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RAPID COMMUNICATION

Removal of Cesium Using Cobalt-Ferrocyanide-Impregnated Polymer-Chain-Grafted Fibers

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KEYWORDS: radiation-induced graft polymerization, cesium ion removal, cobalt ferrocyanides, 6-nylon fiber, adsorbent

I. Introduction

Radioisotopes are currently being released by Fukushima Daiichi nuclear power plant, which was damaged by the magnitude-9.0 earthquake and the tsunami that followed. Cesium-137, cesium-134, and iodine-131 produced by the fission of nuclear fuels are expected to seriously contaminate the sea and ground. Cesium and iodine dissolve in water and seawater in ionic forms of Cs^+ and I^- or IO_3^-, respectively. Cesium-137, with a longer half-life (30 years) than iodine-131 (8 days), should be removed and confined.

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Adsorption is a feasible method of removing radioactive species from water contaminated with radioisotopes. Zeolites and insoluble metal ferrocyanides1) are known as adsorbents capable of specifically capturing cesium-137 ions. Moreover, the insoluble metal ferrocyanides are loaded onto solid supports in bead or granule form such as porous anion-exchange resins2-4), silica gels5,6), and zeolites7). However, fibrous adsorbents are effective for easy operation at sites for processing water contaminated with radioisotopes.

Here, we propose a novel fiber that can immobilize metal ferrocyanides for the removal of cesium ions using a commercially available 6-nylon fiber as a starting material. Precipitates of metal ferrocyanide (M-FC) were formed among the polymer chains grafted onto the 6-nylon fiber. Therefore, the M-FC-impregnated fibers with a small diameter enhance the mass transfer of cesium ions from the bulk of liquid to the M-FC particles, leading to the rapid removal of cesium ions. In addition, the M-FC-impregnated fibers can be fabricated into various fiber modules for easy operation at the sites. In this study, the cobalt ion was used as a metal ion that precipitates with potassium ferrocyanide.

II. Experimental

1. Materials

6-Nylon fiber of 40 μm diameter, which was purchased from Toray Co., was used as the trunk polymer for grafting. Vinyl benzyl trimethylammonium chloride (VBTAC, $CH_2=CHC_6H_4CH_2N(CH_3)_3Cl$) was supplied by AGC Seimi Chemical Co. Sodium styrene sulfonate (SSS, $CH_2=CHC_6H_4SO_3Na$) was purchased from Wako. VBTAC and SSS were used without further purification. Potassium hexacyanoferrate(II) trihydrate and cobalt(II) chloride hexahydrate were purchased from Wako. The other chemicals were of analytical grade or higher. Cesium chloride was dissolved with seawater to yield a concentration of 10 mg-Cs/L. Seawater obtained offshore of Odawara in Kanagawa Prefecture, Japan was supplied by the Research Institute of Salt and Sea Water Science.

2. Impregnation of Cobalt Ferrocyanide onto VBTAC- and SSS-Fibers

Two impregnation schemes of cobalt ferrocyanide onto VBTAC- and SSS-grafted 6-nylon fibers are shown in **Figs. 1 (a) and (b)**, respectively. Each scheme consists of four steps. (1) Electron-beam irradiation[8,9]: Nylon fiber or 6-nylon fiber was irradiated with an electron beam in nitrogen atmosphere at ambient temperature. The dose was 200 kGy. (2) VBTAC or SSS grafting: The irradiated Nylon fiber was immersed in 0.5 M VBTAC or 0.5 M SSS aqueous solution for a prescribed reaction time at 313 K. The degree of VBTAC or SSS grafting was evaluated from the mass gain of the fiber as

$$\text{Degree of VBTAC or SSS grafting (\%)} = 100\,(W_1 - W_0)/W_0 \qquad (1)$$

where W_0 and W_1 are the masses of the trunk and VBTAC- or SSS-grafted fibers, respectively. The resulting VBTAC- and SSS-grafted fibers are hereafter referred to as the VBTAC and SSS fiber, respectively. From the viewpoint of the physical strength of the VBTAC and SSS fibers, dgs were set at 25 and 73%, respectively. (3-a) Binding of ferrocyanide ions to the trimethylammonium group of the VBTAC fiber: The VBTAC fiber was immersed in 0.1 M potassium ferrocyanide aqueous solution at 298 K for 30 min. (3-b) Binding of cobalt ions to the sulfonic group of the SSS fiber: The SSS fiber was immersed in 0.11 M $CoCl_2$ aqueous solution at 298 K for 1 h. (4-a) Precipitation of cobalt ferrocyanide onto the VBTAC fiber: The ferrocyanide-ion-bound fiber was reacted with 0.11 M $CoCl_2$ aqueous solution at 298 K for 3 h to precipitate cobalt ferrocyanide (Co-FC). (4-b) Precipitation of cobalt ferrocyanide onto the SSS-fiber: The cobalt-ion-bound fiber was reacted with 0.11 M potassium ferrocyanide aqueous solution at 298 K for 1 h to precipitate Co-FC.

After the fibers were immersed in a 1.0 M NaCl aqueous solution and washed repeatedly with water, they were vacuum-dried. The resultant Co-FC-impregnated fibers prepared via VBTAC and SSS grafting onto the nylon fibers are hereafter referred to as the VBTAC- and SSS-Co-FC fibers, respectively. The content of Co-FC impregnated was evaluated from the mass gain of the fiber as

$$\text{Content of Co-FC impregnated (\%)} = 100\,(W_2 - W_1)/W_2 \qquad (2)$$

where W_2 is the mass of the VBTAC- or SSS-Co-FC fiber.

The crystalline phases of the VBTAC- and SSS-Co-FC fibers were identified by X-ray diffractometry (XRD, Bruker, D8 Advance) using CuKα radiation. The distributions of ferrocyanide and cobalt ions inside the ferrocyanide-ion-bound VBTAC and VBTAC-Co-FC fibers were determined by scanning electron microscopy/energy-dispersive X-ray spectroscopy system (SEM/EDS. JEOL, JSM-6510A).

3. Cesium Adsorption in Batch Mode Using VBTAC- and SSS-Co-FC Fibers

As a preliminary experiment, the cesium adsorption experiment using 10 mg-Cs/L cesium chloride dissolved with a 0.5 M NaCl aqueous solution was performed to confirm high selectivities of the VBTAC- and SSS-Co-FC fibers. Approximately 0.2 g of the VBTAC- or SSS-Co-FC fiber was immersed in 20 mL of 10 mg-Cs/L cesium solution. After gentle stirring at 298 K for a prescribed contact time, the supernatant was sampled and the cesium concentration in seawater was determined by ICP-MS. The contact time ranged from 3 to 60 min. The removal percentage (R) of cesium from the solution and the distribution coefficient (K_d) were evaluated as

$$\text{Removal percentage (\%)} = 100\,(C_i - C_t)/C_i \tag{3}$$

$$\text{Distribution coefficient (cm}^3\text{/g)} = [(C_i - C_f)\,V/W]/C_f \tag{4}$$

where C_i and C_f are the initial and final cesium concentrations, respectively, and C_t is the cesium concentration after the prescribed contact time. V and W are the volume of the solution and weight of the VBTAC- or SSS-Co-FC fiber, respectively.

III. Results and Discussion

The contents of VBTAC- and SSS-Co-FC impregnated were 5.1 and 7.3%, respectively, which were lower than that (21%) of nickel-ferrocyanide impregnated onto zeolite7). The diameter of the Nylon fiber (40 μm) in the dry state increased to the diameters of the VBTAC (45 μm) and SSS (56 μm) fibers in the dry state. The XRD patterns of 6-nylon, VBTAC-, and SSS-Co-FC fibers are shown in **Fig. 2**. Although apparent diffraction peak of Co-FC was not observed on the diffraction pattern of the VBTAC-Co-FC fiber (**Fig. 2(b)**), the formation of $K_2Co[Fe(CN)_6]$ (ICDD Card No. 00-031-1000) was confirmed on the SSS-Co-FC fiber (**Fig. 2(c)**).

The distribution of iron across the ferrocyanide-ion-bound VBTAC fiber is shown in **Fig. 3 (a).** The distributions of iron and cobalt across the VBTAC-Co-FC fiber measured using EDS are shown in **Figs. 3 (b) and (c)**, respectively. The uniform Fe or ferrocyanide distribution across the ferrocyanide-ion-bound VBTAC fiber corresponds to the uniform distribution of the poly-VBTAC chain grafted to the Nylon fiber. On the other hand, Fe and Co were observed only in the periphery of the VBTAC-Co-FC fiber, which was treated with 1.0 M NaCl.

The adsorption rates of cesium ions in seawater onto the VBTAC- and SSS-Co-FC fibers were evaluated in batch mode. As shown in **Table 1**, after immersing the fibers in seawater for 30 min, the cesium concentrations became lower than the detection limits of ICP-MS (0.2 mg-Cs/L). This is indicative of the rapid mass transfer of cesium ions to the Co-FC impregnated onto the fibers. From the results of Fig. 3 and Table 1, Co-FC phase was evidently formed on the VBTAC-Co-FC fiber. The Co-FC phase with small size and low crystallinity will be formed on the periphery of the VBTAC-Co-FC fiber. The recovery percentages of the VBTAC– and SSS-Co-FC fibers in seawater were higher than 98% and the distribution coefficients were at least 4.9×10^3. The VBTAC– or SSS-Co-FC fiber as an adsorbent for the removal of cesium ions should be selected on the basis of the production cost and mechanical strength of the fiber.

The mass-transfer characteristics of the fibers are advantageous because the fibers can be regarded as a strand of small beads10). Moreover, the flow resistance of the fiber module is adjustable simply by controlling the packing density of the fibers. The Co-FC-impregnated fibers prepared in this study are promising for the rapid removal of cesium ions from cesium-ion-containing solutions by an easy operation.

IV. Conclusion

Sparingly soluble metal ferrocyanide (M-FC) salts are formed in liquid by mixing a metal salt solution with potassium ferrocyanide solution. Therefore, for use as an adsorbent, M-FCs have thus far been impregnated onto various solid supports such as porous ion-exchange beads, silica gel, and activated carbon. To achieve the rapid capture of cesium ions and easy processing of highly radioactive water, we prepared a novel M-FC-impregnated fiber by radiation-induced graft polymerization and subsequent chemical modifications.

Ferrocyanide and cobalt ions were bound to vinyl benzyl trimethylammmonium chloride- and sodium styrene sulfonate-grafted 6-nylon fibers, respectively, via an ion-exchange interaction. Subsequently, the bound ferrocyanide and cobalt ions were reacted with cobalt and potassium ferrocyanide ions, respectively, to form insoluble or sparingly soluble cobalt-ferrocyanide (Co-FC). The resultant Co-FC-impregnated fibers exhibited a high affinity to cesium ions in seawater. Such fibers can be fabricated into various fiber modules suitable for the removal of radioisotopes at sites.

References

1) G. B. Barton, J. L. Hepworth, E. D. McClanahan, R. L. Moore, H. H. Van Tuyl, "Chemical processing wastes; Recovering fission products," *Ind. Eng. Chem.*, **50**[2], 212-216 (1958).

2) K. Watari, M. Izawa, "Separation of radiocesium by copper ferrocyanide-anion exchange resin," *J. Nucl. Sci. Technol.*, **2**, 321-322 (1965).

3) K. Watari, K. Imai, M. Izawa, "Radiochemical application of iron ferrocyanide-anion exchange resin," *J. Nucl. Sci. Technol.*, **5**, 309-312 (1968).

4) K. Tanihara, "Preparation of insoluble hexacyanoferrate(II)-macroporous ion exchange resin composites and comparison of their performance as a regenerable ion exchanger for cesium,"*Nippon Kagaku Kaishi*, **9**, 835-841 (1996), [in Japanese].

5) K. Tanihara, "Selective separation of cesium from strongly acidic nitrate media by repeated use of cupric ferrocyanide-silica gel composite ion exchanger of redoxtype," *Reports of the Kyushu National Industrial Research Institute*, No. 61, 23-28 (1998).

6) H. Mimura, M. Kimura, K. Akiba, Y. Onodera, "Selective removal of cesium from highly concentrated sodium nitrate neutral solutions by potassium nickel hexacyanoferrate(II)-loaded silica gels," *Solvent Extr. Ion Exch.*, **17**, 403-417 (1999).

7) H. Mimura, M. Kimura, K. Akiba, Y. Onodera, "Separation of cesium and strontium by potassium hexacyanoferrate(II)-loaded zeolite A," *J. Nucl. Sci. Technol.*, **36**, 307-310 (1999).

8) K. Saito, T. Sugo, *Delicious Recipe for Graft Polymerization*, Maruzen, Tokyo (2008), [in Japanese].

9) S. Asai, K. Miyoshi, K. Saito, "Modification of a porous sheet (MAPS) for the high-performance solid-phase extraction of trace and ultratrace elements by radiation-induced graft polymerization," *Anal. Sci.*, **26**, 649-658 (2010).

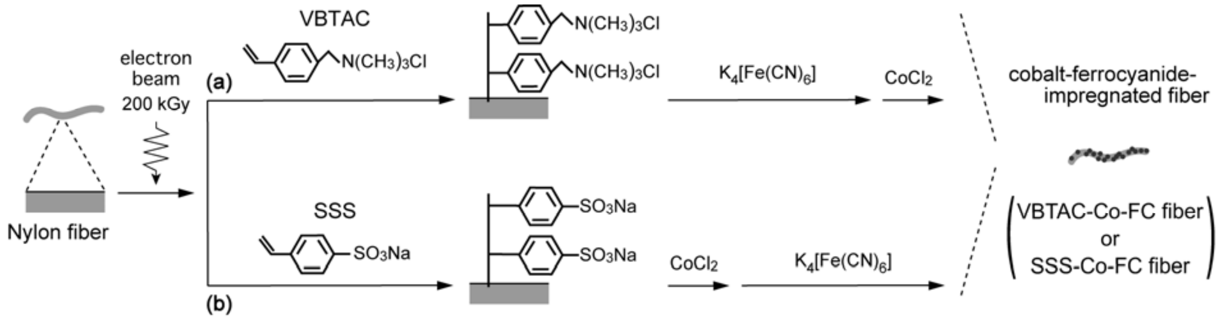
10) K. Ikeda, D. Umeno, K. Saito, F. Koide, E. Miyata, T. Sugo, “Removal of boron using nylon-based chelating fibers,” *Ind. Eng. Chem. Res.*, **50**, 5727-5732 (2011).

Figure captions

Fig. 1 Two preparation schemes of cobalt-ferrocyanide (Co-FC)-impregnated fiber

Fig. 2 XRD patterns of 6-nylon, VBTAC-Co-FC, and SSS-Co-FC fibers
(a) 6-nylon, (b) VBTAC-Co-FC fiber, (c) SSS-Co-FC fiber; the peaks identified by ▽ correspond to $K_2CoFe(CN)_6$

Fig. 3 Distributions of Fe and Co across ferrocyanide-ion-bound VBTAC fiber and VBTAC-Co-FC fiber
(a) Fe across ferrocyanide-ion-bound VBTAC fiber, (b) Fe across VBTAC-Co-FC fiber, (c) Co across VBTAC-Co-FC fiber



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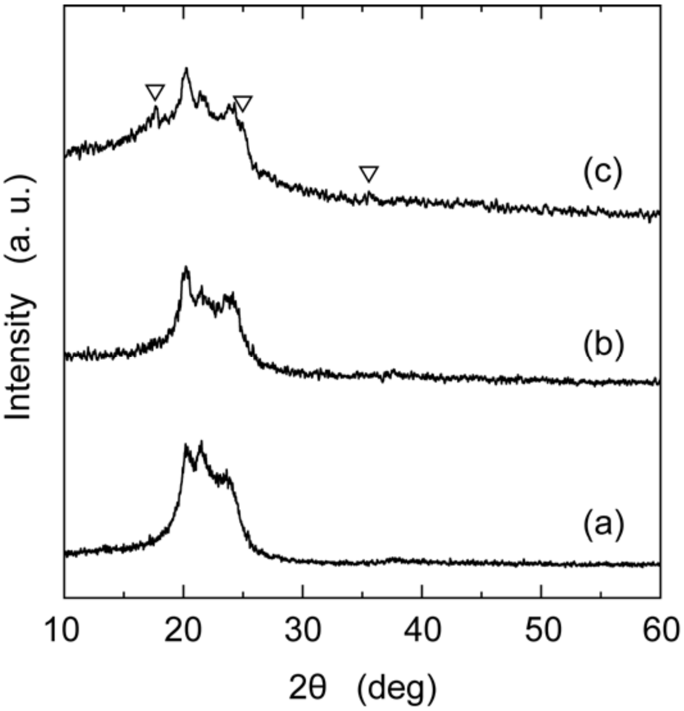

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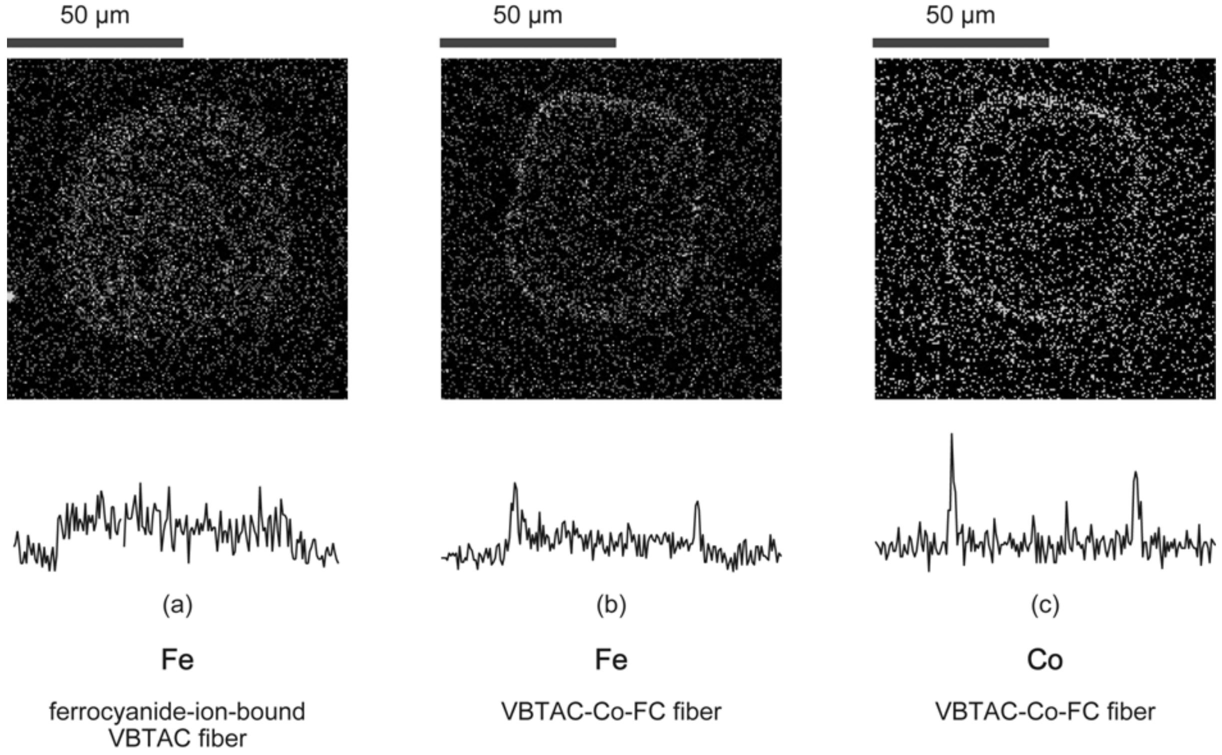

Fig.3 Distributions of Fe and Co across ferrocyanide-ion-bound VBTAC fiber and VBTAC-Co-FC fiber

(a) Fe across ferrocyanide-ion-bound VBTAC fiber, (b) Fe across VBTAC-Co-FC fiber, (c) Co across VBTAC-Co-FC fiber

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Table 1 Cesium concentration decay in seawater

	Cesium concentration in seawater [mg-Cs/L]				
t (min)	0	3	10	30	60
SSS-Co-FC fiber	9.7	0.8	0.3	< 0.2	< 0.2
VBTAC-Co-FC fiber	9.7	4.9	2.8	< 0.2	< 0.2