doi:10.1246/cl.2011.806

Published on the web June 25, 2011

Specific Sorption Behavior of Actinoids on Biogenic Mn Oxide

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We made sorption experiments of actinoids on Mn oxide in dilute NaCl solution. Sorption affinity of actinoids on synthetic Mn oxide was Th(IV) > U(VI) > Np(V). The specific sorption behavior of actinoids on biogenic Mn oxide was observed. Thorium sorbed on biogenic Mn oxide was desorbed into solution with increasing time. Neptunium was not sorbed on biogenic Mn oxide. The specific sorption behavior is possibly due to organic ligands released from microorganisms and surface properties of biogenic Mn oxide.

Uranium and plutonium are used to produce electricity in nuclear power plants. As a result of nuclear power generation, many radioactive wastes are produced. Release of actinoids from radioactive wastes into natural environments would be a serious problem for humans. Therefore, prediction of actinoid behavior in natural environments is of serious concern.[1,2] Oxidation state of actinoids ranges from trivalent to hexavalent states. Solubility, complexation, and sorption of actinoids on mineral surfaces depend on their oxidation state. Therefore, knowledge of the chemical natures of actinoids in different oxidation states is essential for modeling their migration in aqueous systems.

Sorption of dissolved actinoid species on mineral surfaces is an important process which retards their migration in natural environments. In particular, Mn(IV) oxide has received considerable attention because of its strong sorption and ubiquity in natural environments.[3,4] Recently, it is accepted that the formation of Mn oxide is microbially mediated in most Mn oxide deposits.[5] Considering the microbial formation of Mn oxide, sorption behavior should be investigated using biogenic Mn oxide. However, actinoid sorption on Mn oxide has been examined using abiotically synthesized analogues.[3,4,6] Therefore, in this study, we made sorption experiments of actinoids on biogenic Mn oxide produced by a Mn(II)-oxidizing microorganism.

Sorption experiments of actinoids on Mn oxide were carried out in 10 mmol L^{-1} NaCl solution. *Acremonium* sp. strain KR21-2, a Mn-oxidizing fungus, was cultured to prepare biogenic Mn oxide. Detailed procedures for the cultivation of strain KR21-2 have been described in our earlier work.[7] The biogenic Mn oxide was not separated from fungal cells. Abiotic Mn oxide (δ-MnO_2) was synthesized according to Villalobos et al.[8] Measurement of X-ray diffraction patterns for the biogenic and synthetic Mn oxides showed that both had poorly crystalline structures.[7,8] The specific surface areas of the biogenic and synthetic Mn oxides were 113 and 27.8 m^2 g^{-1}, respectively.[4,9] Stock solution with 0.5 mmol L^{-1} ^{232}Th(IV), ^{237}Np(V), and ^{238}U(VI) each was prepared. First, the biogenic or synthetic Mn oxide was put into 50 mL of 10 mmol L^{-1} NaCl solution. We used PFA Teflon bottles to minimize sorption of actinoids on container walls. The total amount of the harvested biogenic Mn oxide for each sorption experiment corresponded to ca. 2.8 mg of Mn with 6.3 mg of fungal cells.[7] Therefore, 2.8 mg/50 mL = 56 mg L^{-1} of solid Mn as biogenic Mn oxide was used for each experimental run. The amount of δ-MnO_2 added to the 10 mmol L^{-1} NaCl solution was 44 mg L^{-1} of solid Mn. Finally, the actinoid stock solution was added to the solution. Initial concentration of each actinoid in the solution was 1 μmol L^{-1}. Initial pH values were adjusted with HCl or NaOH solution. Solutions after different time were sampled by filtration with a 0.2 μm filter to measure actinoid concentrations with an ICP-MS (HP4500). An internal standard of Bi was added to each sample solution to be 10 ng mL^{-1}. Signal intensities of ^{209}Bi, ^{232}Th, ^{237}Np, and ^{238}U were detected. Sorption amount was calculated by the following equation:

$$\text{Actinoid sorption (\%)} = ([\text{An}]_{\text{initial}} - [\text{An}]_{\text{measure}})/[\text{An}]_{\text{initial}} \times 100 \quad (1)$$

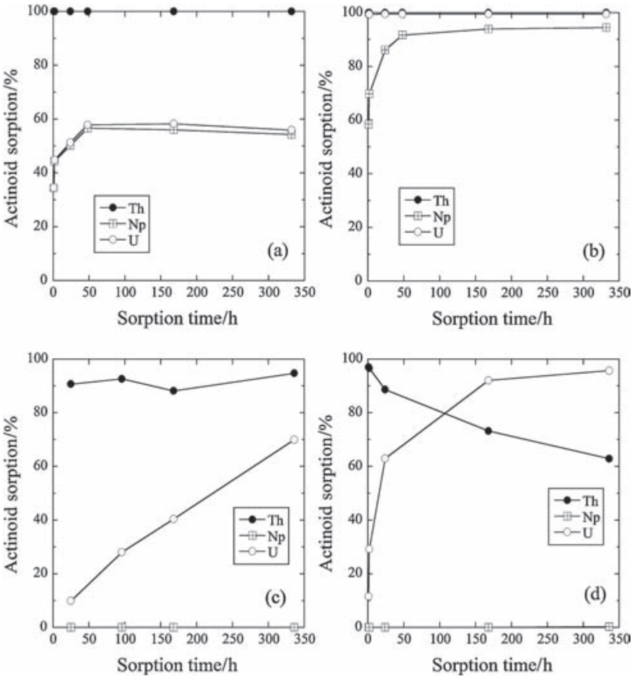

Figure 1. Sorption kinetics of actinoids using (a) synthetic Mn oxide at pH 2.8, (b) synthetic Mn oxide at pH 6.1, (c) biogenic Mn oxide at pH 2.9–3.1, and (d) biogenic Mn oxide at pH 3.4–5.9.

The results of sorption kinetics of Th(IV), Np(V), and U(VI) on Mn oxide are shown in Figure 1. At pH 2.8, all Th in solution was sorbed quickly on synthetic Mn oxide within an hour (Figure 1a). Np and U sorption increased until 48 h and then remained contant. At pH 6.1, U as well as Th was sorbed quickly on synthetic Mn oxide (Figure 1b). The sorption kinetics of Np at pH 6.1 was similar to that at pH 2.8 although total amount sorbed

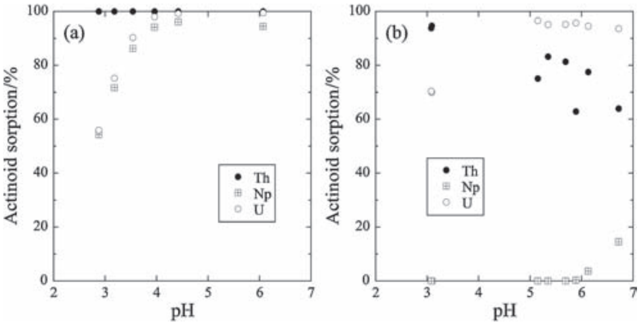

Figure 2. Sorption of Th(IV), Np(V), and U(VI) on (a) synthetic and (b) biogenic Mn oxides as a function of pH after 2 weeks.

on Mn oxide was larger at pH 6.1 (Figures 1a and 1b). The pH values of reacting solutions increased during sorption experiments using biogenic Mn oxide (2.9–3.1 and 3.4–5.9, Figures 1c and 1d), whereas those were relatively constant using synthetic Mn oxide. The increase in pH was possibly caused by release of organic molecules from fungal cells as was observed in our previous work on REE sorption on biogenic Mn oxide.[7] Sorption kinetics of actinoids on biogenic Mn oxide was quite different from that on synthetic Mn oxide. Neptunium was not sorbed on biogenic Mn oxide at all (Figures 1c and 1d). Sorption of U on biogenic Mn oxide increased with increasing sorption time. Difference of sorption behavior on biogenic Mn oxide between U and Np is striking relative to synthetic Mn oxide. Under lower pH condition (pH 2.9–3.1), about 90% of Th was sorbed on biogenic Mn oxide after 24 h, and sorption did not increase significantly during the sorption experiment (Figure 1c). Under higher pH condition (pH 3.4–5.9), the amount of Th sorbed on biogenic Mn oxide decreased with increasing time (Figure 1d), indicating that Th sorbed on biogenic Mn oxide was desorbed into solution phase.

Figure 2 shows sorption of Th(IV), Np(V), and U(VI) on synthetic and biogenic Mn oxides after 2 weeks as a function of solution pH. Thorium was strongly sorbed on synthetic Mn oxide between pH 3 and 6 (Figure 2a).[3] Sorption of U and Np increased with increasing pH from 3 to 4.5. Uranium sorption on biogenic Mn oxide was greater at pH higher than 5 than that at pH 3 (Figure 2b). Neptunium was not sorbed on biogenic Mn oxide at all between pH 3 and 6, although it was sorbed a little at pH higher than 6. Thorium sorption on biogenic Mn oxide decreased with increasing pH.

The results of this study clearly show that sorption properties of synthetic and biogenic Mn oxides for actinoids are quite different (Figures 1 and 2). Since the tetravalent Th is a highly insoluble element, the strong sorption on synthetic Mn oxide is quite reasonable throughout the pH conditions studied here (Figure 2a).[3] However, a decrease in Th sorption on biogenic Mn oxide was observed with increasing pH (Figure 2b), indicating that Th is more stable in solution phase at higher pH. Tetravalent actinoids form strong complexes with organic ligands,[10,11] but we did not add any organic ligands to experimental solutions at the beginning of each experimental run. In our previous work, we reported that Ce(IV) was stabilized in solution phase by complexation with organic ligands released from fungal cells.[7] The Ce(IV)–organic ligand complexation was stronger under higher pH conditions. Similarly, it is possible that complexation of Th(IV) with organic ligands increased solubility of Th(IV) especially under higher pH conditions (Figure 2b). Desorption of Th from biogenic Mn oxide suggests that organic ligands were gradually excreted from fungal cells with increasing time (Figure 1d). Our previous work showed that complexation of Ce(IV) with organic ligands occurred within 24 h.[7] Therefore, the desorption of Th(IV) from 1 to 24 h is reasonable (Figure 1d).

The sorption behavior of U and Np on synthetic Mn oxide showed similar trend (Figures 1a, 1b, and 2a). Difference of actinoid sorption on biogenic Mn oxide is striking relative to synthetic Mn oxide (Figures 1c, 1d, and 2b). Similarly to Th(IV), it is possible that U(VI) and Np(V) are also complexed with organic ligands released from fungal cells. However, it is unlikely that U(VI)–organic ligand complex is more stable than Th(IV)–organic ligand complex because U(VI) was sorbed more strongly on biogenic Mn oxide (Figures 1d and 2b). Possibly, Np(V) forms fewer complexes with organic ligands than Th(IV) and U(VI) do. Therefore, the difference of Np sorption on synthetic and biogenic Mn oxides may be attributed to sorption properties of surfaces of the Mn oxides. The coexistence of fungal cells with biogenic Mn oxide may also affect sorption behavior. Further studies are needed to clarify the sorption behavior of U and Np on biogenic Mn oxide.

Other researchers have conducted sorption experiments using actinoids separately in different experimental runs.[3,6] In this study, we carried out sorption experiments using Th(IV), Np(V), and U(VI) simultaneously in the same experimental system. This made it possible to compare the sorption behavior of different actinoids directly. As a result, we found clearly the differences in sorption behavior among Th(IV), Np(V), and U(VI) (Figures 1 and 2). Knowledge of actinoids with different oxidation states can be a basis to understand the behavior of Pu, which has complicated redox chemistry, because Th(IV), Np(V), and U(VI) as analogues correspond to Pu(IV), Pu(V), and Pu(VI), respectively.

In this study, we first found the specific sorption behavior of actinoids on biogenic Mn oxide (Figures 1 and 2). Apparent sorption affinity of actinoids on δ-MnO_2 is stronger than that on biogenic Mn oxide. This is possibly due to organic ligands released from fungal cells and surface properties of biogenic Mn oxide. Most Mn oxides occurring in natural environments is of biogenic origin.[5] Therefore, more detailed studies should be done not only using synthetic Mn oxide but also using biogenic Mn oxide.

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