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-

dinov and Rehr, 2000) to yield a radial structure function (RSF) and the curve fitting was performed for k^3 -weighted $\chi(k)$ at the wave number interval 2.5–12.5 Å⁻¹. For the first shell fitting, the value of distance ($r \pm 0.02$ Å) and coordination number ($N \pm 20\%$) is provided (Sayers and Bunker, 1988; De Leon et al., 1991; Fendorf and Sparks, 1996; Fitts et al., 1999). Multiple backscattering effects were not considered in this study.

3. Results and discussion

3.1. Batch experiments

The sorbed amount of Cu on three minerals and equilibrated pH of batch experiments are shown in Table 1. The amount of Cu sorbed by gibbsite, pyrolusite, and amorphous silica ranged from 595 to 15462 µg g⁻¹, 10,557 to 15,770 µg g⁻¹, and 335 to 15418 µg g⁻¹, respectively. The equilibrium pH of batch experiments ranged from 5.36 to 6.54 with the exception of an equilibrated pH of 8.86 present in pyrolusite suspension. In our study, with increasing pH, the amounts of Cu sorbed on the surface of these three minerals increased. Only 4.4–67.0% of Cu added was removed from solution at pH below 5.63, while 97.8–100.0% of Cu added was removed from solution at pH above 5.63. Meanwhile, the amount of Cu sorbed decreases proportionally with increasing amount of sorbents, meaning that the surface coverage decreases with increasing oxides.

Table 1
The sorbed amount of Cu on three minerals and equilibrium pH of batch experiments

Sorbent	Sorbent concentration (g L ⁻¹)	Sorbed amount (µg g ⁻¹)	Removed from solution (%)	Equilibrium pH
Al(OH) ₃	2	937	5.9	5.48
		15,462	98.1	6.54
	5	595	9.4	5.36
MnO ₂	2	6185	98.1	6.22
		10,557	67.0	5.63
	5	15,770	100.0	8.86
SiO ₂	2	687	4.4	5.60
		15,418	97.8	6.25
	5	335	5.3	5.54
		6165	97.8	6.43

Fig. 1. The first derivatives of Cu(II) K-edge XANES spectra of three representative samples.

Similar trends have also been reported previously (Chang et al., 2002).

3.2. XANES spectra analysis

Fig. 1 shows the first derivatives of K-edge XANES spectra of three representative samples and the pre-edge peak, indicating the first inflection point of the absorption K-edge of Cu (8979 eV). XANES spectra of both octahedral and tetrahedral metal complexes possess the pre-edge peak and its intensity increases with distortion, which removes the symmetric center and results in d - p orbital mixing (Lytle et al., 1988; Xia et al., 1997). On the other hand, each first derivative spectrum also shows obvious split peaks in Fig. 1, revealing that there is a strong shoulder structure in the region half-way up the edge due to $1s$ - $4p$ transitions (Bianconi et al., 1982). Cu(II) has nine 3d electrons, with a low probability for that bound state transition, so the pre-edge is always small but its size will depend on the degree of distorted. It will be smallest symmetrical octahedral, larger for distorted octahedral, and largest for tetrahedral. The shoulder on the edge step has been attributed to multiple low scattering effects (Strange et al., 1990). Miessler and Tarr (1991) also demonstrate that Cu(II) commonly shows significant Jahn–Teller effects which may cause the structure of Cu(II) complex to vary from tetrahedral through square planar to distorted octahedral. Therefore, the binding structure of Cu(II) in the samples studied is likely to be

tetragonal-distorted octahedral (Xia et al., 1997; Fitts et al., 1999; Dubbin et al., 2000; Manceau et al., 2000).

3.3. EXAFS spectra analysis

The normalized and background-subtracted k^3 -weighted $\chi(k)$ curves of six representative samples are shown in Fig. 2. EXAFS spectra oscillations are due to photoelectron scattering from atoms surrounding the target of Cu(II) ion. At equilibrated pH of suspension below 5.63, samples A and E show the same amplitude, frequency, and phase for each EXAFS spectrum. This indicates that the local chemical environment of Cu(II) in these two samples is very similar even though the sorbent types and concentrations are different. On the other hand, at pH above 5.63, samples B, C, D, and F all show strong similarities in their EXAFS spectra, but are distinguished from samples A and E by an extra peak at $k=7.6$ – 7.8 . This peak seems to be characteristic of the type of Cu environment in $\text{Cu}(\text{OH})_2$ (e.g., compared with EXAFS spectra of Fitts et al. (1999) and Xia et al. (1997)). Therefore, the local structural environments surrounding Cu are different at equilibrated pH of suspension below or above 5.63. According to solution equilibrium calculations using equilibrium constants (Lindsay, 1979; Smith and Martell, 1976), Harter (1983) indicates that free Cu^{2+} is the dominant species (>96%) in the solution at pH

below 6.0, while both free Cu^{2+} and $\text{Cu}(\text{OH})_2^\circ$ are the predominant species and CuOH^+ is the minor species (2–7%) at pH 6–7. For solution with pH above 8.0, Cu(II) exists as $\text{Cu}(\text{OH})_2^\circ$ (>92%). However, McBride and Blasiar (1979) demonstrated that increase in total Cu(II) at higher pH was not accompanied by an activity increase, indicating that most of the Cu(II) (around 17% of total soluble Cu^{2+}) was in complexed form above pH 5.0. In addition, the EXAFS study of Xia et al. (1997) reported polynuclear copper hydroxide clusters precipitated on silica surface during the sorption process with equilibrated pH at 5.5 and low surface coverage (0.8% of a monolayer). Fig. 3 shows the EXAFS spectra of Cu(II) sorbed on gibbsite, pyrolusite, and amorphous silica under different pH conditions. It reveals that the local chemical structure of Cu(II) would change at equilibrium pH greater than 5.6 (gibbsite system), 5.6 (pyrolusite system, Fig. 2), or 5.7 (amorphous silica system). Therefore $\text{Cu}(\text{OH})_2^\circ$ may exist as the main sorbed species for solutions with pH greater than 5.6.

The radial structure function (RSF) of Cu(II) sorbed by three oxides, together with the best fit of the Fourier transforms of the EXAFS spectra (uncorrected for phase shift), at different pH and sorbent concentrations are shown in Fig. 4. The structure parameters of best fits are summarized in Table 2. At equilibrium pH below 5.63, the best fits for Cu on both gibbsite and amorphous silica samples show four nearest O atoms (i.e., coordination number is 4.0) at the distance of 1.98–2.04 Å and 1.92–2.00 Å completing the first coordination sphere, respectively. Schofield et al. (1994) and Alcacio et al. (2001) reported that the longer distance is partly due to scattering from the two longer apical oxygen. Coordination numbers for distorted sites are often anomalously small. In Table 2, the best fit data also show that there are two more shells with one and four coordination numbers at the distances of 2.65 and 3.34 Å, respectively. The second shell distance of 2.65 Å is consistent with the local structure of plancheite, $\text{Cu}_8(\text{Si}_4\text{O}_{11})_2(\text{OH})_4(\text{H}_2\text{O})$, and shattuckite, $\text{Cu}_5(\text{SiO}_3)_4(\text{OH})_2$ previously reported (Farquhar et al., 1996). The Cu on this shell is bridged by two oxygen atoms to form “ribbons” of oxygen bridged chain and this Cu–Cu distance is very short due to constriction by the

Fig. 2. Normalized and background-subtracted k^3 -weighted EXAFS spectra of (A) 2 g L⁻¹ Al(OH)₃, pH 5.32, (B) 5 g L⁻¹ Al(OH)₃, pH 6.22, (C) 2 g L⁻¹ MnO₂, pH 5.63, (D) 2 g L⁻¹ MnO₂, pH 8.86, (E) 5 g L⁻¹ SiO₂, pH 5.54, and (F) 2 g L⁻¹ SiO₂, pH 6.25.

Fig. 3. Effect of pH on EXAFS spectra of Cu(II) sorbed on $\text{Al}(\text{OH})_3$ at (A) pH 5.32, (B) pH 5.48, (C) pH 5.70, (D) pH 6.54, (E) pH 6.54; on MnO_2 at (F) pH 5.63, (G) pH 7.60, (H) pH 8.86, (I) pH 9.12; and on SiO_2 at (J) pH 5.54, (K) pH 5.60, (L) pH 5.87, (M) pH 5.98, (N) pH 6.25.

surrounding aluminosilicate matrix (Charnock et al., 1995; Farquhar et al., 1996). Therefore, the Cu of this second shell is consistent with a sorbed Cu species with this type of structure. The third shell may be attributed to either Cu or the center atom of sorbent (Al or Si), because their backscattering properties are too similar to allow distinction (Parkman et al., 1999). On the other hand, at equilibrium pH above 5.63, $\text{Cu}(\text{OH})_2^\circ$ exists in all samples. The best fits for Cu

on all samples are the same as those for pH below 5.63; however, an extra shell, with coordination numbers close to 2.0 at the distance of 2.95 Å, is found. This shell is attributed to the backscattering of Cu in $\text{Cu}(\text{OH})_2^\circ$. This indicates that both sorbed (Cu^{2+}) and precipitated ($\text{Cu}(\text{OH})_2$) species exist on oxides at pH above 5.63. Meanwhile, all evidence shows that

Fig. 4. Radial structure function (RSF) and best fit of Cu(II) sorbed on (A) $\text{Al}(\text{OH})_3$, (B) MnO_2 , and (C) SiO_2 along with Fourier transforms of the EXAFS spectra (uncorrected for phase shift).

Table 2

Atoms, coordination numbers (N), bond distances (r), Debye–Waller factors (σ^2), and R -factors obtained from the curve fitting procedure for the local Cu surrounding

Sorbent	Sorbent conc. (g L ⁻¹)	Equilibrium pH	Atom	r (Å)	N	σ^2 (Å ²)	(R)-factor* (%)
Al(OH) ₃	2	5.48	O	2.04	4.0	0.005	1.32
			Cu	2.64	1.2	0.015	
			Cu/Al	3.30	4.5	0.019	
		6.54	O	1.96	4.0	0.003	0.12
			Cu	2.65	1.0	0.009	
			Cu	2.95	2.0	0.006	
	5	5.36	Cu/Al	3.34	4.0	0.008	1.16
			O	1.98	4.0	0.005	
			Cu	2.62	1.2	0.020	
		6.22	Cu/Al	3.36	4.8	0.022	0.17
			O	1.95	4.0	0.005	
			Cu	2.65	1.1	0.019	
MnO ₂	2	5.63	Cu	3.01	2.0	0.011	
			Cu/Al	3.27	4.0	0.008	
			O	1.97	4.0	0.001	0.34
		8.86	Cu	2.60	1.0	0.006	
			Cu	2.93	2.1	0.002	
			Cu/Mn	3.28	4.2	0.000	0.23
	5		O	1.97	4.0	0.008	
			Cu	2.65	1.0	0.010	
			Cu	2.95	2.0	0.006	
		5.60	Cu/Mn	3.34	4.0	0.016	0.41
			O	2.00	4.0	0.004	
			Cu	2.63	1.3	0.038	
SiO ₂	2	6.25	Cu/Si	3.32	4.1	0.021	0.68
			O	1.96	4.0	0.003	
			Cu	2.64	1.2	0.017	
	5	5.54	Cu	2.90	2.0	0.003	
			Cu/Si	3.36	3.8	0.013	
			O	1.92	4.0	0.006	0.87
		6.43	Cu	2.66	1.0	0.026	
			Cu/Si	3.31	5.0	0.026	
			O	1.95	4.1	0.014	0.71
			Cu	2.65	1.0	0.002	
			Cu	2.95	2.0	0.005	
			Cu/Si	3.34	4.0	0.005	

* R -factor is the overall goodness-of-fit.

there is no significant effect of sorbent types and sorbent concentrations on the EXAFS spectra.

4. Conclusions

Cu(II) was reacted with three important soil components—gibbsite, pyrolusite, and amorphous silica at different equilibrated pH and sorbent concentrations. The pH significantly affects the species of Cu sorbed on the surface of these oxides. At

equilibrated pH of suspensions below 5.63, the sorbed species of Cu with the best-fits bond distance and coordination number are as follows: Cu–O, 1.95 Å and 4; Cu–Cu, 2.65 Å and 1; and Cu–Cu/M (M is the center atom of sorbent, Al, Mn, or Si in this study), 3.34 and 4. On the other hand, at equilibrated pH of suspension above 5.63, Cu(OH)₂[°] was the major species present in the solution, therefore, both adsorbed and precipitated species might exist on the surface of oxides. The best-fit bond distances and coordination numbers were as follows: Cu–O, 1.95 Å

and 4; Cu–Cu, 2.65 Å and 1; Cu–Cu, 2.95 Å and 2; and Cu–Cu/M, 3.34 Å and 4. According to the EXAFS spectra and the results of best fit, there is no significant difference between the three oxides and the two sorbent concentrations.

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