

Mechanism of cadmium adsorption to goethite in the presence of inorganic and organic ligands

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The speciation and mobility of cadmium is important due to the toxicity of the metal and its widespread discharge from industrial processes. Iron (oxyhydr)-oxides are notable sorbents for Cd^{2+} and hence retard its mobility. In natural solutions, the presence of anionic ligands have been shown to enhance the adsorption of Cd^{2+} . The pH edge for cadmium adsorption is generally shifted to a lower pH in the presence of an anion. However, the mechanism of cation adsorption enhancement has remained controversial. Three mechanisms have been suggested: (1) enhancement by electrostatic interaction (e.g. Benjamin and Leckie, 1981); (2) formation of a ternary cation-anion-surface complex (e.g. Schindler, 1990); and (3) formation of a surface precipitate (e.g. Stumm *et al.*, 1963). Electrostatic enhancement is believed to occur by the reduction of the positive surface charge following the adsorption of negative anions, thus resulting in a more attractive surface for adsorption of cations. A ternary cation-anion-surface complex may be inner sphere (directly bonded to the surface after one or more water molecules are shed from the hydration sphere of the aqua ion) or outer sphere (held to the surface of the sorbent by electrostatic attraction; ion fully hydrated). The formation of a surface precipitate results in a three dimensional lattice containing Cd^{2+} . Precipitation may be particularly enhanced in the presence of a

sorbent which acts as a template for formation of a new solid phase.

Experimental data describing these complex ternary systems are scarce and an accurate interpretation of titration data is difficult without confirming which of the three mechanisms above is controlling adsorption enhancement. Understanding the microscopic mechanisms of co-adsorption will enable a better interpretation of experimental sorption data to be made and hence allow more accurate forward modelling of natural systems.

Extended X-ray Absorption Fine Structure spectroscopy (EXAFS) provides information about the structure and coordination of metals on mineral surfaces. Here we present EXAFS data for the adsorption of Cd^{2+} in the presence of the ligands sulphate, phosphate, humate, citrate, and oxalate because these ligands are all present in the natural environment. Oxalate and citrate also contain carboxylic functional groups which represent those found on humic- and fulvic acids. All of the ligands, with the exception of citrate, have previously been shown to enhance adsorption of Cd^{2+} to iron(oxyhydr)oxide (e.g. Hoins *et al.*, 1993). This investigation determines which of the three sorption

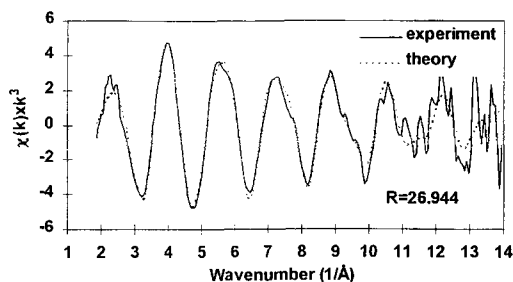


FIG. 1. EXAFS spectrum of Cd^{2+} adsorbed on goethite in the presence of phosphate at pH 5.0.

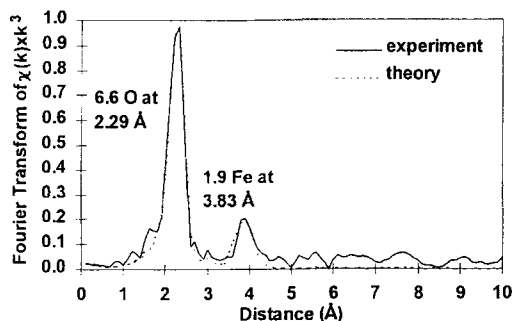


FIG. 2. Radial distribution function (RDF) of the EXAFS function shown in Fig. 1, Cd^{2+} adsorbed on goethite in the presence of phosphate at pH 5.0.

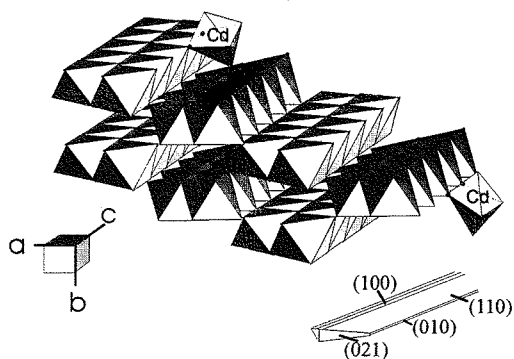


FIG. 3. Structure of the proposed $\text{Cd}(\text{OH}_2)_4^{2+}$ complex sorbed by 'double-corner-sharing' to the (110) face of goethite.

mechanisms of enhancement given above is dominant in each system.

Results

In the case of phosphate, sulphate and humate Cd was surrounded by a first shell of 6 ± 1 O atoms at 2.3 ± 0.1 Å (Figs 1, 2). A second shell of approximately 2 Fe atoms at 3.8 ± 0.1 Å was also observed. This we interpreted as showing that Cd^{2+} is inner-spherically bound to the surface of goethite by octahedral-double-corner-sharing to sites on the (110) surface of goethite (Fig. 3) (Randall *et al.*, 1998). For citrate we conclude that Cd^{2+} is most probably adsorbed in a similar manner, although the formation of a ternary complex cannot be ruled out. In contrast Cd^{2+} appears to form a surface precipitate in the presence of oxalate (Fig. 4).

The enhancement mechanism of the extent of Cd^{2+} in the presence of sulphate and phosphate is solely by electrostatic interaction. This implies that the ligands adsorb to different sites than Cd^{2+} , but we do not

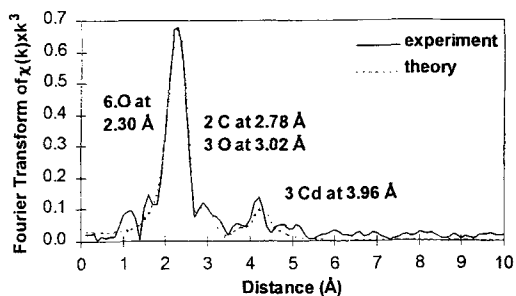


FIG. 4. RDF of the EXAFS function of Cd^{2+} sorbed on goethite in the presence of oxalate at pH 5.3.

know which sites attract the ligands. Electrostatic enhancement of the sorption of Cd^{2+} to iron (oxyhydr)oxides is important in soils, particularly those which are treated with inorganic fertilisers. However, this enhancement is likely to be reversible and ionic strength dependent as a surface precipitate is not formed. For remediation of contaminated land, flushing with low pH water ($\text{pH} < 4$) is likely to be effective for removal of Cd^{2+} , even in the presence of sulphate and phosphate over a time-scale related to adsorption-desorption reactions (hours) rather than to dissolution (weeks).

References

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