Characterization of Eu(III) Adsorbed onto Chitin and Chitosan by Time-resolved Laser-induced Fluorescence Spectroscopy

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Chitin and chitosan exhibited high distribution coefficients for Eu(III). On the other hand, analysis by time-resolved laser-induced fluorescence spectroscopy showed that the hydration states of Eu(III) on chitin and on chitosan were significantly different. Europium(III) on chitin interacted with its coordination sites in an inner-spherical manner while that on chitosan interacts in an outer-spherical manner.

Chitin and chitosan are very attractive as adsorbents for metals, because they are ecologically acceptable and potentially inexpensive. Interaction mechanism between these biopolymers and metals has been widely investigated, showing that the amine nitrogen is the active site for metal ion coordination.[1] However, the effects of key process variables on metal adsorption behavior are still not well characterized. To develop the derivatives with higher capacities, the properties of the adsorbents as well as the chemical state of the metal adsorbed should be clearly understood.

Several studies were performed on the interaction of chitin and chitosan with lanthanides and actinides.[2,3] However, we have limited knowledge on the coordination structure around the adsorbed metals. Study on the interaction mechanisms between these biopolymers and lanthanides is very important with regard to the removal of these elements from radioactive contaminants. Importance of deep understanding of the mechanism is undoubtedly true from the viewpoint that lanthanides are good analogues to trivalent actinides.

Time-resolved laser-induced fluorescence spectroscopy (TRLFS) has an advantage in terms of its high selectivity and sensitivity for trivalent lanthanides and actinides, and applicability to adsorbed species on materials with complicated structure in the presence of aqueous phase.[4] The fluorescence lifetime of Eu(III) excited is related to the number of water molecules in the inner-sphere (N_{H_2O}).[5] The relative intensity of the $^5D_0 \rightarrow {}^7F_1$ (electric dipole) and $^5D_0 \rightarrow {}^7F_2$ (magnetic dipole) emissions ($R_{E/M}$) is an indicator for strength of the ligand field of Eu(III).[6] Unknown coordination environments of Eu(III) can be characterized including both the inner- and outer-sphere simply by plotting $R_{E/M}$ and ΔN_{H_2O} ($= 9 - N_{H_2O}$) on the coordination-environment diagram (CE diagram).[7]

In the present study, the adsorbent properties of chitin and chitosan were examined with regard to the chemical state of Eu(III) by batch experiments and TRLFS. TRLFS was applied to characterization of the coordination environments of adsorbed Eu(III) based on the CE diagram.

We used commercially available chitin and chitosan, whose degree of deacetylation was approximately 25 and 70%, respectively. For distribution experiments, 80 mg of the biopolymers and ^{152}Eu(III) was mixed in 8 cm^3 of distilled water which had been bubbled with N_2 gas for 24 h to remove dissolved CO_2. pH of the solutions was adjusted with a small amount of NaOH or $HClO_4$. The solution was shaken at a room temperature with a constant shaking at 150 rpm. After one week of shaking, the suspending solution was centrifuged, and distribution of ^{152}Eu(III) was determined radiometrically.

TRLFS experiments were conducted for Eu(III) adsorbed on the biopolymers. Eighty mg of the biopolymers was mixed with 8 cm^3 of 0.01 mol dm^{-3} of Eu(III). The solution was shaken at 150 rpm and at a room temperature for one week. A small amount of the biolpolymers was stuck in a quartz cell for the laser irradiation. Emission spectra and lifetimes of Eu(III) were measured by TRLFS system described elsewhere.[8] The luminescence decay curves, which was measured by the emission at $^5D_0 \rightarrow {}^7F_1$, were fitted by a monoexponential function. The N_{H_2O} of Eu(III) in the biopolymers and the solution was estimated according to the equation:

$$N_{H_2O} = 1.05k_{obs} - 0.44$$

where k_{obs} (ms^{-1}) is the decay constant.[8] The relative peak intensity ratio ($R_{E/M}$) is defined as

$$R_{E/M} = I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$$

where $I(^5D_0 \rightarrow {}^7F_2)$ and $I(^5D_0 \rightarrow {}^7F_1)$ are calculated from the peak areas.

Figure 1 shows logarithmic distribution ratios, $\log K_d$ (g^{-1} cm^3), of Eu(III) for chitin and chitosan. Adsorption onto cellulose was also determined in consideration that chitin and chitosan are the derivatives of cellulose, so that the roles of functional groups on the biopolymers in Eu(III) adsorption can be better clarified. The reported pH values are those measured after adsorption. For chitin, $\log K_d$ was approximately 2

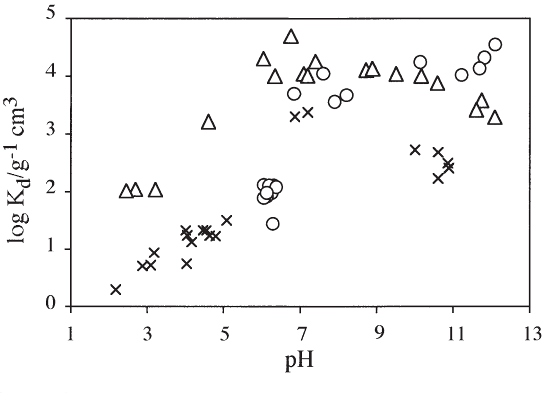

Figure 1. Adsorption of Eu(III) by chitin (△), chitosan (○), and cellulose (×). Volume of solutions and weight of the biopolymers are 8 cm^3 and 80 mg, respectively.

at around pH 3 and increased with an increase in pH up to 7, reaching its maximum ($\geq$4). $\log K_d$ was decreased over pH 8, because the formation of anionic Eu(III) species by hydrolysis proceeds in the alkaline pH region. For chitosan $\log K_d$ increased with an increase in pH. Chitosan dissolves in the acidic pH region. Measurement of the adsorption on chitosan; therefore, was not conducted below pH 6. Cellulose showed a maximum in $\log K_d$ in the neutral pH region (approximately 3.5). Lower $\log K_d$ was observed for cellulose than that for chitin and chitosan. This fact indicates that the amine nitrogen on chitin and chitosan have a stronger affinity for Eu(III) compared with that of the hydroxyl oxygen in cellulose.

The CE diagram of Eu(III) adsorbed on chitin, chitosan and cellulose obtained at pH 6–8 is shown in Fig. 2. ΔN_{H_2O} in the figure was calculated by the equation $\Delta N_{H_2O} = 9 - N_{H_2O}$. Here, the coordination number of Eu(III) ion is assumed to be unchanged and 9. Coordination number of Eu(III) is difficult to be clearly elucidated in complicated systems, even with the analytical methods, such as EXAFS and NMR. As for the research in which coordination number has been successfully evaluated, values raging from 8–10 are reported in most cases.[9] The energy transfer from Eu(III) excited to functional groups other than water molecules was negligible, which we ascertained by using Eu(III)–D_2O solutions in the place of Eu(III)–H_2O solutions. The discussion based on the CE diagram is sufficiently reliable. Thus, ΔN_{H_2O} represents the number of coordination sites occupied in the inner-sphere of Eu(III) by the ligands other than water molecules. It is reported that Eu(III) exhibits extremely large k_{obs}, in some cases, especially in the high-alkaline pH region where hydrolysis of Eu(III) occurs.[10] In the present study, results with k_{obs} smaller than 9 ($N_{H_2O} \leq 9$), which was obtained in the samples with their pHs below 8.0, are plotted. In this pH region, almost complete Eu(III) adsorption was attained and contribution on the $R_{E/M}$–ΔN_{H_2O} plots from Eu(III) dissolved in the liquid phase is considered to be negligible. k_{obs} smaller than 9 assures that no precipitation was formed after one week of incubation.

$R_{E/M}$–ΔN_{H_2O} plots for the Eu(III) adsorbed on chitin are distributed on the upper left area of the CE diagram, showing that approximately 5–7 water molecules were removed from the inner-sphere of Eu(III). The hydration state of Eu(III) adsorbed on chitosan is different from that on chitin. $R_{E/M}$–ΔN_{H_2O} plots for Eu(III) adsorbed on chitosan distributed mostly on the lower right area in the CE diagram, showing ΔN_{H_2O} ranging from 1.5 to 3. These findings indicate that larger number of water molecules is replaced by ligands from the inner-sphere of Eu(III) on chitin compared with that on chitosan. The Eu(III) on chitin is possibly coordinated with the amine nitrogen as well as the carbonyl oxygen. As for $R_{E/M}$, values as large as 5 were observed for chitosan due to the lowered symmetry in the coordination environment of adsorbed Eu(III), whereas $R_{E/M}$ for chitin was less than 3. The CE diagram indicates that $R_{E/M}$–ΔN_{H_2O} plots in the upper left area result from predominantly inner-spherical interactions, while those in the lower right area are attributable to an outer-spherical one.[7] According to this interpretation, the interaction between Eu(III) and chitin is an inner-spherical one while that between Eu(III) and chitosan is an outer-spherical one. The inner-spherical coordination of Eu(III) observed for chitin may be due to the existence of the carbonyl oxygen, which has a hard character showing the high affinity for the hard cation, Eu(III). The structure of cellulose resembles that of chitin and chitosan, except that the hydroxyl groups in position 2 have been replaced by amino or acetylamino groups. Both $R_{E/M}$ and ΔN_{H_2O} exhibited smaller values, however, for Eu(III) adsorbed on cellulose compared to that on chitin for ΔN_{H_2O} plots, and that on chitosan for $R_{E/M}$ plots, respectively. This observation strongly suggests that the coordination of Eu(III) to cellulose is weaker than that to chitin or chitosan.

Interactions between biopolymers and metals are divided into weaker and stronger ones, according to the functional groups in the polymers.[11] Chitin and chitosan are both classified into stronger adsorbents. In this investigation, high distribution coefficients of these biopolymers were obtained by the distribution experiments. By TRLFS, however, large differences in the hydration state of Eu(III) were observed between the ones adsorbed on chitin and chitosan. Our investigation implies that the adsorbent properties of these polymers are not governed by the affinity of the amine nitrogen for metals alone, but some other factors, such as the carbonyl oxygen and the macromolecular steric effect, should be taken into consideration for the precise estimation of the properties.

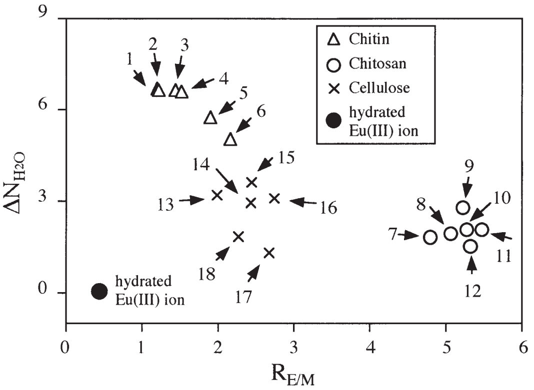

Figure 2. Coordination-environment diagram obtained for Eu(III) adsorbed on chitin, chitosan, and cellulose. The large closed circle represents the result obtained for hydrated Eu(III) ion with no interaction other than water molecules. pH values are as follows: (1) 6.66, (2) 7.14, (3) 7.03, (4) 7.11, (5) 7.12, and (6) 7.46 for chitin, and (7) 7.17, (8) 7.30, (9) 7.26, (10) 7.18, (11) 7.30, and (12) 7.82 for chitosan, and (13) 6.44, (14) 6.46, (15) 6.69, (16) 6.92, (17) 6.73, and (18) 6.86 for cellulose.

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