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Fine Fibrous Amidoxime Adsorbent Synthesized by Grafting and Uranium Adsorption–Elution Cyclic Test with Seawater

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ABSTRACT

Fibrous amidoxime adsorbents were prepared by radiation-induced co-grafting of acrylonitrile (AN) and methacrylic acid (MAA) and subsequent amidoximation. Adsorption of uranium in seawater was evaluated by pumping seawater into the adsorbent column. The best monomer ratio of AN and MAA was 7 : 3 for continual usage of uranium adsorption. Though hydrochloric acid is an effective eluting agent for the metals adsorbed on the adsorbent, amidoxime groups were simultaneously damaged after five cycles of adsorption–desorption.

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This deterioration was reduced by an alkaline treatment of the adsorbents after each elution. Furthermore, various organic acids were examined as elution agents. It was found that the 80% of adsorption activity was still maintained after five cycles of adsorption–desorption when tartaric acid was used for eluting agent.

Key Words: Amidoxime adsorbent; Co-grafting; Adsorption; Uranium; Cyclic test; Alkaline treatment; Tartaric acid.

INTRODUCTION

Some ppb of valuable rare metals such as vanadium and uranium are solved in seawater. However, the total amounts of these metals are extremely huge. For example, the uranium amount is 4.5 billion which is equivalent to 1000 times of mine uranium.[1,2] Hence, the recovery of rare metals like uranium from seawater has been considered as one of the useful techniques for energy security for atom power plant in the future. If we succeeded to collect such kinds of rare metals effectively from seawater, our country could not suffer from the shortage of rare metals.

Radiation induced graft polymerization is a useful technique for the preparation of metal and gas adsorbent by using polymer fibers and films as trunk polymer.[3–7] The process of making adsorbents consisted of three steps. First, irradiation by an electron beam or gamma ray was conducted to produce radicals initiating the graft polymerization. Second step was grafting where the vinyl monomers were reacted with the radicals and the graft chains were propagated from the radicals in the trunk polymer. After grafting, the introduced graft chains were chemically modified to functional group having the selective affinity to the aiming metal ion.

Amidoxime (AO) adsorbents are considered as the most promising material for the recovery of uranium from seawater.[8–11] Adsorbents having AO groups exhibits a high selectivity against uranium which exists as tricarbonate–uranyl(VI) complex, $[UO_2(CO_3)_3]^{4-}$, in seawater.[12–14] The adsorbed uranyl ions are easily eluted with acid solutions.[14–17] Though the repetition use of the adsorbent is important on the point of economical view,[18,19] there is no information of the damage of the cyclic test of the adsorption and elution for the AO adsorbents.

The objective of the present work is to optimize the composition of cografting for the recovery from seawater, to evaluate the damage and mechanism of the adsorbent using inorganic acid as an eluting agent and to minimize the damage of the adsorbent by means of alkaline treatment and organic eluting agent.

EXPERIMENTAL

Material

Polyethylene-coated polypropylene nonwoven fiber (NF) supplied by Kurashiki Textile Manufacturing Co., Okayama Japan, was used as a trunk polymer for co-grafting. The average diameter of the NF was 13 μm. Acrylonitrile (AN) and methacrylic acid (MAA) were purchased from Kanto Chemical, Tokyo Japan and used without further purification. Hydroxylamine hydrochloride (HA) and organic acids such as tartaric acid, malic acid, and oxalic acid of reagent grade were purchased from Kanto Chemical, Tokyo, Japan.

Preparation of AO Adsorbents

The preparation scheme of the AO adsorbent is illustrated in Fig. 1.[20,21] First, NF was irradiated with 200 kGy of 2.0 MeV and 1 mA electron beam in nitrogen atmosphere at ambient temperature. After irradiation, the irradiated NF was immersed in 50% (w/w) solution of the mixture monomers of AN and MAA in dimethyl sulfoxide (DMSO) which had previously deaerated with nitrogen gas. The weight ratio of the monomers of AN and MAA was changed from 60/40 to 80/20 to optimize the adsorption activity. The graft polymerization was carried out at 313 K. The grafting time was determined to yield the 4 mol/kg of AO groups after chemical modification. The grafted NF was washed repeatedly with dimethylformamide and methanol and dried under the reduced pressure before it was weighted. The degree

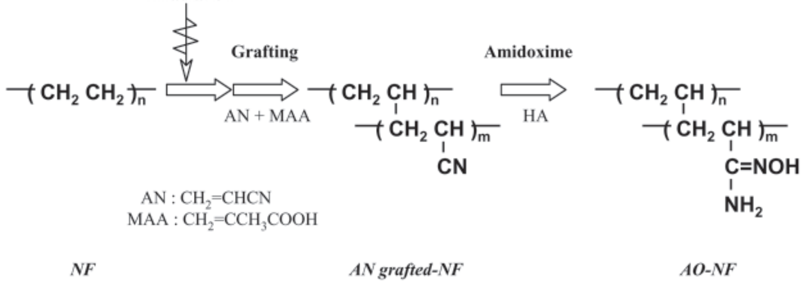


Figure 1. Preparation process of the AO adsorbent.

of co-grafting was calculated from the weight increment as follows:

$$\text{Degree of co-grafting: dg}(\%) = 100\frac{W_1 - W_0}{W_0}$$

where W_0 and W_1 are the dry weights of NF and co-grafted NF, respectively.

The cyano groups introduced were converted into AO groups by immersing the co-grafted NF in 3% (w/w) aqueous HA solution at 350 K for 45 min. After the reaction, the AO–NF was washed repeatedly with deionized water. Then, the grafted-NF was dried under the reduced pressure, and its weight was measured. The density of AO groups was defined from the following equation:

$$\text{AO group density (mol/kg)} = 1000\frac{(W_2 - W_1)}{33, W_2}$$

where W_1 and W_2 are the dry weights of the co-grafted NF before and after amidoximation, respectively. After the amidoximation, the adsorbent was treated with 2.5% (w/w) potassium hydroxide solution at 353 K for 30 min.

Adsorption Test for Seawater

In order to evaluate the adsorbent with natural seawater at pH 8.0, the equipment of the column adsorption was set-up at the quay of Mutsu works, JAERI, in Aomori prefecture. The column size is 40 mm in inner diameter and 90 mm in height, respectively, as illustrated in Fig. 2. Into the column,

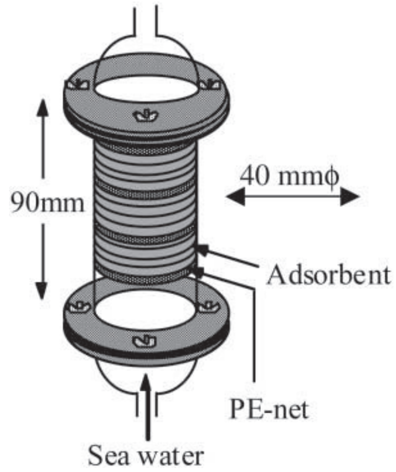


Figure 2. Stacking of adsorbent in column test.

12 adsorbents, 40 mm in diameter and 2 mm thick, were stacked with polyethylene nets in top, bottom, and every three adsorbents. The filling height of adsorbents was totally set to 30 mm. The seawater was directly pumped out from the sea near the quay after being filtered through 25 μm pore size polypropylene filters (Toyo Filter Co., Japan). Filtered seawater was fed into the column at flow rate of 3 L/min. The seawater temperature was controlled at 298 K using a heat exchanger in advance.

Elution with Acids

After adsorption of uranium in the seawater, all adsorbents were taken out of the column. The marine organisms in the adsorbent were washed out using the supersonic waves generator for 15 min. Then the adsorbents were immersed in acid solution to elute the adsorbed uranium at 150 rpm using magnetic stirrer. As an inorganic eluting agent, 0.5 M hydrochloric acid was used. Tartaric acid, oxalic acid, malic acid, maleic acid, phthalic acid, and formic acid were used as organic acids. Immersing time of the adsorbent in the eluting agent was 1 hr at ambient temperature. After the elution of uranium, the adsorbent could be regenerated with alkali solution and used repeatedly for the adsorption of uranium.[14] To evaluate the distribution of uranium in the adsorbents packed in the column, the adsorbents were divided into three parts in the direction of the column height.

Analysis

The adsorbed metals were quantitatively analyzed by inductively coupled plasma analysis after they were eluted from the adsorbents.

Physical damage of the adsorbent was observed by scanning electron microscope (SEM), after the adsorbent was dried under reduced pressure. Chemical damage on the adsorbent was estimated by ^{13}C-NMR spectrometry.

RESULT AND DISCUSSION

Monomer Ratio in Co-grafting

The adsorbents prepared by different ratio of AN/MAA were packed in the column. After 2 days contact with seawater the adsorbed uranium of adsorbents were 141, 145, and 135 mg of uranium per kilogram of dry adsorbent corresponding to AN/MAA = 60/40, 70/30, and 80/20, respectively. No difference was observed at one time adsorption. To optimize the ratio of AN/MAA adsorption–elution cyclic test was carried out five times. The amount of uranium on AN/MAA adsorbents against adsorption time was shown in Fig. 3. Total uranium adsorptions in five cyclic tests were 272, 292, and 245 mg U/kg dry adsorbent (hereafter termed kg-ad) for AN/MAA = 60/40, 70/30, and 80/20. As a result, the adsorbents of the ratio of AN/MAA = 70/30 was highest performance. Hence, the optimum ratio of the monomers was decided to AN/MAA = 70/30.

The images of the NF and the AO adsorbent, which had dg of 120%, prepared from NF grafted in AN/MAA = 70/30 observed by SEM are shown in Fig. 4. The NF had the opening space of 81%. The adsorbent still had the opening space of 85%. Grafting can make the fibrous adsorbent having high opening space.

Efficiency of Uranium Adsorption

The seawater was pumped into the adsorbent column to evaluate the efficiency of uranium adsorption. Figure 5 shows the effect of pumping

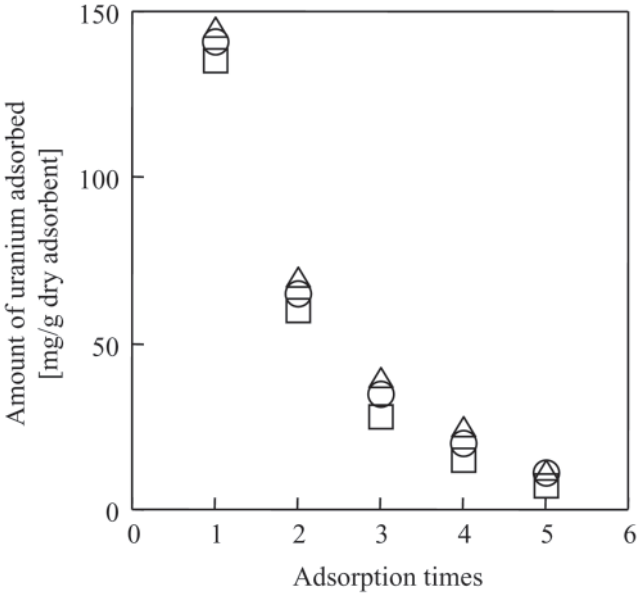
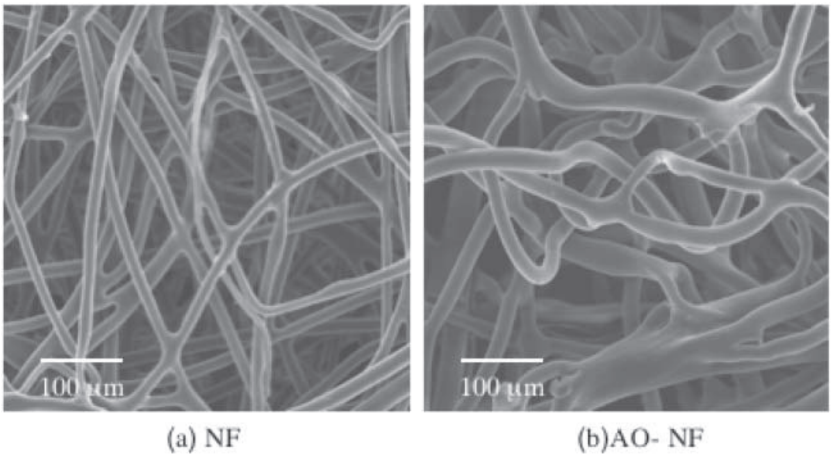


Figure 3. Uranium adsorption as a function of repetition usage. *Key:* ○, AN/MAA = 60/40; △, AN/MAA = 70/30; □, AN/MAA = 80/20.



(a) NF (b)AO- NF

Figure 4. SEM images of trunk and AO fibers (a) NF (b) AO–NF.

time on the uranium uptake. It could be seen that the amount of uranium adsorbed increased with pumping time. After 7 days, the amount of adsorbed uranium reached 300 mg U/kg ad. To measure the distribution of adsorbed uranium, 12 adsorbents were divided into three parts. Three adsorbents from bottom were

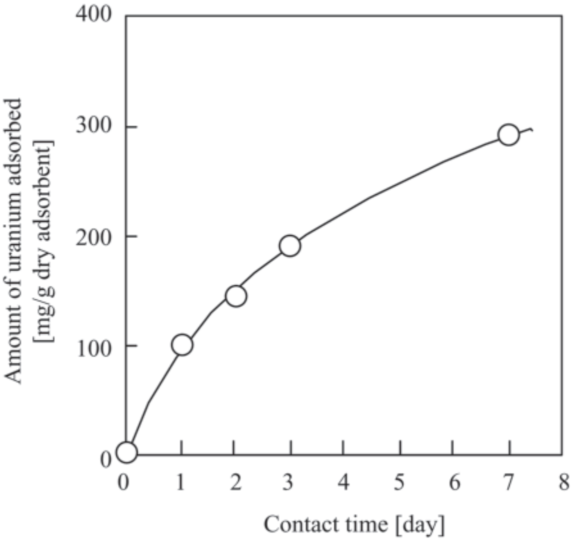


Figure 5. Uranium uptake from seawater as a function of contact time.

termed by first layer. Middle three and top three adsorbents were termed by second and third layers, respectively. Figure 6 shows the uranium adsorption in different layers of the adsorbents after 7, 3, and 2 days of column adsorption. There were no differences of uranium adsorption in the three layers. The efficiency of uranium adsorption from seawater was calculated from the amount of the adsorbed uranium on the adsorbent divided by uranium amount in the seawater passing through the adsorbent column. The efficiencies of uranium adsorption were at 0.8%, 1.1%, and 1.3% for 7, 3, and 2 days of column adsorption, respectively. Hence, the following adsorption–elution cycles were carried out with 2 day of column adsorption.

Durability Test of Adsorption–Elution Cycles with Alkaline Treatment

The seawater was pumped into the adsorbent column for 2 days and then the adsorbed uranium was eluted by hydrochloric acid. Regeneration

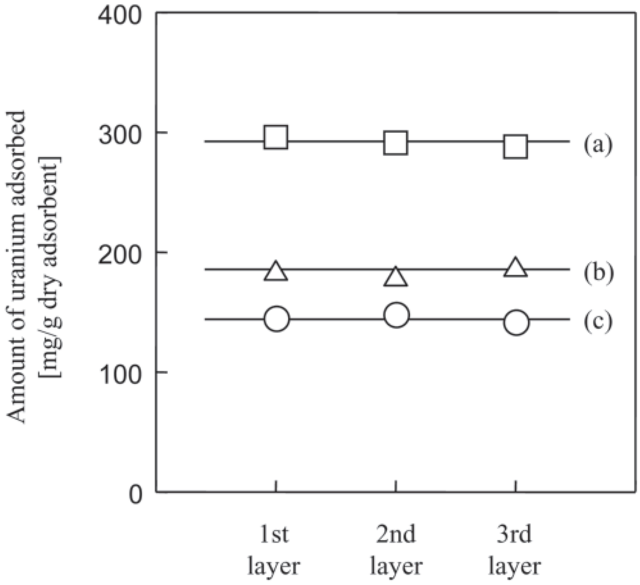


Figure 6. Adsorption distributes of uranium in the column; contact time (a) 7 days, (b) 3 days, and (c) 2 days.

with alkaline solution was investigated. Figure 7 shows the plot of the normalized uranium uptake against the repetition number of adsorption and elution. Without alkaline treatment after elution of the uranium, the uranium uptake considerably decreased with the increment of the number of adsorption–elution cycles. After five repetitions, the adsorbent lost its adsorption capacity. Instead, the uranium uptake with alkaline treatment of the adsorbent gradually decreased with the increment of the number of adsorption–elution cycles. As a result, uranium uptake after five cycles still maintained 73% of the initial activity of uranium adsorption. The effect of alkaline treatment was investigated on the point of view of chemical damage. Figure 8 shows the ^{13}C-NMR spectra after amidoximation (a), after elution with HCl (b), and after alkaline treatment (c), respectively. In Fig. 8(a), the AO carbon appeared in the range 155–159 ppm and the imidedioxime near 147 ppm.[22–24] In Fig. 8(b), the peak of AO decreased and the carbonyl region 175–185 ppm was detected. However, the peak of AO was reappeared and carbonyl region was disappeared by alkaline treatment [Fig. 8(c)]. For this reason, the alkaline treatment is effective on the reduction of chemical damage in the elution with HCl solution.

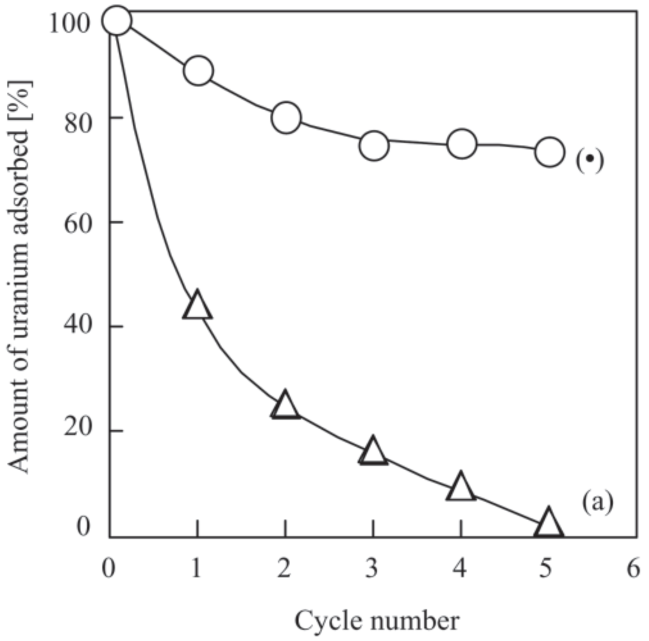


Figure 7. Uranium uptake vs. number of repeated usage using by HCl solution (a) without alkaline treatment (b) with alkaline treatment.

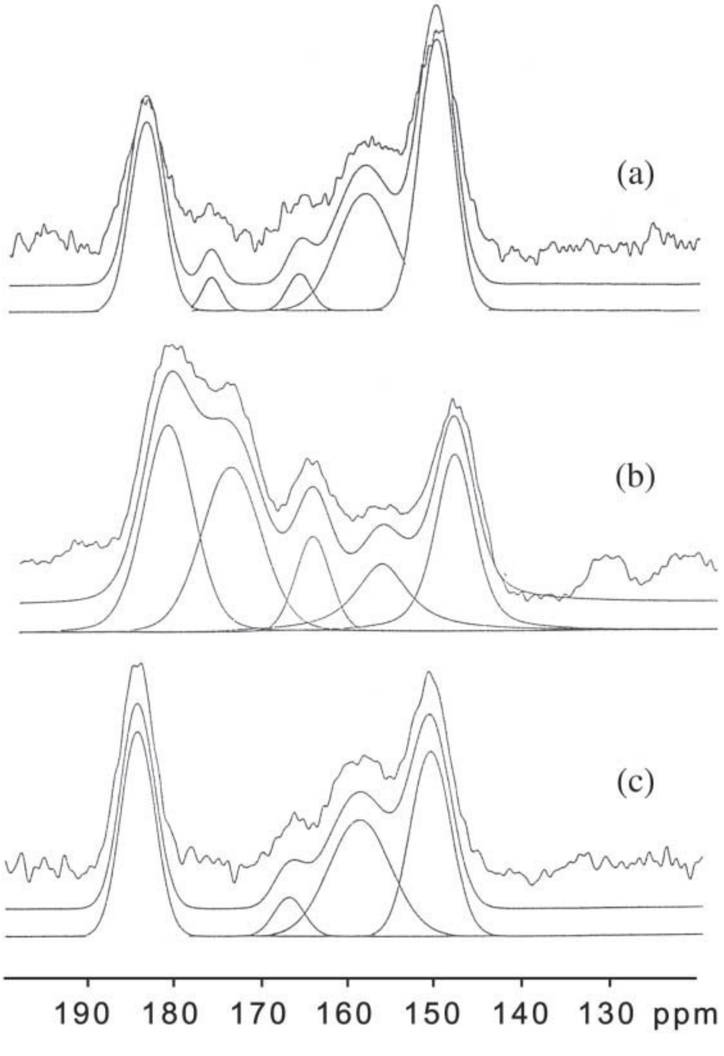


Figure 8. ^{13}C-NMR chemical shifts of AO groups (a) after amidoximation, (b) after elution with HCl solution, and (c) alkaline treatment.

Durability Test for Adsorbent using by Organic Acid

The elution with HCl solution gave the serious damage to the AO group in the adsorbent. The eluting agents of chelate type have been tried as possibility of eluting agent for uranium on AO adsorbent. Table 1 summarized the list of

Table 1. Lists of the eluting agent.

Eluting agent	Elution (%)	C.N.	S.C.
Tartaric acid	100	6	9.73
Oxalic acid	100	6	9.10
Malic acid	100	6	5.50
Maleic acid	90	6	5.15
Phthalic acid	80	6	4.38
Sulfuric acid	100	6	3.14
Acetic acid	80	6	2.70
Formic acid	70	6	2.61
Nitric acid	100	6	0.72
Hydrochloric acid	100	6	0.05

Note: C.N., coordination number; S.C., stability constant.

eluting agents, coordination number, and stability constant against uranium ion.[25] In the elution with 1 M tartaric acid, 1 M oxalic acid, and 1 M malic acid as eluting agent, the uranium was eluted 100%. Then the following cyclic test was carried out by using these three agents. Figure 9 shows the

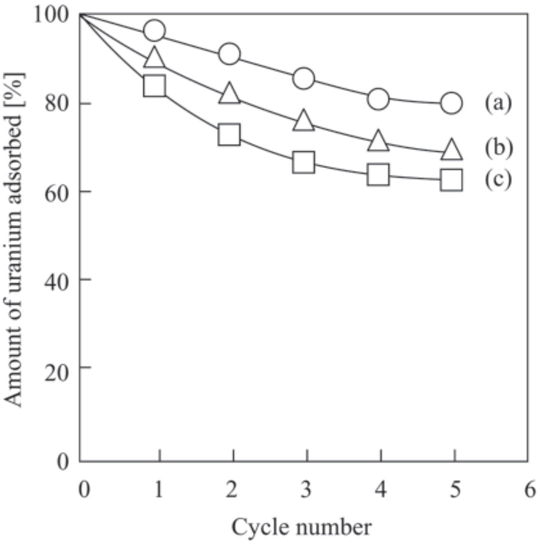


Figure 9. Uranium uptake vs. number of repeated usage using by organic acid (a) tartaric acid, (b) malic acid, and (c) oxalic acid.

performance of adsorbent using three kinds of organic acids as eluting agents. Tartaric acid seemed to be the most effective for maintaining the adsorption activity.

Physical Damage

The adsorbents were observed by SEM after elution of uranium with HCl and tartaric acid. Figure 10 shows the repetition of adsorption and elution at

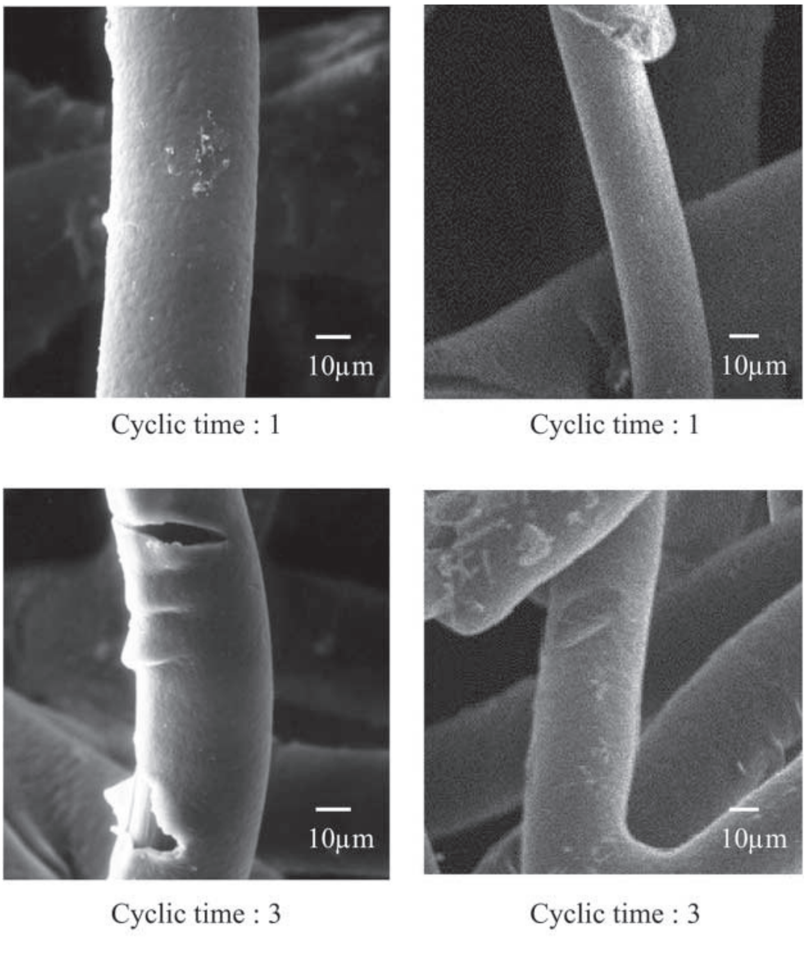


Figure 10. SEM images of adsorbent after eluted by HCl solution and tartaric acid.

one and three times. After the first elution, the difference of damage on the surface of the adsorbents could not be observed. The surface layer came off after third elution with HCl. In the case of tartaric acid, such damage on the surface of the fiber was reduced when compared with HCl as an eluting agent. In the plenty times of repetition usage of adsorbent, tartaric acid was found to be the best eluting agent.

CONCLUSIONS

From the experimental data using fibrous AO adsorbent prepared by radiation-induced graft polymerization in a column mode of uranium adsorption–elution cycles, the conclusions could be drawn as follows:

1. The AO adsorbent prepared at a monomer composition of AN/MAA = 70/30 in a weight ratio provided the highest amount of uranium adsorbed onto the adsorbent in a column mode.
2. The deterioration of the adsorption performance during the uranium adsorption–elution cycles could be minimized by means of alkaline treatment after each elution with HCl solution procedure.
3. The chemical change observed with ^{13}C-NMR revealed that the AO group was regenerated with alkaline treatment.
4. The damage of adsorbent structure after recycle could be effectively minimized when tartaric acid of chelate type was used as an eluting agent.
5. The tartaric acid depressed the mechanical damage of the adsorbent also.

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