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Kinetics of Adsorption of Uranium on Amidoxime Polymers from Seawater

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Abstract

Distributions of uranium adsorbed on amidoxime polymers crosslinked with tetraethyleneglycol dimethacrylate (4EGDM) and/or divinylbenzene (DVB) from seawater were examined by x-ray microanalysis in order to elucidate the diffusion behavior of uranium into the polymer matrix. The uniform distribution of the ligands on the polymers was confirmed by the distribution of Cu(II) adsorbed from copper(II) dichloride solutions. It was found that the distribution of uranium adsorbed is changed significantly by the composition of 4EGDM and DVB. Thus, the polymer crosslinked with 4EGDM exhibits a uniform distribution of uranium; however, as the ratio of DVB to 4EGDM increases, a more predominant distribution of uranium near the periphery of the polymer particle appears and the intensity decreases. This suggests that the adsorption rate of uranium is governed by the diffusion of uranium into the polymer matrix, explaining well the dependence of the adsorption rate on the hydrophilicity of the polymer. On the basis of these results, the diffusion constant of uranium into the polymer matrix was estimated to be 3.3×10^{-7} cm^2/s.

INTRODUCTION

Polymers bearing amidoxime groups exhibit a high selective adsorptivity toward uranium (*1–3*) which is present as an assumed species of tricarbonatouranate(VI) ion, $[UO_2(CO_3)_3]^{4-}$, in seawater (*4*), suggesting their usefulness for the recovery of uranium from seawater. This characteristic feature is principally due to the metal ion-complexing nature of the ligand, which forms a more stable complex with a metal ion of a more hard acid character (*5*). In previous papers (*3*, *6*, *7*) it was reported that an adsorption rate of uranium from seawater on the amidoxime polymer, which is crosslinked with hydrophilic tetraethyleneglycol dimethacrylate (4EGDM) and/or hydrophobic divinylbenzene (DVB), increases with an increasing ratio of 4EGDM to DVB. Furthermore, the adsorption capacity of uranium at the adsorption equilibrium increases in the same order. On the basis of the dependence of the adsorption rate on the porosity and hydrophilicity, it is presumed that the adsorption rate is primarily governed by the diffusion of uranium into the polymer matrix (*3*, *7*), and the hydrophobicity of the polymer matrix containing DVB unit reduces the possibility of chelation of $[UO_2(CO_3)_3]^{4-}$ with the ligands.

In the adsorption of uranium on the amidoxime polymers from seawater, the attainment of adsorption equilibrium is estimated to require a very long period, probably due to the very low concentration of uranium (3 $\mu g/dm^3$) in seawater. This situation prevents the practical examination on the diffusion behavior of uranium into the polymer matrix by the usual analysis of time dependence of uranium adsorption. However, the radial distribution of uranium adsorbed on the amidoxime polymer may provide direct information on the diffusion behavior of uranium. Accordingly, in the present study the radial distributions of uranium adsorbed on amidoxime polymers crosslinked with DVB and/or 4EGDM from seawater were examined with respect to the diffusion behavior of uranium into the polymer matrix.

EXPERIMENTAL

Materials

Spherical particles of poly(acrylonitrile) crosslinked with DVB and/or 4EGDM were prepared by suspension polymerization as described in the literatures (*3*, *7*). The particles were treated with hydroxylamine in

methanol at 60°C for 8 h to afford a polymer having amidoxime groups. The amidoxime polymer was washed thoroughly with methanol and then with distilled water.

The particles of amidoxime polymer thus prepared were sieved in water, and the fraction of 0.4–0.59 mm diameter was employed in the present experiments.

Adsorptive Capacity for Cu(II)

The adsorptive capacity for Cu(II) was determined by the following method. A 0.05 mol/dm^3 copper(II) dichloride solution was maintained at pH 4.5 with an acetic acid–sodium acetate buffer solution. Amidoxime polymer (0.1 g) immersed in 25 cm^3 of the Cu(II) solution was sealed and maintained at 25°C for 48 h with shaking. After filtration, the concentration of Cu(II) in the filtrate was determined with a Perkin-Elmer 403 atomic absorption spectrophotometer. The adsorptive capacity was obtained from the difference between the initial and the final concentration of Cu(II).

Adsorption of Uranium from Seawater

Amidoxime polymer (5 g) was loaded in a glass column (inner diameter, 2.5 cm; height, 20 cm), and seawater was passed upward through the column at a flow rate of 250 ± 10 cm^3/min at 25 ± 2°C. This flow rate exhibited the maximum adsorption rate of uranium. After a prescribed time the polymer particles were collected and washed thoroughly with distilled water. The adsorbed uranium was eluted with a 1 mol/dm^3 HCl solution with reflux; the uranium concentration in the filtrate was determined by fluorometry using an Aloka Model FMT-3B fluorometer to give the amount of uranium adsorbed.

X-Ray Microanalysis

X-ray microanalysis of the amidoxime polymer samples was performed with a Shimadzu Model EMX-SM x-ray microanalyzer. The crystals used for resolution of the spectra were pentaerithritol, lithium fluoride, and rubidium hydrogenphthalate for UM_α, Fe and CuK_α, and MgK_α, respectively. All the measurements were carried out under constant electron energy (20 keV) and current (10 nA).

The polymer sample was buried in an acrylic resin and cut to obtain a maximum cross section. The cross-sectional surface of the specimen was coated by vacuum-evaporated aluminum to prevent charging on the specimen. By moving the specimen at a constant velocity (100 μm/min), the relevant x-ray intensity was obtained on a chart recorder.

Porosimetry

The pore volume and surface area were determined by the mercury intrusion method using a Carlo Erba Model series 200 porosimeter.

RESULTS AND DISCUSSION

Characterization of Amidoxime Polymer

Adsorptive capacities of Cu(II) on the amidoxime polymers are listed in Table 1. This value is 1.17–2.55 mmol/g, which is satisfactorily referred to the amount of amidoxime groups on the polymer (*3*). The polymer crosslinked with DVB exhibits a smaller adsorptive capacity than do the other polymers.

The present amidoxime polymers, which were prepared by treatment of poly(acrylonitrile) with hydroxylamine in methanol, do not necessarily assure a uniform distribution of the ligands in the polymer matrix, which is different from the case of the polymerization of monomers having functional groups. Then, x-ray microanalyses of Cu(II) adsorbed on the amidoxime polymers were carried out in order to examine the distribution of the ligands on the polymers. The result for Polymer Sample 3 is shown in Fig. 1. This shows a practically uniform distribution of Cu(II) on the polymer, leading to a uniform formation of amidoxime groups. Similar uniformities were observed for the other polymer samples. It is, therefore, confirmed that the amidoxime ligands are formed uniformly on the resulting polymers. The smaller adsorptive capacity of Cu(II) of Polymer 1 compared to the others suggests that the hydrophobic DVB unit inhibits the reaction of hydroxylamine with nitrile groups in the polymer matrix.

The porous properties of the amidoxime polymers are illustrated in Table 1. Note that the porosity decreases with an increasing ratio of DVB to 4EGDM.

TABLE 1
Cu(II) Adsorptive Capacities and the Porous Properties of Amidoxime Polymers

Polymer sample	Crosslinking (wt%)		True density (g/cm^3)	Cu(II) adsorptive capacity (mmol/g)	Surface area (m^2/g)	Pore volume (cm^3/g)	Mean pore radius[a] (nm)
	DVB	4EGDM					
1	30	0	—	1.17	71.7	0.626	17.5
2	27	13	1.13	2.55	84.2	0.836	19.9
3	5	35	1.11	2.41	56.2	0.885	31.5
4	0	40	1.09	2.08	39.3	1.52	77.4

[a]This value is defined as $2V_p/S_p$, where V_p and S_p are the pore volume and the surface area, respectively.

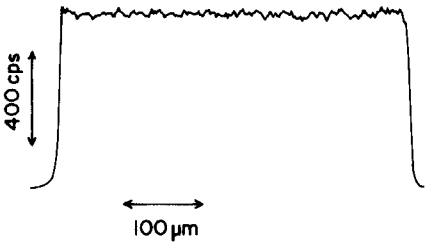

FIG. 1. Distribution curve of Cu(II) adsorbed on the Amidoxime Polymer 3.

Radial Distribution of Uranium Adsorbed from Seawater

Under the present conditions, the adsorption rate of uranium on the amidoxime polymer from seawater is supposed to be hardly affected by the diffusion process of uranium in the boundary layer between the outer surface of the spherical polymer particle and the bulk seawater because the high flow rate of seawater secures the maximum adsorption rate. Moreover, the chelation rate of uranium with the ligands is assumed to be extremely fast because of the chelation of uranium with acetamidoxime as a monomeric ligand (*5*). Therefore, uranium adsorption under the present conditions is assumed to be affected significantly by the diffusion of uranium into the polymer matrix.

According to Kunin's definition (*8*), the present polymers can be assumed to consist of two distinct phases: one is the pore phase, referred to as a pore domain and resulting from pores as shown in Table 1, and the other is the gel phase of the polymer network. Thus, the two diffusion processes of uranium into these two phases of the polymer matrix must be taken into account.

The amounts of uranium adsorbed on the polymer samples employed for x-ray microanalysis are listed in Table 2; these values are far from those at adsorption equilibrium (*7*). The distribution curves of uranium adsorbed on the polymers are shown in Fig. 2. It is worth noting that a uniform distribution of uranium is observed in Polymer 4 which is crosslinked with hydrophilic 4EGDM. However, as the ratio of DVB to 4EGDM increases, a predominant distribution of uranium near the periphery of the polymer particle is observed. For Polymer 1 crosslinked with only DVB, the intensity at any position is suppressed to almost zero, while uranium adsorption on Polymer 2 exhibits a wider distribution which becomes smoother with increasing adsorption time, as shown in Fig. 3. These characteristic distributions are presumed to reflect the

TABLE 2
Amidoxime Polymer Samples Employed for X-Ray Microanalysis

Polymer sample	Adsorption time (d)	Uranium adsorbed (mg/g)
1	86	0.27
2-1	134	0.94
2-2	169	1.21
2-3	365	1.55
3	155	1.50
4	180	4.54

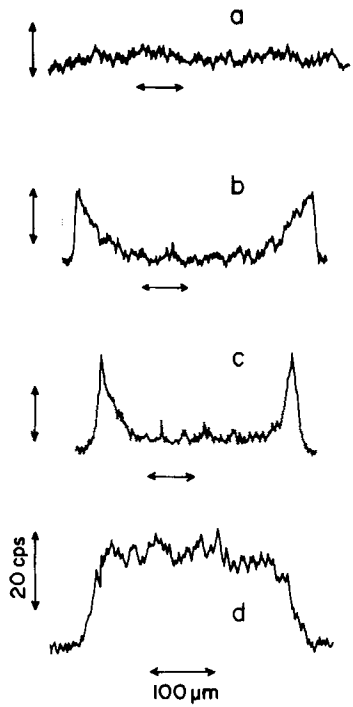

FIG. 2. Distributions of uranium adsorbed on the amidoxime polymers from seawater. Polymer samples: 1 (a), 2-2 (b), 3 (c), and 4 (d).

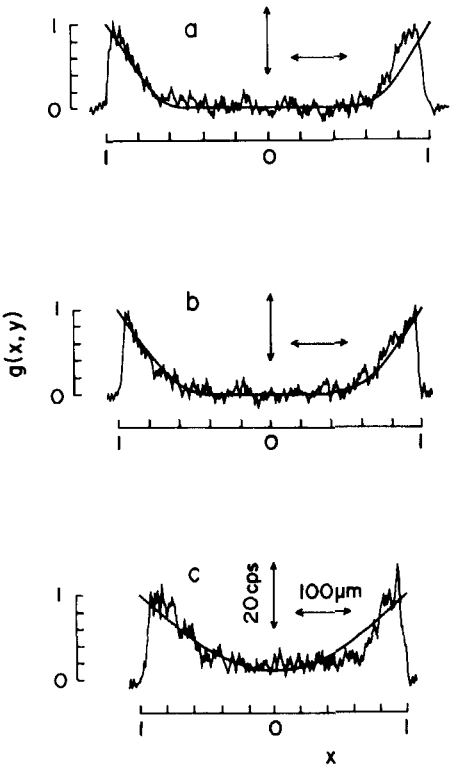

FIG. 3. Time dependence of distribution of uranium adsorbed on the amidoxime polymer 2 from seawater. Adsorption time in days: 134 (a), 169 (b), and 365 (c). The smooth lines were determined in order to obtain best fits of $g(x,y)$ by using y values in Table 4.

diffusion behavior of uranium into the polymer matrix because a uniform distribution of ligand groups is assumed.

The uniform distribution of uranium on Polymer 4 shows that the rate of uranium adsorption is primarily governed by diffusion into the gel phase rather than the pore phase. As the ratio of DVB to 4EGDM increases, uranium adsorption becomes more significantly affected by diffusion into the pore phase as well as into the gel phase, judging from the decreasing peak height and the shift of the adsorption peak to the periphery. The behavior of the adsorption peak with time as shown in Fig. 3 shows the difficulty of uranium diffusion into the gel phase containing DVB units. Moreover, in Polymer 1 (crosslinked with only DVB), uranium diffusion into both the gel phase and the pore phase is

significantly suppressed, and this reflects its low adsorption rate and low adsorption capacity (*3*, *7*). As pointed out previously (*3*, *5*, *9*), the amidoxime ligands are assumed to be present as neutral species in seawater (pH: 8.1–8.3) and, therefore, the amidoxime polymer has a lower hydrophilicity than ordinary ion-exchange resins. The hydrophobicity of the polymer matrix containing DVB units prevents significant diffusion of the ionic species $[UO_2(CO_3)_3]^{4-}$ into the pore phase and the gel phase. Furthermore, the possibility of chelation of $[UO_2(CO_3)_3]^{4-}$ with the ligands would also be reduced by the hydrophobic field of the gel phase.

Distribution curves of Mg(II) and Fe(III) adsorbed on Polymer 3 from seawater are shown in Fig. 4. Mg(II) distributes uniformly on the polymer, and this result is consistent with the ready diffusion of Mg(II) and therefore the ready attainment of adsorption equilibrium. On the other hand, the distinct distribution of Fe(III) is observed only near the periphery; similar results are observed on the other samples, but cannot

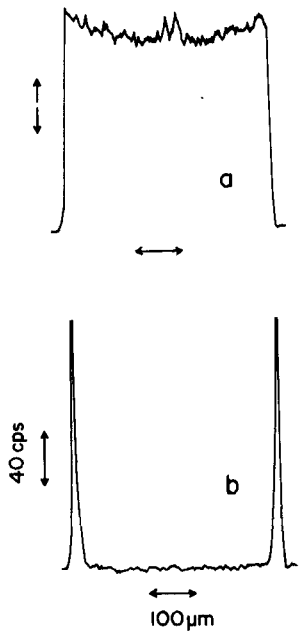

FIG. 4. Distribution curves of Mg(II) (a) and Fe(III) (b) adsorbed on the Amidoxime Polymer 3 from seawater.

be satisfactorily explained although the Fe(III) species is assumed to undergo chemical changes after chelation.

Diffusion Constant of Uranium into Polymer Matrix

As described above for Polymer Sample 2, the adsorption layer of uranium develops with increasing adsorption time, while the maximum intensity of the distribution curve is almost constant. In this case, the overall diffusion constant of uranium into the polymer matrix, D_p, can be estimated from the distribution curve. If the adsorption rate of uranium is assumed to be governed by uranium diffusion into the spherical polymer matrix, the uranium diffusion is expressed by Eq. (1), satisfying the boundary conditions of Eqs. (2)–(5):

$$\rho_p(\partial/\partial t)q(R,t) = D_p\{(\partial^2/\partial R^2) + (2/R)(\partial/\partial R)\}C(R,t) \quad (1)$$

$$C(R,0) = 0 \qquad (0 \leqslant R < R_0) \quad (2)$$

$$C(R,\infty) = C_0 \qquad (0 \leqslant R \leqslant R_0) \quad (3)$$

$$C(R_0,t) = C_0 \qquad (0 \leqslant t) \quad (4)$$

$$(\partial/\partial R)C(R,t)|_{R=0} \qquad (0 \leqslant t) \quad (5)$$

where ρ_p is an apparent density of the polymer; R_0 and R are the radius and the radial position, respectively; t is time; C_0 and $C(R,t)$ denote the concentrations of uranium in the bulk seawater and in the solution phase at R and t, respectively; and $q(R,t)$ is the amount of uranium adsorbed at R and t. Here, the following Freundlich-type adsorption formula is assumed to hold between $q(R,t)$ and $C(R,t)$, similar to the case of inorganic adsorbents (*11*),

$$q(R,t)/q_0 = [C(R,t)/C_0]^{1/n} \quad (6)$$

where q_0 is the adsorption capacity of uranium at the adsorption equilibrium and n is a constant larger than zero. When we assume $n = 1$ on the basis of the result of adsorption equilibrium of uranium from aqueous solutions containing $[UO_2(CO_3)_3]^{4-}$ on Polymer 2 (*11*), the following equation expressed in terms of the dimensionless variables is derived from Eqs. (1) and (6),

$$(\partial/\partial y)f(x,y) = \{(\partial^2/\partial x^2) + (2/x)(\partial/\partial x)\}f(x,y) \quad (7)$$

where x, y, $f(x,y)$, and $g(x,y)$ are defined as follows:

$$x = R/R_0 \tag{8}$$

$$y = D_p C_0 t/(R_0^2 \rho_p q_0) \tag{9}$$

$$f(x,y) = C(R,t)/C_0 \tag{10}$$

$$g(x,y) = q(R,t)/q_0 = f(x,y) \tag{11}$$

Equation (7) can be solved under the above boundary conditions to yield

$$f(x,y) = 1 + 2\sum_{i=1}^{\infty} (-1)^i \exp(-i^2\pi^2 y) \sin(i\pi x)/(i\pi x) \tag{12}$$

and the dimensionless adsorption amount of uranium, $g(y)$, is given by

$$g(y) = 1 - (6/\pi^2)\sum_{i=1}^{\infty} \exp(-i^2\pi^2 y)/i^2 \tag{13}$$

Thus, if the y value is determined by fitting $g(x,y)$ to the experimental distribution curve, the diffusion constant can be obtained through Eq. (9), although the q_0 value must be known.

The q_0 value cannot be determined experimentally. In the present study this value was estimated from the distribution curve shown in Fig. 3 as follows. Since the maximum intensity is almost equal at any time, it was assumed that this intensity is attained at any position after the adsorption equilibrium is reached. $I(t)$, defined by

$$I(t) = \int_0^{R_0} 4\pi R^2 I(R,t) dR/(4\pi R_0^3/3) \tag{14}$$

is related to the adsorption amount of uranium at t, where $I(R,t)$ is the intensity of distribution curve at R and t. The $I(t)$ value was calculated by smoothing the distribution curve. The results are listed in Table 3. Thus, the q_0 value was evaluated as follows:

$$q_0 = C_{p.U}[I(t)/I(\infty)]^{-1} \tag{15}$$

where $C_{p.U}$ is the adsorption amount of uranium determined experimentally as listed in Table 3. The average value of q_0 is estimated to be 2.55 mg/g.

The y values were determined by curve-fitting of $g(x,y)$ to the

TABLE 3
Estimation of Adsorption Capacity of Uranium from Seawater on Amidoxime Polymers

Polymer sample	Time (d)	$C_{p,U}$(mg/g)	$I(t)/I(\infty)$	q_0(mg/g)
2-1	134	0.944	0.37	2.55
2-2	169	1.21	0.45	2.68
2-3	365	1.55	0.64	2.42

experimental results shown in Fig. 3, and the results are listed in Table 4. Thus, the diffusion constant D_p is evaluated to be 3.3×10^{-7} cm^2/s, as shown in Table 4, where the experimental values $\rho_p = 0.32$ g/cm^3 and $C_0 = 2.8$ μg/dm^3 are employed. This value of D_p is close to that of the inorganic adsorbent (*10*), being much smaller than an inherent diffusion constant of uranium in artificial seawater: 3.43×10^{-6} cm^2/s (*12*).

The present study shows that the distribution of uranium adsorbed on the amidoxime polymer from seawater changes significantly by the composition of hydrophilic 4EGDM and hydrophobic DVB. This result suggests that the adsorption rate of uranium is governed primarily by uranium diffusion into the polymer matrix, and also that the chelation of ionic $[UO_2(CO_3)_3]^{4-}$ with amidoxime ligands is affected significantly by the hydrophilic properties of the gel phase. Therefore, the design of the pore and gel structure and the hydrophilicity of the polymer matrix seem to be essential for the development of a functional amidoxime polymer for the recovery of uranium from seawater.

TABLE 4
Evaluation of Diffusion Constant of Uranium into Amidoxime Polymer

Polymer sample	Time (d)	$C_{p,U}$ (mg/g)	R_0,[a] (mm)	y^b	$10^7 \times D_p^b$ (cm^2/s)
2-1	134	0.944	0.275	0.015 (0.015)	2.9 (2.9)
2-2	169	1.21	0.275	0.025 (0.024)	3.7 (3.6)
2-3	365	1.55	0.241	0.070 (0.059)	3.7 (3.2)

[a]These values are the average radius of 10 samples.
[b]The values in parentheses were obtained by using Eq. (13).

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