

An EXAFS investigation of the mechanism of Cd attenuation on Fe and Mn (oxyhydr)oxide minerals

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The structure of aqueous cadmium sorption complexes on the iron oxyhydroxide minerals goethite (α -FeOOH), lepidocrocite (γ -FeOOH), akaganeite (β -FeOOH), schwertmannite ($\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$), and cryptomelane ($\text{KMn}_8\text{O}_{16}$) have been determined *in situ* (in the presence of water) using Extended X-Ray Adsorption Fine Structure (EXAFS) spectroscopy. Sorption on these minerals may limit the mobility of Cd in soils and groundwater.

Experimental

All minerals were prepared in our laboratory according to methods reported in the literature. Samples for EXAFS analysis were prepared by adding a known concentration of Cd stock solution to suspensions of the chosen mineral and equilibrating for approximately 24 h. CO_2 -free conditions were maintained throughout the adsorption step of sample preparation to prevent the formation of $\text{CdCO}_3(\text{s})$.

EXAFS data were collected at the CLRC Synchrotron Radiation Source (SRS) at Daresbury Laboratory, U.K. Spectra were collected in multiple fluorescence mode scans at the Cd K-edge under room temperature conditions on station 9.2. Samples

were presented to the X-ray beam as a wet paste held by Sellotape in a 2 mm thick plastic slide with a 4×15 mm sample slot. EXAFS data were also collected from β -Cd(OH) $_2(\text{s})$, for use as a reference standard in later curve fitting.

EXAFS data reduction and analysis was performed using native Daresbury Laboratory software packages (EXCALIB, EXBACK, and EXCURV92) (Binsted *et al.*, 1991). All reported atomic shells are significant at the 1% level. The phase shift functions used in the curve fitting were derived by *ab initio* methods in EXCURV92.

Results

The EXAFS results show that in all adsorption samples and the β -Cd(OH) $_2(\text{s})$ standard, Cd is surrounded by an inner atomic shell containing approximately 6 O,OH,OH $_2$ groups (EXAFS cannot distinguish between these three possibilities) at a distance of 2.24–2.28 Å. At least one additional atomic shell containing Fe or Mn atoms is observed outside the O shell but within 4 Å of the central Cd atom, showing that Cd must adsorb *via* an inner sphere mechanism. There is no evidence for a Cd shell in theoretical fits to experimental data from the adsorption samples, and this indicates that Cd did not

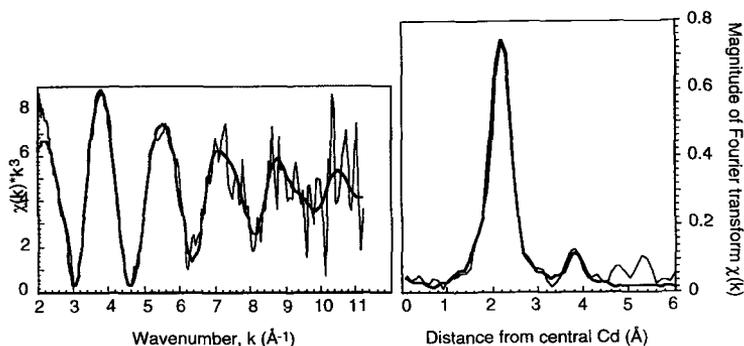


FIG. 1. Representative EXAFS plot (left) and radial distribution function (right) for Cd adsorbed on goethite.

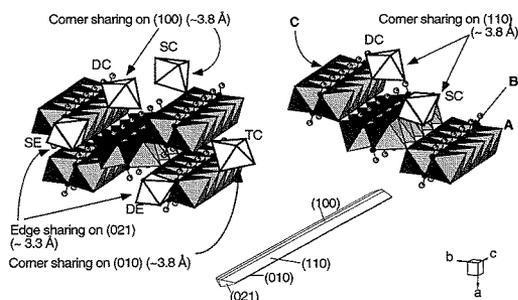


FIG. 2. Interpretation of EXAFS results for Cd adsorbed on goethite.

adsorb *via* the precipitation of a solid phase such as $\text{Cd}(\text{OH})_2(\text{s})$ or $\text{CdCO}_3(\text{s})$. These results are in general agreement with an earlier EXAFS-based study of Cd sorption on goethite and hydrous ferric oxide by Spadini *et al.* (1994).

The EXAFS results for various 'wet paste' goethite adsorption samples are effectively the same regardless of pH (pH 5.4 to 9.3 range) or surface loading (24–53% range). In all cases, a shell containing between 1.1 and 1.8 Fe atoms is present between 3.75 and 3.80 Å from the central Cd atom in addition to the O shell (Fig. 1). This Cd-Fe separation suggests that Cd adsorbs *via* a corner-sharing mechanism, and there is no support for an Fe shell at 3.3 Å, which would indicate edge-sharing adsorption.

Corner-sharing adsorption can occur if adsorbed Cd forms a bidentate bridge between two adjacent A-type hydroxyls or undergoes monodentate adsorption with one C-type hydroxyl (Fig. 2). These two mechanisms are regarded as double corner (DC) and single corner (SC) adsorption, respectively, and can occur on both the dominant (110) faces and the much smaller (110) faces of goethite. Because these DC and SC adsorption complexes result in identical Cd-Fe separations and Fe coordination numbers, they are indistinguishable by EXAFS. However, the supposed inertness of the C-type hydroxyls suggests that adsorption is most likely to occur by DC bridging of two A-type hydroxyls.

Edge-sharing adsorption is thought to be energetically favoured over corner-sharing adsorption, and the fact that edge sharing is not observed (even at a surface loading as low as 24%) is consistent with the morphology of goethite crystals: edge sharing can only occur on the (021) faces which constitute just

~5% of the total surface area.

In contrast to the results from goethite, the Fe shell in the lepidocrocite samples contains 1.1–1.5 Fe atoms at 3.26–3.30 Å (indicative of edge-sharing adsorption) rather than the 3.75–3.80 Å. This difference can be explained in terms of crystal morphology: Lepidocrocite crystals are typically more platy and broad than the narrow acicular goethite needles. As a consequence, far more edge-sharing sites are available on lepidocrocite, and it is these which Cd preferentially bonds to. Relatively small changes in pH (6.0–7.0) and surface loading (27 %–45 %) have no significant effect on the EXAFS results from lepidocrocite.

Cryptomelane consists of a framework structure containing 2×2 tunnels ~4.6 Å in diameter which are partly occupied by K^+ and H^+ . This mineral was able to sorb up to two thirds of the available Cd^{2+} from solution at pH as low as 2.0, with a concomitant release of H^+ to maintain charge balance (although no K was released during Cd sorption). The EXAFS results show that Cd is surrounded by one shell containing 6.5 O atoms at 2.24 Å, and another containing 4.9 Mn at 3.65 Å. These results indicate that Cd sorbed at sites within cryptomelane's tunnel structure, but that it shifted off the ideal tunnel cation position (on the tunnel axis) to allow bonding with O atoms in the tunnel walls.

Akaganeite and schwertmannite are both structurally similar to cryptomelane, but differ in that the tunnel sites are occupied by Cl^- and SO_4^{2-} , respectively, and crystal growth along the needle axis is poor in schwertmannite. EXAFS results for Cd on akaganeite and schwertmannite both show the omnipresent shell of six O atoms at 2.28 Å and a contribution from an Fe shell(s) between 3 and 4 Å. Unfortunately, data quality was not sufficient to resolve an exact Cd-Fe separation, and the only firm conclusion that can be drawn is that Cd sorbed to both of these minerals *via* an inner sphere mechanism.

References

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 Spadini, L., Manceau, A., Schindler, P.W., and Charlet, L. (1994) *J. Colloid Interf. Sci.*, **168**, 73–86.