X-Ray Microanalysis of Uranium on Fibrous Amidoxime-type Adsorbent

Takao Kitamura,* Koji Sakane, and Shunsaku Katoh

Government Industrial Research Institute, Shikoku 2-3-3 Hananomiyacho, Takamatsu 761

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Synopsis. The adsorption process for uranium from sea water was studied by X-ray microanalysis on polyacrylamidoxime fiber, whose functional group was found to distribute uniformly. Uniform distribution of uranium was observed on cross sections of the adsorbents, which had contacted with sea water for 14 and 55 d. It was deduced that intrafiber diffusion of uranium is not the rate determining step in adsorption.

Recently much higher interest is around on the organic polymer adsorbents because of their high adsorption rate and versatile possibilities in organic synthesis.[1–4] Among these adsorbents the ones with amidoxime functional groups have the highest adsorption rate for uranium from sea water.

Improvement of adsorptive properties for practical application necessitates knowledges about uranium adsorption process from sea water, which hitherto were not obtained from direct analysis of distribution of adsorbed uranium. In this note, distributions of functional groups and uranium were measured by X-ray microanalysis of copper(II) and uranium, respectively, and the uranium adsorption process is briefly discussed.

Experimental

Adsorbent. Adsorbent was obtained by reacting commercially available acrylic fiber of *ca.* 15 μm diam. with hydroxylamine by the usual method to form amidoxime functional groups.[5] Then the fiber was treated for 24 h with a 1 M (1 M = 1 mol dm^{-3}) NaOH solution for conditioning. The amount of the functional group in the adsorbent was determined from copper(II) ion adsorption capacity.[6] Adsorption of copper(II) ion was carried out by shaking 0.1 g of the adsorbent for 3 d at 25 °C in a solution of 0.05 M $CuCl_2$ (25 cm^3), which is buffered to pH 4.5 with CH_3COOH–CH_3COONa.

Uranium Adsorption. Uranium was adsorbed from filtered natural sea water in columns of 2.5 cm inner diam. and 20 cm length at linear flow rate of 20 cm min^{-1} for 55 d. The uranium content in the adsorbent was determined by fluorometry on an Aloka fluorimeter FMT-3B after desorption with diluted HCl solution.[6]

X-Ray Microanalysis. Apparatus used was JEOL JXM-50A scanning electron microscope-X-ray microanalyser. Crystals used for resolution of spectra were pentaerithritol for U *Mα*, and lithium fluoride for Cu *Kα*. Standard samples for Cu and U analyses were the cross sections of wires supplied by JEOL.

Sample Preparation for X-Ray Microanalysis. Fibrous adsorbent was buried in an acrylic resin. After hardening the cylindrical resin of 5 mm diam. was cut to 5 mm height. Electrical contact of the specimen was attained by coating vacuum-evaporated aluminum, which was found to serve more satisfactorily than gold and platinum in minimizing X-ray absorption and preventing charging of the specimen. In some cases one end of the fiber was buried in a resorcinol resin, the other end being razored and coated with aluminum.

Results and Discussion

Characterization of Adsorbent. Secondary electron image of the adsorbent in Fig. 1 shows a smooth surface and existence of a notch in the direction of axis. This notch gave a typical shape of the cross section for most of the fibers as in Figs. 2—4. Amount of the functional group of the fiber was determined to be 2.6 mmol g^{-1}. Distribution of the functional group was measured on a cross section of the adsorbent by measuring Cu *Kα* radiation of adsorbed copper(II). Figure 2 shows the secondary electron image and Cu *Kα* micrography across a section. The image was observed under the same electron beam conditions with that for X-ray measurement, *i.e.*, at high electron beam intensity of 2×10^{-8} A and accelerating voltage of 25 kV, which were necessary to measure characteristic X-rays of elements at rather low concentration. This resulted in low resolution of the secondary electron image, which in turn reflects approximately the resolution of the line profile. Constant counting rate of Cu *Kα*

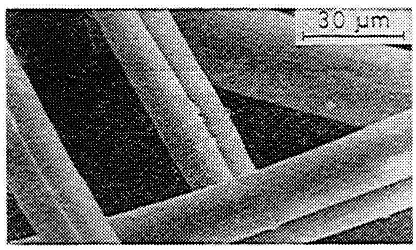

Fig. 1. Secondary electron image of the fibrous adsorbent.

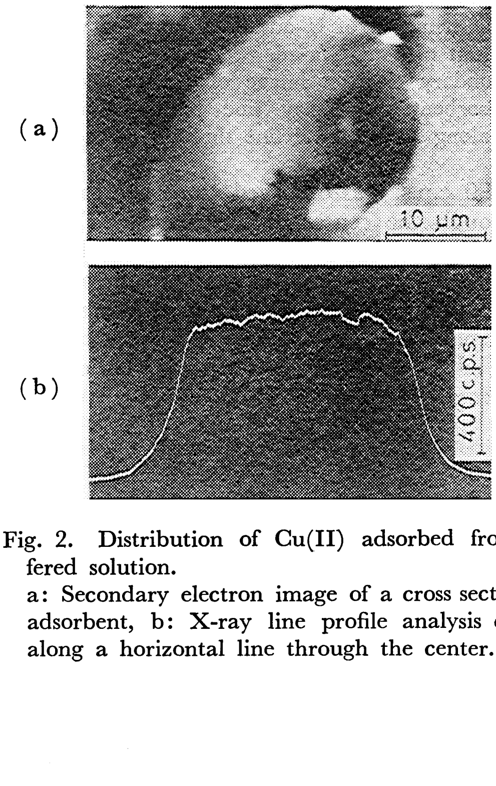

Fig. 2. Distribution of Cu(II) adsorbed from a buffered solution.
a: Secondary electron image of a cross section of the adsorbent, b: X-ray line profile analysis of Cu *Kα* along a horizontal line through the center.

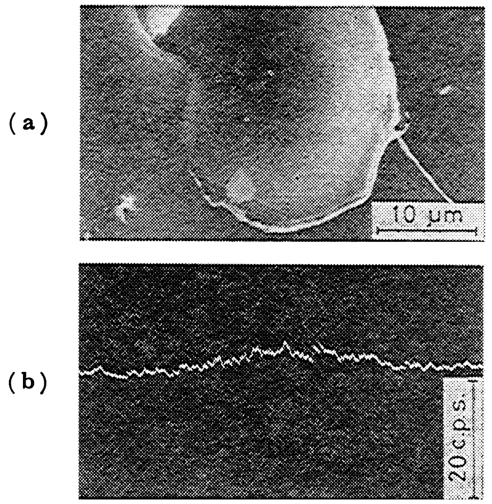

Fig. 3. Distribution of U adsorbed from sea water to an amount of 2 mg-U/g-ad.
a: Secondary electron image of a cross section of the adsorbent, b: X-ray line profile analysis of U $M\alpha$ along a horizontal line through the center.

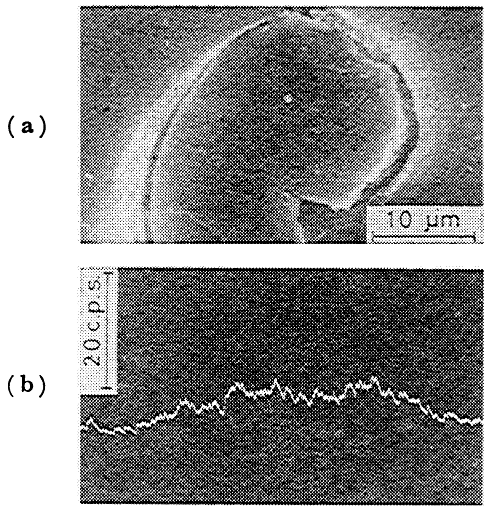

Fig. 4. Distribution of U adsorbed from sea water to an amount of 5 mg-U/g-ad.
a: Secondary electron image of a cross section of the adsorbent, b: X-ray line profile analysis of U $M\alpha$ along a horizontal line through the center.

of about 490 c.p.s. was observed along the line, which passed through the center of the image. This result shows a uniform distribution of copper(II), hence the uniform formation of functional group in the adsorbent. The counting rate of Cu $K\alpha$ of the standard sample was 7500 c.p.s. under the same conditions. The concentration of Cu(II) in the adsorbent was calculated to be 165 mg g^{-1}, giving correction factor⁷⁾ G of 2.5. This rather large G value can be attributed to the effect of absorption of electron and X-ray by coating materials.

Microanalysis of Uranium. The adsorbents at two different durations of uranium adsorption *i.e.* 14 and 55 d were examined. The former contained 2 mg g^{-1} and the latter 5 mg g^{-1} of uranium. Figure 3 shows a secondary electron image and U $M\alpha$ X-ray line analysis of a cross section of the adsorbent after 55 d adsorption. Although the observed line is a little scattered, the counting rate around the center is nearly as high as that around the edge of the section. From the results observed above, it is found that the distribution of uranium in the fiber is approximately uniform. A similar observation with lower counting rate was made with adsorbents after 14 d adsorption as in Fig. 4. The above results of apparently uniform distribution of uranium for the two adsorbents at different durations of adsorption suggest that a boundary layer of adsorbed uranium does not exist, and intrafiber diffusion of uranium is not the rate determining step in adsorption from sea water.

For 0.3 mm diam. particle of hydrous titanium oxide adsorbent,⁸⁾ uranium-adsorbed layer of 0.03 mm thickness was calculated from the curve of adsorption rate, whereas the layer was not detected with the fibrous adsorbent, that is, the whole volume of the adsorbent was effective for uranium adsorption. The rate of uranium adsorption was 2 mg g^{-1} in 14 d with the fibrous adsorbent, whereas the rate with the hydrous titanium oxide adsorbent was 0.18 mg g^{-1} in 20 d.⁸⁾ These two characteristics of high adsorption rate and high effectivity can be denoted as the advantages of the fibrous amidoxime-type adsorbent for adsorption of uranium from sea water.

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