EXAFS Studies about the Sorption of Cadmium Ions on Montmorillonite

Rieko Takamatsu,*[1] Kiyotaka Asakura,[2] Wang-Jae Chun,[2] Tsuyoshi Miyazaki,[3] and Masashi Nakano[4]
[1]*School of Veterinary Medicine and Animal Sciences, Kitasato University, 35-1 Higashi23bancho, Towada 034-8628*
[2]*Catalysis Research Center, Hokkaido University, Kita 21-10, Kita-ku, Sapporo 001-0021*
[3]*Graduate School of Agricultural and Life Sciences, The University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-8657*
[4]*Research Institute of Soil Science and Technology, 1-27-201 Misora-cho, Otsu 520-0023*

(Received October 19, 2005; CL-051325; E-mail: takamats@vmas.kitasato-u.ac.jp)

We investigated local structures around cadmium (Cd) sorbed on montmorillonite at various pH values by EXAFS (extend X-ray absorption fine structure). We found two sorption types, an outer-sphere complex and a surface precipitate. The outer-sphere complex was mainly formed at a lower pH which had an identical structure to aqueous Cd^{2+}, while the surface precipitate was found at high pH which had a one-layer $Cd_5(OH)_8(NO_3)_2(H_2O)_2$-like structure.

Cadmium (Cd) is a toxic heavy metal that results in significant pollution of many soil and groundwater systems. Furtherworse, Cd is known to bioaccumulate. Since the mobility and bioavailability of Cd in polluted systems are strongly related to its sorption structures, it is important to understand the sorption structures on clay minerals which are main soil components. Montmorillonite is a dioctahedral smectite mineral that is prevalent in soil environments and has a high surface area and cation-exchange capacity (CEC). Over past several decades, macroscopic investigation on the sorption mechanisms of metals on montmorillonite presented many thermodynamic models such as "surface complexation models" to describe metal sorption reactions at the solid–water interface.[1] The models explained the pH-dependent sorption properties on the montmorillonite.[2–4] Outer-sphere complex is mainly formed on permanent charge sites on the interlayer of montmorillonite at low pH values while inner-sphere complex formation occurs at high pH values, where the metals are fixed to deprotonated surface hydroxides on the edge of montmorillonite. However, we have to determine the molecular structures of the sorbed species directly in order to reveal the real sorption mechanism. Recent studies using EXAFS (extend X-ray absorption fine structure) have shown that heavy metals are sorbed on clay and oxide surfaces accompanied by the formation of multinuclear or polynuclear surface complexes (i.e., surface precipitate) much more frequently than previously expected based on the thermodynamical models.[5–9] These microscopic studies have promoted our understanding of the real sorption mechanism. EXAFS analyses of Cd species on the montmorillonite, however, have never been reported in spite of its importance for soil pollution mainly because the K-edge EXAFS requires X-rays with higher energy than 23 keV. We carried out K-edge Cd EXAFS measurements for Cd sorbed on montmorillonite in a vertical Wiggler beam line in SPring-8 and Photon Factory beam line, which provide a high energy X-ray. EXAFS provides only averaged local structure information for all coexisting metal species having the same absorption edge. We varied the pH values in order to change the sorption species continuously and applied a regression analysis to quantitatively evaluate the composition of each sorption structure.

Cd was sorbed on Na-montmorillonite (Kunipia-F, Kunimine Industries Co.) using a batch technique at several different pH values. $Cd(NO_3)_2$ ($0.002\,mol\,L^{-1}$) and $NaNO_3$ ($0.004\,mol\,L^{-1}$) solutions were applied and the reaction time was 24 h (295 ± 1 K). The pH values were pH 3.2, 4.8, 7.1, and 10.2. The clay samples were washed three times with distilled water and were stored as wet pastes in glass sample holders. β-$Cd(OH)_2$ powder, $Cd(NO_3)_2$ solution ($0.1\,mol\,L^{-1}$, $NaNO_3$ $0.2\,mol\,L^{-1}$, pH 5.2) and bulk precipitate ($Cd(NO_3)_2$ 0.1 $mol\,L^{-1}$, $NaNO_3$ $0.2\,mol\,L^{-1}$, pH 8.0) were used as references for the EXAFS measurements. X-ray diffraction data for the freeze-dried bulk precipitate showed that it had a $Cd_5(OH)_8(NO_3)_2(H_2O)_2$ crystalline structure.[10]

Cd K-edge EXAFS spectra were obtained at BL01B1 of SPring-8 (JASRI) and BL14A of Photon Factory (KEK-PF). A Si(311) double crystal monochromator was used. The spectra were collected in a transmission mode at room temperature. The EXAFS analyses were carried out by REX2000 (Rigaku Co.) using phase shift and amplitude functions derived from the date of β-$Cd(OH)_2$.[11]

Figure 1 shows the k^3-weighted EXAFS oscillations and their Fourier transforms for the clay samples at various pH

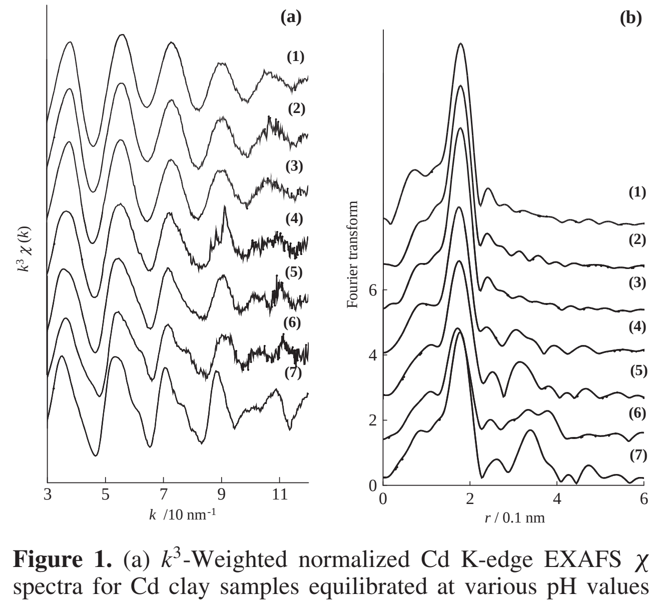

Figure 1. (a) k^3-Weighted normalized Cd K-edge EXAFS χ spectra for Cd clay samples equilibrated at various pH values and for references. (b) Fourier transforms of the EXAFS oscillations, $\Delta k = 30$–$120\,nm^{-1}$. (1) Cd^{2+}(aq) (reference), (2) Clay sample 1 (pH 3.2), (3) Clay sample 2 (pH 4.8), (4) Clay sample 3 (pH 7.1), (5) Clay sample 4 (pH 10.2), (6) Cd bulk precipitate (reference), (7) β-$Cd(OH)_2$ (reference).

Table 1. Coefficients A and B in regression analyses of eq 1 and local atomic structure parameters of separated surface precipitate [S.P.] for clay samples at pH 7.1 and 10.2

	pH	A^a	B^a	CN(Cd–O)^b	r(Cd–O)^c / 0.1 nm	CN(Cd–Cd)^d	r(Cd–Cd)^c / 0.1 nm
Clay 3 [S.P.]	7.1	0.58	0.42	5.8	2.31^e	4.2	3.39
Clay 4 [S.P.]	10.2	0.34	0.66	6.0	2.31	4.0	3.39
Bulk precipitate				6.0	2.31	2.7	3.41
						4.6	3.90

[a] The coefficients indicate the ratios of surface formation (outer-sphere complex (A) and surface precipitate (B)). [b] Coordination number, error is ±0.5. [c] Radial distance, error is $\pm 0.02\,\mathrm{nm}^{-1}$. [d] Coordination number, error is ±0.8. [e] Coordination number is fixed.

values, and those for the Cd reference compounds. Similarity of the spectra for the clay samples at pH 3.2 and 4.8 to that of the Cd solution indicates that the local structure around the sorbed Cd at low pH is similar to that of the Cd aquo complex and an outer-sphere complex is formed at low pH range. The outer-sphere complex is mainly present in the interlayer space because the interlayer possesses permanent negative charges and a large surface area.

Meanwhile the spectra at pH 7.1 and pH 10.2 were similar to those of β-Cd(OH)$_2$ and the bulk precipitate. The second shell peak in the Fourier transforms is corresponding to Cd–Cd bonding, indicating the formation of polynuclear Cd species. EXAFS oscillations at pH 7.1 and at 10.2 are more identical to the one in the bulk precipitate in the k-range of 90–110 nm^{-1} than that of the β-Cd(OH)$_2$. The first shells corresponding to Cd–O are larger than those of the bulk precipitate and β-Cd(OH)$_2$, probably due to coexisting of the outer-sphere complex. In order to remove the effect of the outer-sphere, we carried out regression analysis using following equation.

$$k^3\chi_{\mathrm{ob}}(k) \approx Ak^3\chi_{\mathrm{o.c.}}(k) + Bk^3\chi_{\mathrm{s.p.}}(k) \quad (A + B = 1), \qquad (1)$$

where $\chi_{\mathrm{ob}}(k)$, $\chi_{\mathrm{o.c.}}(k)$, and $\chi_{\mathrm{s.p.}}(k)$ are EXAFS oscillations for observed data, the outer-sphere complex, the surface identical structure to the Cd solution, we used the EXAFS of the Cd solution as $\chi_{\mathrm{o.c.}}(k)$. $\chi_{\mathrm{s.p.}}(k)$ was unknown. We postulated it was similar to the oscillation of bulk precipitate for the first approximation. We obtained A and B using eq 1 (Table 1) and then extracted $\chi_{\mathrm{s.p.}}(k)$ by removing the contribution of the outer-sphere complex from $\chi_{\mathrm{ob}}(k)$ using the A coefficients. Taking error bars into consideration, A's and B's redetermined by using the extracted $\chi_{\mathrm{s.p.}}$ agreed with the original A's and B's within the precipitate, respectively. Thus, the extracted $\chi_{\mathrm{s.p.}}$ could be applied for the further structural analyses.

We carried out the curve-fitting analyses on the extracted $\chi_{\mathrm{s.p.}}$ (Table 1). The coordination numbers and bond distances for Cd–O were almost the same as those of the bulk precipitate. The second Cd–Cd shell gave only one type of Cd–Cd distance in the clay samples while we found two types of Cd–Cd distances in the bulk precipitate. As mentioned above the bulk precipitate is $Cd_5(OH)_8(NO_3)_2(H_2O)_2$. In this structure, Cd octahedron is linked with its edge sharing to form a layer structure in which Cd–Cd distance was found at 0.341 nm in our EXAFS. Another Cd^{2+} ion was located on the Cd octahedron layers which connect the next layer though NO_3^- counter cation and OH^- group. The distance between the absorbed Cd and the Cd in the octaheron layer was observed in 0.390 nm in the EXAFS of $Cd_5(OH)_8(NO_3)_2(H_2O)_2$. On the other hand, we could not observe the long Cd–Cd distance at 0.390 nm in the clay samples. The lack of the long Cd–Cd bond in the clay samples indicated that only single Cd octahedron layer structure might grow on the montmorillonite. The Cd layer was formed on the edge of the montmorillonite where the deprotonated hydroxide site was located. The deprotonated hydroxide could be the nucleation site of the layer growth. The surface precipitate layer should be fixed in the parallel manner to the montmorillonite sheet with direct a Cd–O–Al bond.

In this paper, we carried Cd K-edge EXAFS analysis on the Cd species sorbed on montmorillonite in different pH conditions. At low pH, the outer-sphere Cd complex was sorbed, while we found the surface precipitate at high pH. We determined the surface precipitate which should have the $Cd_5(OH)_8(NO_3)_2$-$(H_2O)_2$-like single layer structure formed on the edge of montmorillonite. We revealed that the clay edge influenced the surface precipitate formation and their growth. The findings will give the new structural information on the surface precipitate and advance the sorption models to explain sorption behavior and mobility of Cd in the soil system.

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