

Preparation of Fibrous Adsorbents Containing Amidoxime Groups by Radiation-Induced Grafting and Application to Uranium Recovery from Sea Water

N. KABAY,^{1,*} A. KATAKAI,¹ T. SUGO,¹ and H. EGAWA²

¹Japan Atomic Energy Research Institute, Takasaki Radiation Chemistry Research Establishment, Takasaki, Gunma 370-12, Japan; and ²Kumamoto University, Faculty of Engineering, Department of Applied Chemistry, Kumamoto 860, Japan

SYNOPSIS

Polypropylene fibers and polyethylene hollow fibers were used as trunk polymers and were irradiated by electron beams with a dose of 200 kGy under N₂ atmosphere. Grafting of acrylonitrile to those irradiated fibers was carried out at 40°C for different periods of time. The degree of grafting was determined as a function of time. The fibrous adsorbents containing amidoxime groups were prepared by the reaction of acrylonitrile-grafted polymers with 3% hydroxylamine in a methanol–water mixture (1 : 1). Distribution of copper ions complexed with amidoxime groups at various adsorption times was obtained by electron-probe X-ray microanalysis. The amidoxime groups are homogeneously distributed in the cross section of fibrous adsorbents. The fibrous adsorbents based upon polypropylene fiber of 40 μm showed a remarkable kinetic behavior for Cu²⁺. Even after 15 min, the adsorption capacity was 2.32 mmol Cu²⁺ per gram of fiber. Also, the functionalization with hydroxylamine was carried out at different conditions to compare the adsorption characteristics of the resultant adsorbents. Despite having superficially different properties (elemental microanalysis, ion-exchange capacities, adsorption capacity for UO₂²⁺), the polypropylene-based fibrous adsorbents showed similar adsorption properties for uranium from sea water. The adsorption tests proved the performance of the polypropylene-based fibrous adsorbents as a promising material for uranium recovery from sea water. In addition, uranium uptake of fibrous adsorbents increased in proportion to the volume of sea water. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Owing to the worldwide interest in the extraction of uranium from sea water, there have been many papers dealing with this subject. Amidoxime-containing adsorbents have been shown to be usable for this purpose, and this has prompted a number of papers dedicated mainly to synthesis of these materials.

Egawa et al.^{1–3} prepared a number of macroreticular chelating resins containing amidoxime groups

by reacting acrylonitrile–divinylbenzene copolymer beads with hydroxylamine. It was reported that these resins have a high capacity for uranium in sea water. Also, several research groups have continued this line of work, developing and testing the various kinds of adsorbents containing amidoxime groups.^{4–6}

The fibrous adsorbents containing amidoxime groups have been shown to exhibit superior adsorption characteristics, especially in view of the high adsorption rate.^{5,7–12} However, it was reported that the fibrous adsorbents have poor mechanical stability when they were contacted with alkali.¹³ This was supposed to have resulted from the high swelling of the fiber and decrease in its mechanical strength, based upon the hydrolysis of the residual cyano group in the polymer network. With this in mind, radiation-induced grafting was developed to control

* To whom correspondence should be addressed at Ege University, Institute of Nuclear Sciences, 35100 Bornova, Izmir, Turkey.

the introduction of the amidoxime group in the prescribed part of the fibrous material, keeping the original mechanical strength, and, thus, to synthesize more stable fibrous adsorbents. Several types of fibrous adsorbents were prepared by changing the grafting conditions and were applied to the recovery of uranium from sea water.¹³⁻¹⁶

Saito et al.¹⁷⁻²⁰ suggested a novel adsorption system using hollow-fiber adsorbents containing amidoxime groups by radiation-induced grafting of acrylonitrile onto polyethylene hollow fiber.

The present work deals with radiation-induced grafting of acrylonitrile onto polypropylene fiber and polyethylene hollow fiber for the purpose of finding (1) the optimum reaction conditions to obtain a maximum degree of grafting; (2) the factors affecting the adsorption properties for copper and uranyl ions; and (3) the optimum reaction conditions during the functionalization with NH_2OH for enhancing the adsorption efficiency.

EXPERIMENTAL

Materials

Polypropylene fibers (ca. 40, 25, and 1–5 μm in diameter) and polyethylene hollow fibers (ca. 0.01 μm in pore size) were used as trunk polymers. All reagents were used as received or were purified by standard methods.

Electron-beam Radiation-induced Grafting

Fibers used for synthesizing adsorbents were dried under vacuum for 16 h and then were packed in a polyethylene bag under nitrogen atmosphere. Samples placed on a stainless-steel plate were irradiated with an electron accelerator (Dynamitron, Model IEA 3000-25-2, Radiation Dynamics Co.) operating at a beam energy of 1.5 MeV and a current of 1 mA at room temperature.

Immediately after irradiation, the fibers were placed into a glass ampule and were evacuated. The introduction of acrylonitrile to those irradiated fibers was carried out under nitrogen atmosphere. The grafting was performed at 40°C. After the grafting, the fibers were immersed in *N,N'*-dimethylformamide at 40°C for 30 min (3 \times) to remove unreacted monomers and homopolymers. Subsequently, the fibers were rinsed with methanol at room temperature (3 \times), air-dried, and then dried under vacuum for 16 h. The grafting yield was calculated by the percentage increase in weight as follows:

$$\text{Degree of grafting (\%)} = [(W_1 - W_0)/W_0] \times 100$$

where W_0 and W_1 represent the weights of initial and grafted fibers, respectively.

Functionalization with Hydroxylamine

The fibers were reacted with 3% hydroxylamine in a methanol–water mixture (1 : 1) at 80°C to convert the cyano groups of grafted chains to amidoxime groups. The preparation of polypropylene-based fibrous adsorbents containing amidoxime groups is shown in Scheme 1.

To investigate the discrepancy in reactive sites of the resulting polymers, the functionalization of polypropylene fiber (1–5 μm) grafted with acrylonitrile was conducted at three different conditions as follows:

Condition A

A methanol–water (1 : 1) solution of hydroxylamine was prepared by adding concentrated KOH into the solution of $\text{NH}_2\text{OH} \cdot \text{HCl}$ in water until pH 7. Polypropylene fiber grafted with acrylonitrile was reacted with hydroxylamine at 80°C for 2 h.

Condition B

The fiber was reacted with hydroxylamine prepared using $\text{NH}_2\text{OH} \cdot \text{HCl}$ and Na_2CO_3 in the presence of an ethanol–water (1 : 1) mixture as a reaction solvent at 90°C for 2 h.

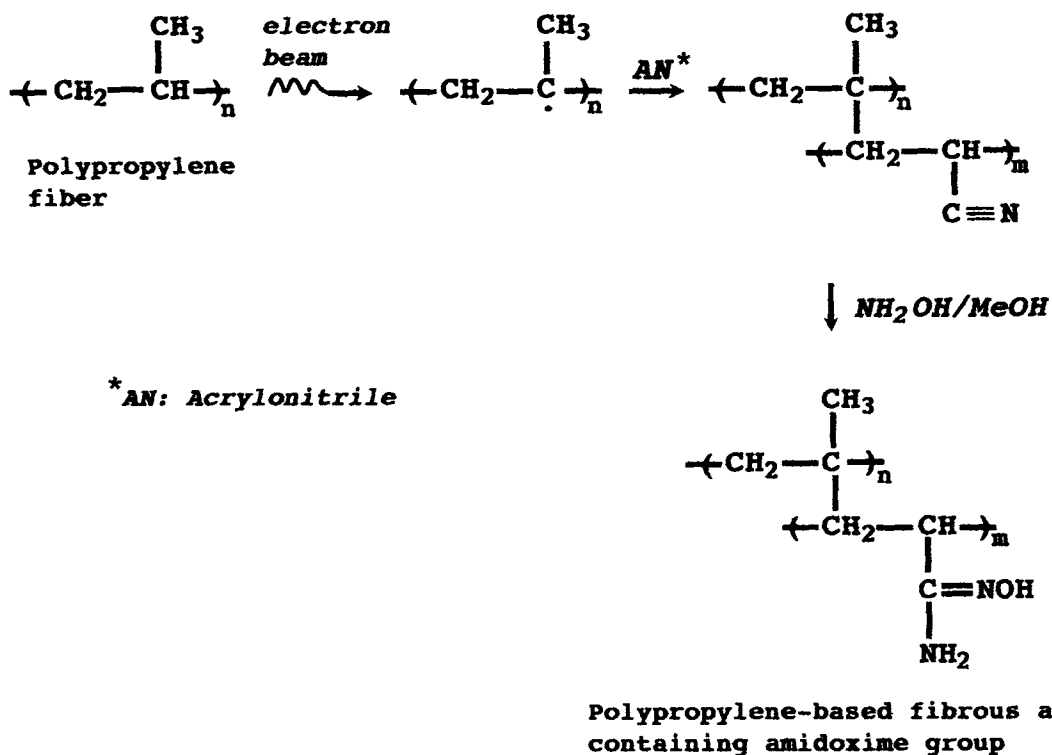
Condition C

The fiber was reacted with a solution of hydroxylamine obtained by the employment of excess $\text{NH}_2\text{OH} \cdot \text{HCl}$ compared to KOH, i.e., acidic condition (pH 4) in the presence of ethanol–water (1 : 1) as a reaction solvent. The reaction was carried out at 90°C for 2 h.

Batchwise Adsorption of Cu^{2+}

Each fibrous adsorbent was subjected to a pretreatment that involved contacting for 1 h with a 2.5% KOH solution at 80°C. A known amount of sample (0.1 g before alkaline treatment) was then contacted with a solution (500 mL) containing Cu^{2+} (10 mM) as its nitrate at pH 6 with continuous stirring at 30°C for 48 h.

To obtain information on the relative performance of each fibrous adsorbent in kinetic terms,



Scheme 1 Preparation of fibrous adsorbent containing amidoxime group.

the adsorption of Cu^{2+} from a nitrate solution containing 10 mmol L^{-1} at pH 6 and 30°C was monitored with time, samples being taken at 5, 10, 15, 30, and 60 min and at 7, 24, and 48 h.

The samples loaded from a solution of Cu^{2+} were stripped batchwise with 10 mL of 1M HCl at 25°C for 2 h ($3\times$). The analysis of Cu^{2+} was performed on a Polarized Zeeman atomic absorption spectrophotometer (Model Z-6100 type). The instrument was calibrated using appropriate standard solutions

of Cu^{2+} , and all solutions for analysis were diluted down to between 0.5 and 5.0 ppm prior to assaying.

The distribution of Cu^{2+} in the fibrous adsorbents was measured with a Jeol electron probe X-ray microanalyzer, EPMA (Model JXA-733).

Batchwise Adsorption of UO_2^{2+}

Each fibrous adsorbent (0.125 g) was equilibrated in a batch process with a solution (50 mL) contain-

Table I Potential Cu^{2+} Adsorption with Fibrous Adsorbents

Symbol ^a	Fiber		Grafting		Reaction with NH_2OH (h)	$[\text{Cu}^{2+}]$ Uptake ^b (mmol/g)
	Diameter (μm)	Time (h)	Degree of Grafting (%)			
PP-1	40.00	3	87.3	3	3.39	
PP-2	25.00	6	89.0	3	3.59	
PP-3	1.00-5.00	5	96.6	2	3.63	
PE-HF	0.01 ^c	6	102.5	2	3.60	

^a PP: polypropylene fiber; PE-HF: polyethylene hollow fiber.

^b Adsorption of copper ions: pH 6, 30°C , 48 h.

^c Pore size.

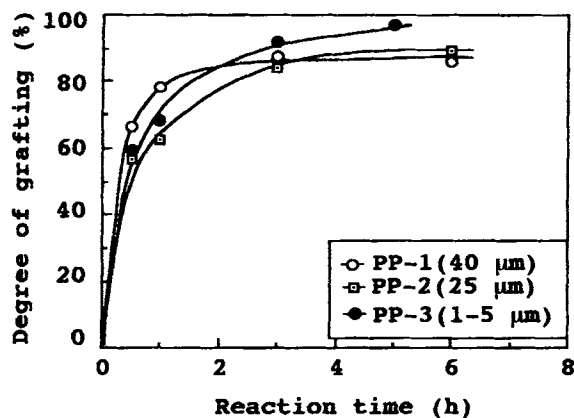


Figure 1 Effect of reaction time on degree of grafting for polypropylene fibers.

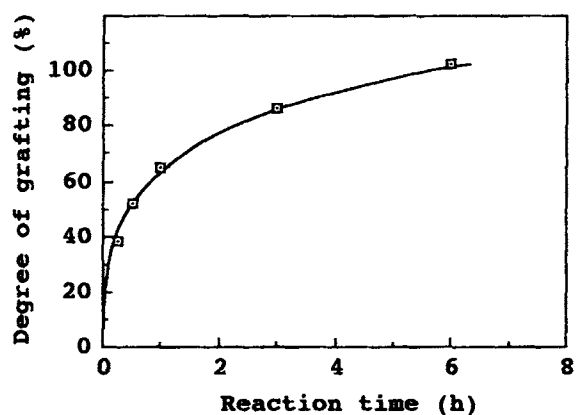


Figure 2 Effect of reaction time on the degree of grafting for polyethylene hollow fibers.

ing UO_2^{2+} (0.01M) as its nitrate with continuous shaking at 30°C for 24 h. The UO_2^{2+} content of the supernatant was determined colorimetrically using sodium salicylate. The amount of UO_2^{2+} adsorbed (i.e., mmol UO_2^{2+} uptake/g of fiber) was calculated from the decrease in concentration of the supernatant.

Batch Extraction of Uranium from Sea Water

Samples (0.1 g) of fibrous adsorbents were contacted initially with 2.5% KOH at 80°C for 1 h. The extraction of uranium from sea water was performed with (a) a batch process using 5 L of natural sea water and (b) a semibatch process by exchanging 5 L of natural sea water intermittently with fresh nat-

ural sea water. The adsorption period was 24 h for each 5 L of sea water.

After contact with sea water, fibrous adsorbents were treated with 1.0M HCl (25 mL) by stirring on a magnetic stirrer for 1 h (2×) to liberate uranium.

Measurement of Anion-exchange Capacity

A 0.5 g sample of fibrous adsorbent and a 100 mL of hydrochloric acid solution (0.1M) were shaken at 30°C for 15 h. The anion-exchange capacity of the fibrous adsorbent was measured by determining chloride in the supernatant by argentometry. To a 10 mL portion of supernatant, 10 mL of 0.2M NaHCO_3 solution and 5 mL of a solution containing 2% starch by weight were added. The resulting so-

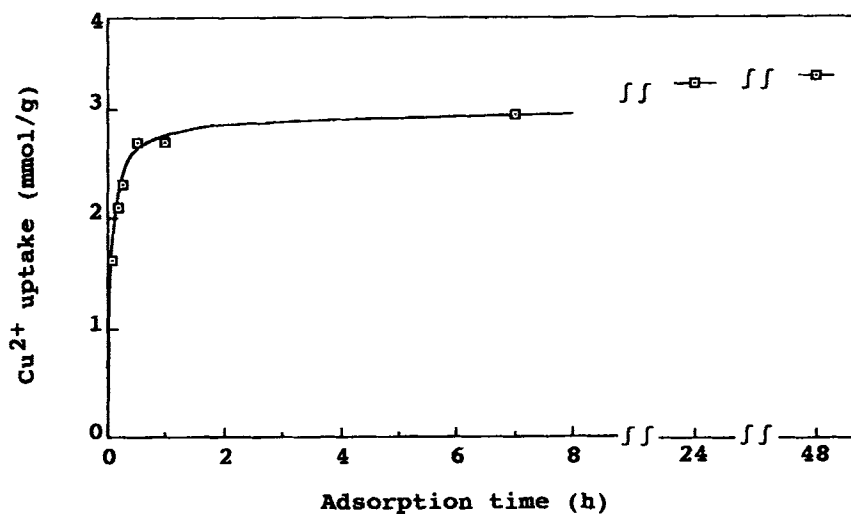


Figure 3 Adsorption of copper ions by polypropylene-based fibrous adsorbent as a function of adsorption time.

Table II Functionalization with Hydroxylamine Using Various Conditions

Condition	Elemental Microanalysis (%)		
	C	H	N
A	60.10	9.80	13.69
B	55.55	8.80	16.54
C	72.14	9.65	13.26

lution was titrated with a 0.1 M solution of silver nitrate using a fluorescein indicator. The anion-exchange capacity of the sample was measured by determining, the chloride released.

Measurement of Cation-exchange Capacity

The fibrous adsorbent used for the measurement of anion-exchange capacity was washed with deionized water until the washings were acid-free, air-dried and then dried at 40°C under vacuum. The resulting sample (0.25 g) and 25 mL of sodium hydroxide solution (0.1 M) were shaken at 30°C for 15 h. A 5 mL portion of supernatant was titrated with a 0.1 M solution of HNO₃ using a methyl orange indicator. After the methyl orange end point was reached, the chloride released was titrated with a 0.05 M solution of AgNO₃ using 0.5 mL of 0.05 M K₂CrO₄ solution for the detection of the end point. The cation-exchange capacity was determined by subtracting the amount of chloride released from the amount of sodium hydroxide exhausted.

Elemental Analysis and IR Spectroscopy

Elemental analyses (C, H, N) were performed on a Yanaco Corder (Model MT-3) instrument. IR spectra were recorded in KBr pellets on a Jasco J-055 spectrophotometer.

RESULTS AND DISCUSSION

Preparation of Fibrous Adsorbents

Grafting of acrylonitrile to the irradiated fibers was carried out at 40°C. Figure 1 shows the relationship between the degree of grafting and reaction time for polypropylene fibers with different diameters. For each fibrous sample, percent graft was increased rapidly in the initial 0.5–3 h and then it leveled off.

Figure 2 shows plots for polyethylene hollow fiber, suggesting that the relationship between the degree of grafting and reaction time displayed a trend similar to those obtained with polypropylene fibers.

Functionalization of the acrylonitrile-grafted fibers with maximum degree of grafting was performed using 3% hydroxylamine solution in MeOH–H₂O (1 : 1 mixture) at 80°C. As summarized in Table I, the resulting fibrous adsorbents containing amidoxime groups remained effective for the adsorption of Cu²⁺ at pH 6.

To obtain some measure of the kinetic performance of fibrous adsorbent based upon polypropylene fiber (40 μm in diameter), the adsorption of Cu²⁺ was monitored with time. The typical loading profile for this adsorbent is shown in Figure 3. The polypropylene-based fibrous adsorbent achieved almost full Cu²⁺ loading quickly in the initial 15 min–1 h. Even after 15 min, the amount of Cu²⁺ loaded was 2.32 mmol Cu²⁺ per gram of fiber.

Figure 4 shows changes in the distribution of Cu²⁺ adsorbed in the cross section of the polypropylene-based fibrous adsorbent (40 μm in diameter) with adsorption time. The amidoxime groups are homogeneously distributed in the cross section of fibrous adsorbent. The discrepancy in adsorption layer was not so apparent after 1 h, showing a correlation with the data in Figure 3. These results highlight the superior performance of polypropylene-based fibrous adsorbents, suggesting a fast exchange for Cu²⁺ was achieved with high efficiency.

Table III The Properties of Polypropylene-based Fibrous Adsorbents

Condition	C _a ^a (meq/g)		C _c ^b (meq/g)		[UO ₂ ²⁺] Uptake ^c (mmol/g)
	NT	AT	NT	AT	
A	2.67	2.58	1.32	2.04	1.36
B	2.12	2.17	1.65	2.20	1.41
C	0.18	0.97	0.31	2.52	1.47

^a Anion-exchange capacity. NT: nontreatment, AT: alkaline treatment.

^b Cation-exchange capacity.

^c Alkaline treatment: 2.5% KOH, 80°C, 1 h.

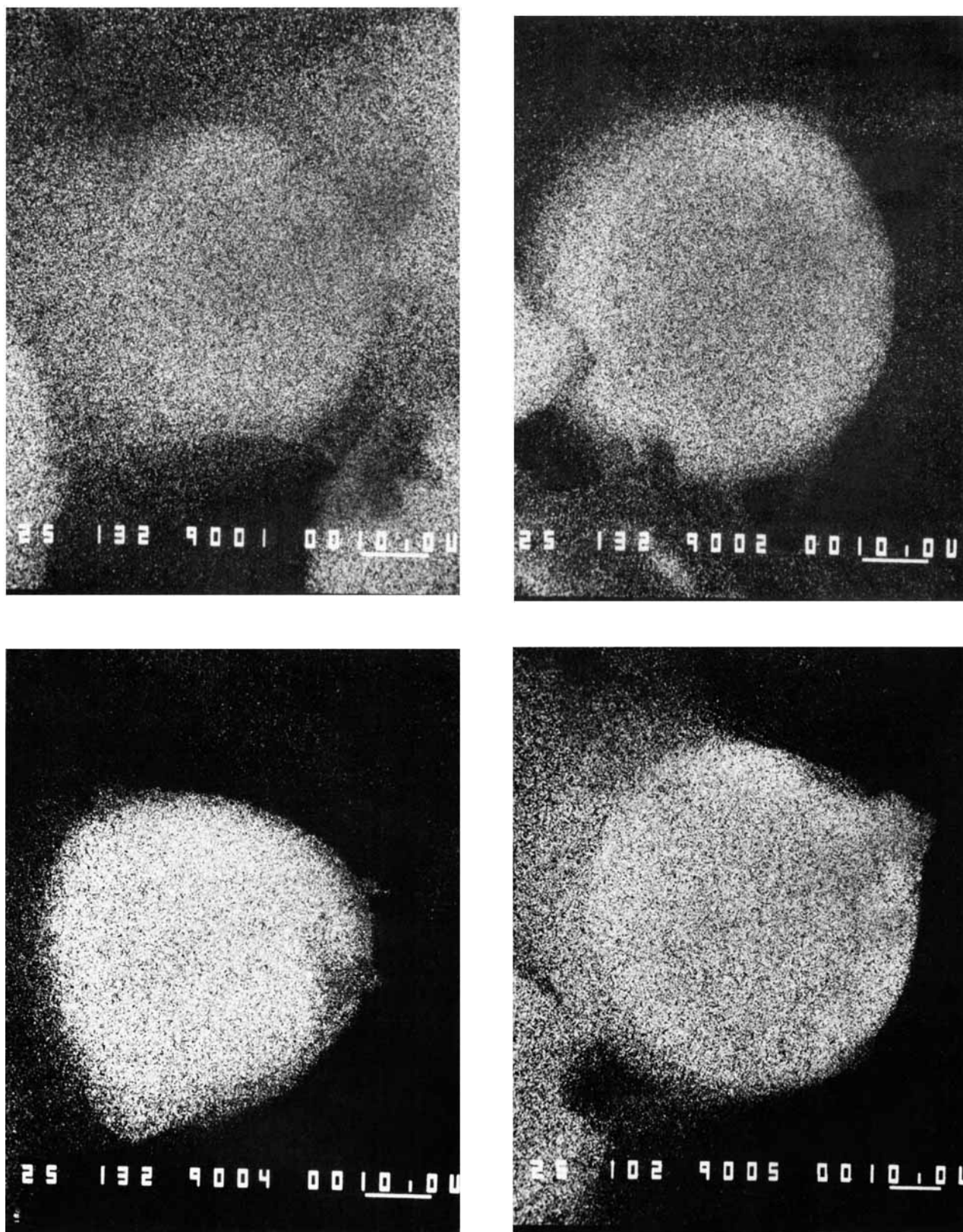


Figure 4 Distribution of copper ions in a polypropylene-based fibrous adsorbent at various contact times: 5, 10, and 30 min; 1, 7, 24, and 48 h.

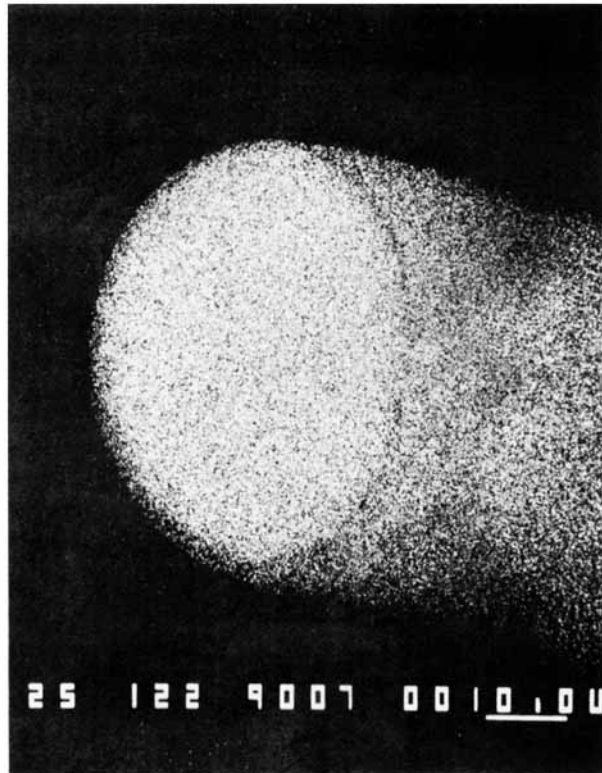


Figure 4 (Continued from the previous page)

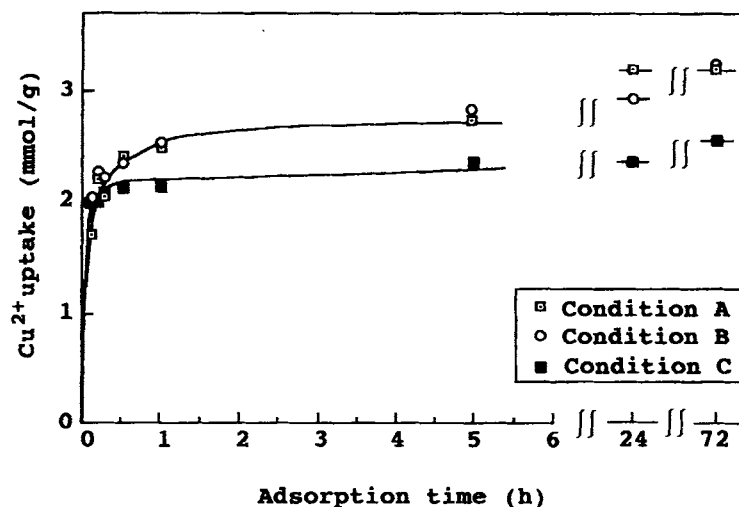


Figure 5 Adsorption profiles of polypropylene-based fibrous adsorbents prepared at various conditions.

Effect of Reaction Conditions

Functionalization of acrylonitrile-grafted polypropylene fiber (1–5 μm in diameter) with hydroxylamine was carried out using various conditions to investigate the optimal conditions for a high efficiency in adsorption properties. The details of three different methods of functionalization (Conditions A, B, and C) are given in the Experimental section.

The results of the elemental microanalyses are summarized in Table II. The elemental analyses suggest that each reaction occurs in a different way, resulting in different changes in the percentage of carbon, hydrogen, and nitrogen.

The IR spectrum of the fibrous adsorbent prepared using Condition C shows a very strong peak at 2235 cm^{-1} , corresponding to the remaining nitrile vibration. Clearly, this is caused by the poor functionalization of fibers with Method C since the neutralization of $\text{NH}_2\text{OH} \cdot \text{HCl}$ was not complete at pH 4 for the preparation of hydroxylamine.

Both elemental analyses and IR spectra can be taken only as a guide to the discrepancy in chemical structures of fibrous adsorbents. From these data

Table IV Uranium Uptake of Fibrous Adsorbents Prepared Using Various Conditions

Condition	Uranium Uptake ($\mu\text{g U/g}$ of fiber/day)
A	152
B	136
C	119

alone, no attempt will be made to draw any conclusions about the mechanism of each reaction. What is clear, however, is that Conditions A and B gave products with larger anion-exchange and cation-exchange capacities than those of Condition C (Table III). On the other hand, as noticed in Table III, a certain increase in cation-exchange capacity was observed by the alkaline treatment, suggesting hydrolysis of the remaining nitrile groups to carboxylic acid. Therefore, the diffusion of uranyl ions increased through micropores and the formation of the uranium complex became easier.

Egawa et al.²¹ previously reported that anion-exchange capacity decreased with the alkaline treatment due to the hydrolysis of amidoxime group. Here, the enhanced hydrophilicity by the alkaline

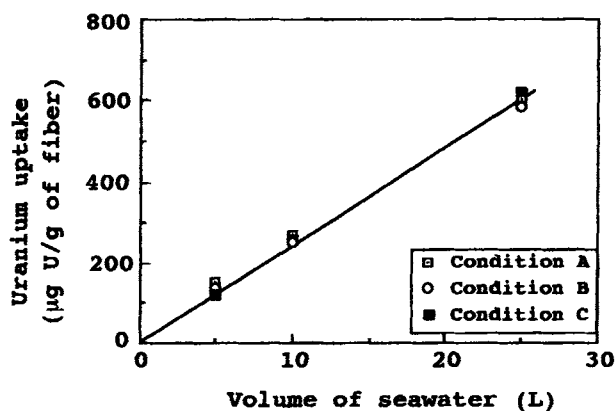


Figure 6 Recovery of uranium from sea water by fibrous adsorbents prepared at various conditions vs. volume of sea water.

treatment hastened the diffusion of hydrochloric acid into the fibrous adsorbent. Therefore, it was supposed that the anion-exchange capacity did not show a significant decrease after the alkaline treatment. On the other hand, the increase in cation-exchange capacity by the alkaline treatment is consistent with results reported in the literature.²¹

To compare the relative performance of each adsorbent prepared using various conditions in kinetic terms, the adsorption of Cu^{2+} was monitored with time. The isotherms are shown in Figure 5. The adsorption of Cu^{2+} seems unchanged after 0.5 h. The difference between Conditions A and B compared with Condition C does not seem remarkable.

To investigate the possible effect of the functionalization conditions on the uranium uptake from sea water, the fibrous adsorbents prepared were immersed in 5 L of sea water. Table IV summarizes the adsorption rate of uranium as μg of U/g of fiber/day. The uranium uptakes of fibrous adsorbents prepared using Conditions A and B are higher than that of Condition C. However, the result corresponding to Condition C was also noticeable. Here, the enhanced diffusion of uranium by the alkaline treatment contributed to the uranium adsorption of fibrous adsorbents.

Figure 6 shows the relationship between the amount of uranium uptake by the polypropylene-based fibrous adsorbents prepared using various conditions and volumes of sea water. In all cases, the amount of uranium uptake is proportional to the volume of sea water.

CONCLUSIONS

The present investigation has shown that the radiation-induced grafting of acrylonitrile to the polyethylene hollow fibers and polypropylene fibers was performed with a high percent graft.

The polypropylene-based fibrous adsorbents containing amidoxime groups achieved a rapid uptake and also a high capacity for Cu^{2+} and UO_2^{2+} . To investigate the possible effect of the functionalization on the uranium recovery from sea water, each fibrous adsorbent prepared using various conditions was tested. Neither elemental analyses nor IR spectra gave distinct information to determine the chemical structure of fibrous adsorbents. To elucidate the precise chemical structure, further investigation should be performed.

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