



An extended X-ray absorption spectroscopy study of copper(II) sorption by oxides

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Abstract

Many important sorption parameters have been determined by isothermal sorption batch experiments; however, only macroscopic and indirect results were obtained. The objective of this study was to derive the species and structural environment of Cu(II) on the surface of gibbsite ($\text{Al}(\text{OH})_3$), pyrolusite (MnO_2), and amorphous silica (SiO_2), using the technique of extended X-ray Absorption Fine Structure (EXAFS) spectroscopy. Results show that the equilibrated pH of suspension affects significantly the species of Cu sorbed on the surface of these oxides. Sorbed species (Cu^{2+}) were present below pH 5.73 and precipitated ($\text{Cu}(\text{OH})_2$) phases above 5.63. On the other hand, there is no EXAFS evidence that sorbent types and concentrations affect the local chemistry environment and species of Cu(II).

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1. Introduction

Isothermal sorption batch experiments are very important in soil science research. Theoretically, maximum monolayer sorption, empirical adsorption constants, and other important adsorption parameters can be determined by this method. Cation-exchange

capacity (CEC) of soils and soil components can also be quantified. Mechanistic interpretations and models have been developed for metal sorption reactions at the soil/water interface; however, they are mostly been developed from macroscopic information without direct atomic-level evidence (Fendorf et al., 1994a, b; Farquhar et al., 1996; Dubbin et al., 2000). Moreover, reactions (particularly sorption reaction) at mineral–water interfaces are major factors in controlling the bioavailability, mobility, toxicity, and fate of added fertilizers, pesticides, herbicides, and pollutants in natural ecosystems (Sparks, 2002).

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According to aquatic chemistry, high solution concentrations or high pH may cause metal hydroxide or carbonate to precipitate onto mineral surfaces (Weesner and Bleam, 1997). Therefore, prediction models require thorough understanding of the composition of relevant surface species, such as identification of the exact species, where they bind to mineral surfaces, and the nature of their precipitate phases (Fitts et al., 1999).

X-ray absorption fine structure (XAFS) spectroscopy has proven to be a powerful method for obtaining the speciation and local structure of elements present in soils (Koningsberger and Prins, 1988; Fendorf and Sparks, 1996). Recent XAFS studies of Cu(II) sorption on mica (Charnock et al., 1995; Farquhar et al., 1996; Kriventsov et al., 1998), silica (Xia et al., 1997; Fitts et al., 1999; Kriventsov et al., 1999), clay minerals (Farquhar et al., 1996; Xia et al., 1997; Parkman et al., 1999; Manceau et al., 2000), and even in aqueous solution with humic substances (Angelo et al., 1998; Korshin et al., 1998; Dubbin et al., 2000; Frenkel et al., 2000; Alcacio et al., 2001) have examined the speciation and local structure of Cu(II). XAFS thereby offers local environmental information, which is unique among the currently available methods. In this study, three major soil components, gibbsite ($\text{Al}(\text{OH})_3$), pyrolusite (MnO_2), and amorphous silica (SiO_2), were equilibrated with Cu(II) using isothermal sorption batch experiments. The objective of this study was to derive the species and structure environment of Cu(II) on the surface of these minerals using the technique of EXAFS spectroscopy.

2. Methods and materials

2.1. Isothermal sorption of batch experiments

The experiments were conducted using three commercial products, which are the most important components in soil, namely $\text{Al}(\text{OH})_3$ (gibbsite, Merck KGaA, Darmstadt; i.e., surface area of 1.5 g m^{-2} , $<1.7 \mu\text{m}$ in size), MnO_2 (pyrolusite, Aldrich Chemical Company; i.e., surface area of 2.0 g m^{-2} , $<40 \mu\text{m}$ in size), and SiO_2 (amorphous silica, Cabot, Tuscolca, IL, i.e., surface area of 204 g m^{-2} , 15–25 nm in diameter) (Kuan et al., 2004) equilibrated with

Cu(II) (CuCl_2 solution). Batch experiments were conducted by mixing 2 or 5 g of gibbsite, pyrolusite, and amorphous silica separately with 1 L of 0.5 mM of CuCl_2 solution in 1 L volumetric flasks. The background solution was 0.1 M NaCl electrolyte solution and the pH of the solution was adjusted to 5.5 and 6.5 ± 0.1 with NaOH and/or HCl solution at 25°C using a Radiometer (Tim 865), titration manager in the set mode. The solution was stirred to achieve equilibrium at 25°C . After 16 h, the equilibrium pH of the suspensions was measured and suspensions were filtered through a cellulose acetate membrane filter of size $0.22 \mu\text{m}$. Copper concentrations in the clear supernatant were analyzed by Induced Couple Plasma (ICP-AES) (Perkin Elmer, Optima 3000).

2.2. Cu K-edge XAFS spectroscopy

XAFS spectroscopy was performed at the National Synchrotron Radiation Research Center (NSRRC), Science-Based Industrial Park, Hsinchu, Taiwan. X-ray absorption spectra at the Cu K-edge (8979 eV) for each sample was collected at beam line (Wiggler-17C). The electron storage ring operated at 1.505 GeV and the currents ranged from 80 to 200 mA. Two parallel Si(111) crystals were used as a monochromator. All the spectra were recorded in fluorescence mode using two ionization chambers with argon as the detectors, which were positioned at 90° to the incident beam. In order to prevent elastic and Compton scattering of the incident X-rays from entering the fluorescence detector, a nickel fluorescence filter ($6 \mu\text{x}$ equivalent) was used for scans at the Cu K-edge (Fendorf and Sparks, 1996). The $0.22 \mu\text{m}$ cellulose acetate membrane filter with filtered sediments was placed at 45° to the X-ray beam. At least three scans were collected for each sample and averaged to improve the signal-to-noise ratio. Each scan was 7–8 min. Energy calibration was monitored by placing a Cu foil behind the ionization chamber to measure the incident X-ray intensity. The first inflection point of the absorption K-edge of the Cu foil was assigned the value of 8979 eV and as the initial point ($k=0$) of the EXAFS spectra. The EXAFS spectra were analyzed by UWXAFS 3.0 software package with phase and amplitude functions generated by FEFF8.10 (Anku-

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