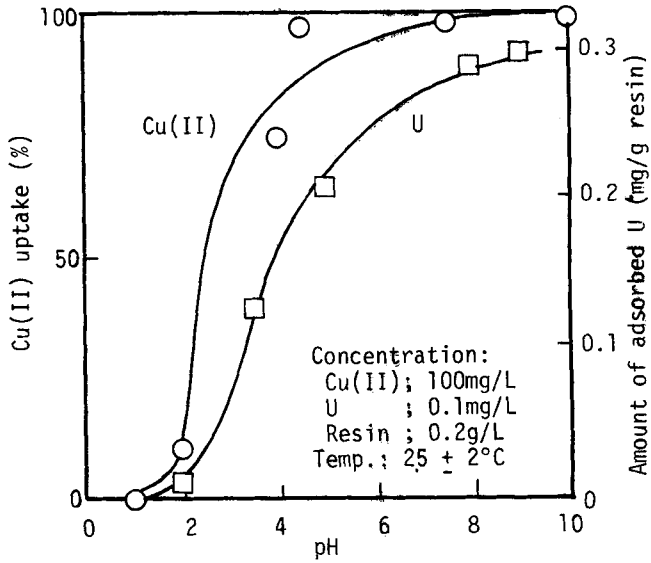

FIGURE 2. The pH dependence of adsorption of Cu(II) and U by AN-DVB-AO resin.

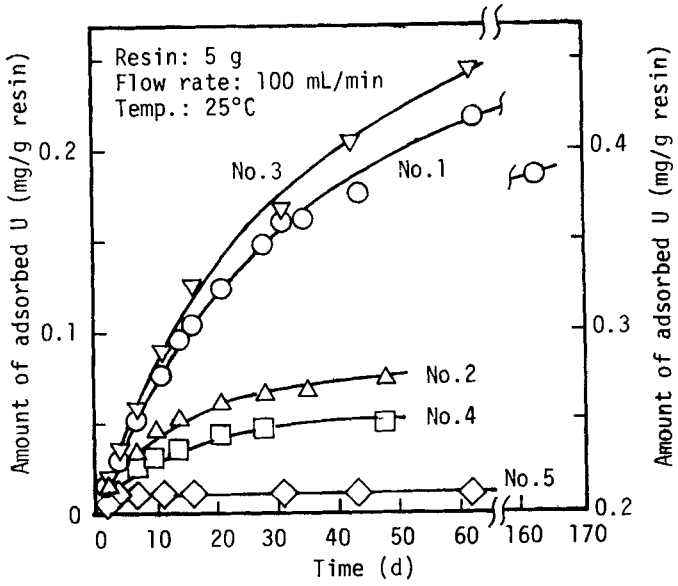

FIGURE 3. The rate of adsorption of uranium by AN-DVB-AO resin.

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column sorption under the following conditions: resin 5 g, flow rate of natural seawater 20 mL/min·g resin, temperature 25 ± 2°C.

The amount of uranium adsorbed by the resin increased with increasing amounts of seawater passed through the resin bed, as shown in Fig. 3. The AN-DVB-AO resin No. 1 adsorbed 0.38 mg U/g resin in 165 days. The rate of uranium adsorption was proportional to the amount of amidoxime group in the resin. During these adsorption experiments, different wettabilities of the resins were observed, the resin with the high uranium adsorptin rate being wetted easily with seawater.

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2. The Hydrophilic Amidoxime Resin (AN-H-AO Resin)

Selection of Cross-linking Agent. From the above results, it was noted that the wettability of the resin is of great importance in the adsorption of uranium from seawater, and that the AN-DVB-AO resin has less wettability owing to the hydrophobic cross-linking agent, divinylbenzene.

To improve the wettability of the resin, hydrophilic co-polymers were synthesized from acrylonitrile and hydrophilic cross-linking agents such as ethylene glycol dimethacrylate (EGDM) and tetraethylene glycol dimethacrylate (TEGDM). Hydrophilic resins were then reacted with hydroxylamine. The AN-H-AO resin with TEGDM as a cross-linking agent gave the highest rate of uranium adsorption from seawater.

3. The Recovery of Uranium from Seawater with the AN-TEGDM-AO Resin

The Adsorption of Uranium from Seawater. It was found that the wettability of the AN-TEGDM-AO resin was improved by treating it with sodium hydroxide solution. A column was charged with 90 mL of AN-TEGDM-AO resin which had been treated with sodium hydroxide solution (1 M), and seawater at 15-25°C was passed through it at a flow rate of 90 bed volumes per hour. The amount of uranium in the resin reached 3.5 mg/g resin as shown in Fig. 6. The adsorption rate was affected by the temperature of the seawater.

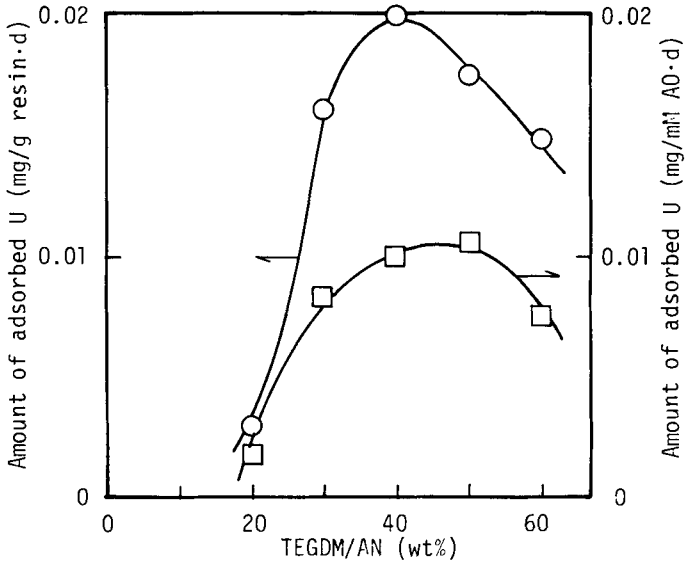

FIGURE 4. Relationship between the rate of uranium adsorption and the ratio of tetraethylene glycol dimethacrylate (TEGDM) to acrylonitrile (AN).

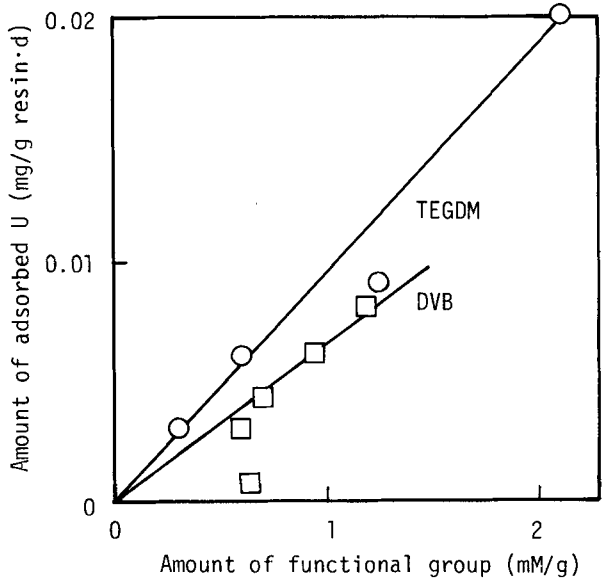

FIGURE 5. Effect of dilution by the cross-linking agent on the uranium adsorption rate.

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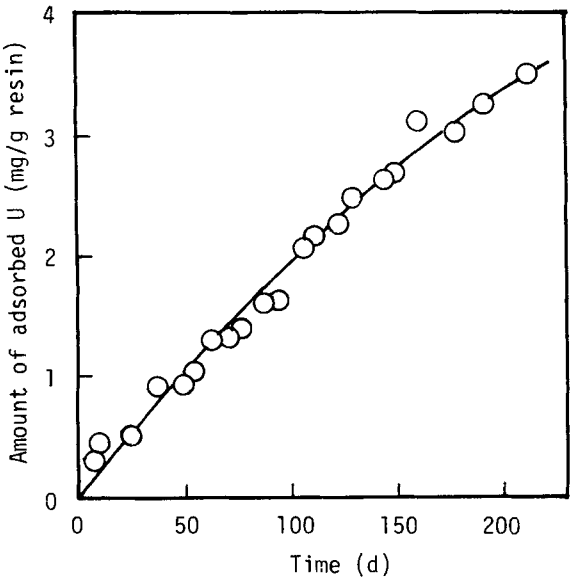

FIGURE 6. Rate of adsorption of uranium by AN-TEGDM-AO resin from seawater (15-25°C).

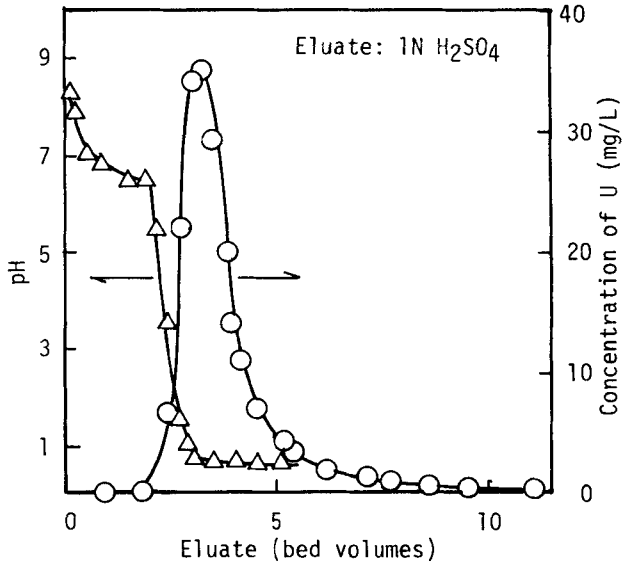

FIGURE 7. Elution of uranium from AN-TEGDM-AO resin at room temperature.

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TABLE 3

Effects of Repeated Adsorption and Desorption

Number of cycles	1	2	3	4	5
Uptake (%)	26	25	25	20	28
Rate of adsorption (mg/g r·d)	0.046	0.045	0.045	0.036	0.042
Desorption (%)	94	93	96	93	94

The Effect of Flow Rate of Seawater on Adsorption of Uranium. The rate of uranium adsorption by the AN-TEGDM-AO resin increased with increasing flow rate, whereas the percent recovery of the uranium decreased. This suggests that the adsorption rate depends on the diffusion of uranyl ions through both the liquid boundary layer and the bulk of the resin.

Desorption of Uranium from the AN-TEGDM-AO Resin. Figure 7 is an elution curve of uranium from the resin with 0.5 M sulfuric acid solution. After two bed volumes, the pH of the eluate dropped sharply, and most of the uranium was eluted in the next three bed volumes.

Recycle of Adsorption and Desorption Processes. On the basis of the above results, the upstream column adsorption from seawater and desorption by sulfuric acid solution were repeated several times. The results, which are summarized in Table 3, show that neither adsorption rate nor recovery were impeded in five cycles of operation.

4. Acrylonitrile-Amidoxime Fiber Adsorbent

To aid in developing another system for the recovery of uranium from seawater, we attempted to provide an amidoxime adsorbent in fiber form.

Properties of the Acrylonitrile-Amidoxime Fiber Adsorbent. Commercial acrylonitrile fibers were used to prepare acrylonitrile-amidoxime fiber (AN-AO-F) by reaction with hydroxylamine in methanol. The properties of the raw materials and an AN-AO-F obtained are summarized in Table 4. The amount of the functional group varied with

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TABLE 4

Properties of AN-AO-F Resin Fibers

No.	Raw Material		AN-AO-F		
	Diameter (μm)	Wet single fiber strength (g)	Diameter (μm)	Wet single fiber strength (g)	Cu(II) adsorbed (mM/g F)
1	15	-	17	-	1.05
2	13	6.6	35	4.3	1.81
3	19	6.0	19	5.4	1.33
4	20	9.1	35	7.0	1.97
5	25	11.3	27	8.4	2.60
6	20	6.4	20	5.3	1.81
7	27	10.5	27	9.6	1.7

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the kind of fiber used, in spite of the same conditions of reaction, as indicated by the extent of Cu(II) adsorption. The strength of single fibers was found not to be greatly decreased by the reaction with hydroxylamine.

The adsorption of uranium from seawater on each AN-AO-F was examined by column sorption at 25°C. The adsorption rates on various AN-AO-F fibers are shown in Fig. 8; the rate was not dependent on the amount of amidoxime which was estimated with Cu(II) adsorptive capacity

Treatment of AN-AO-F by Alkaline Solution. It was found that the rate of adsorption of uranium increased by the treatment of AN-AO-F with alkaline solution, similar to the case of an AN-TEGDM-AO resin. The change in the physicochemical properties of AN-AO-F by an alkaline treatment is shown in Table 5. As the time of alkaline treatment increased, the content of weak acid groups increased, whereas the content of weak base group did not change. The shorter treatment times, up to 8 h, had little efect on the fiber strength, but it decreased at longer treatment times.

ADSORPTIVE PROPERTIES OF ADSORBENTS FOR URANIUM AND OTHER HEAVY METAL IONS

The rates of adsorption of uranium from seawater by AN-TEGDM-AO resin, two AN-AO-F fibers, and titanium-activated carbon composite

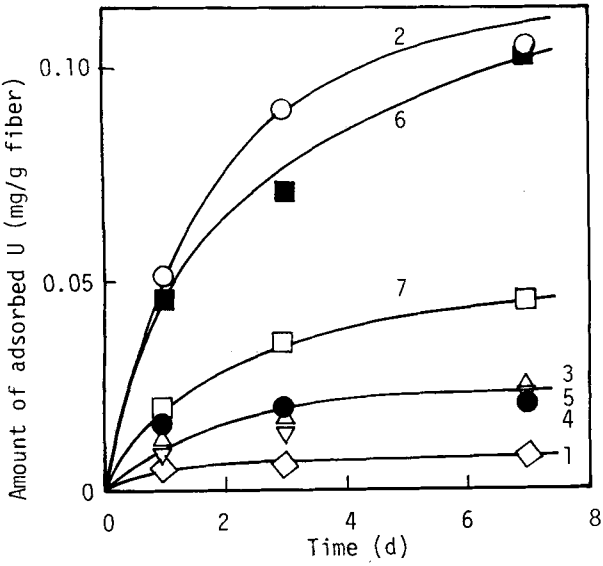

FIGURE 8. Rates of adsorption of uranium by acrylamidoxime fibers at 25°C.

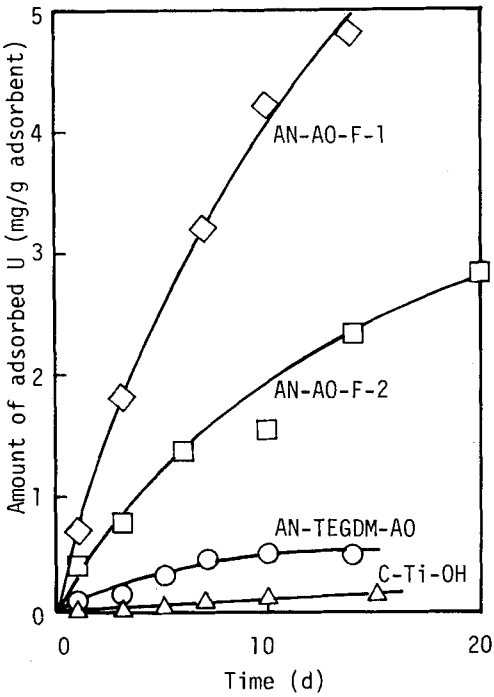

FIGURE 9. Rates of adsorption of uranium by various adsorbents.

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TABLE 5

Effects of Alkaline Treatment of an AN-AO-F Resin Fiber

Time of treatment (h)	Single fiber strength (g)	Cu(II) adsorbed (mM/g-F)	Acid group (meq/g-F)	Base group (meq/g-F)
0	5.2	0.7	0.3	1.6
4	4.6	1.7	1.7	1.1
8	4.5	2.1	2.4	1.2
12	3.8	2.2	3.3	1.2
24	3.2	2.6	4.8	1.7
48	2.6	4.3	-	-

TABLE 6

The Selectivities of Different Types of Adsorbents for Elements in Seawater

Element	Conc. in seawater (mg/L)	Concentration factor (mL/g)		
		AN-AO-F	AN-DVB-AO	Ci-Ti-OH
Mg	1.4×10^{3}	3.7×10	0.3	4.6
Ca	0.4×10^{3}	2.9×10	0.9	3.6×10
Cr	5.0×10^{-5}	4.0×10^{4}	-	1.6×10^{6}
Mn	2.0×10^{-3}	2.5×10^{6}	-	4.0×10^{4}
Fe	1.0×10^{-2}	2.5×10^{5}	1.4×10^{4}	5.3×10^{4}
Cu	3.0×10^{-3}	2.2×10^{5}	1.1×10^{4}	5.5×10^{4}
Zn	1.0×10^{-2}	1.5×10^{5}	9.4×10^{3}	7.4×10^{4}
U	3.0×10^{-3}	4.0×10^{5}	2.3×10^{4}	2.6×10^{4}

adsorbent (C-Ti-OH) are shown in Fig. 9. The selectivities for the heavy metal ions in seawater by three types of adsorbents are shown in Table 6. With the exception of Ca and Cr, the concentration factors are generally higher with AN-AO-F and lower with AN-DVB-AO than with C-Ti-OH.

CONCLUSION

It is concluded from the above results that metal-chelating polymer adsorbents combining the amidoxime group are applicable to the recovery of uranium from seawater.

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