

XAS Study of Sorption of Copper(II) by Oxides

The Extended X-ray Absorption Fine Structure (EXAFS) technique was employed in this study to derive the local structure of Cu(II) sorbed on three soil components. Results show that the equilibrated pH of suspension affects significantly the species of Cu sorbed on the surface of these sorbents. Sorbed species (Cu^{2+}) and precipitated ($\text{Cu}(\text{OH})_2$) phases were formed at the equilibrated pH of suspensions below and above 5.63, respectively.

Isothermal sorption batch experiments are very important in soil science research. Mechanistic interpretations and models have been developed for metal sorption reactions at the soil/water interface; however, they have largely been based on macroscopic information without direct atomic-level evidence. According to aquatic chemistry, high solution concentrations or high pH may cause metal hydroxide or carbonate to precipitate onto minerals surface. 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. Recent XAFS studies have elucidated the mechanism of Cu(II) sorption on mica, silica, and clay minerals. XAFS, an unique method among currently available ones, thereby offers local structural information. 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) solution for isothermal sorption batch experiments. The species and structural environment of Cu(II) on the surface of these sorbents were derived from the EXAFS data.

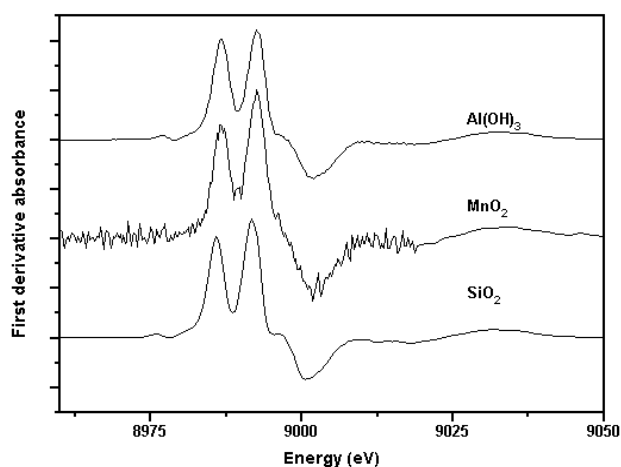


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Figure 1 shows the first derivatives of Cu K-edge XANES spectra of three representative samples, which indicates the first inflection point (around 8979 eV). XANES spectra of both octahedral and tetrahedral metal complexes possess a pre-edge peak and the intensity increases with the extent of distortion, which removes the symmetric center and results in $d-p$ orbital mixing. On the other hand, in Fig. 1, each first derivative spectrum also shows obvious splitting peaks, reflecting a strong shoulder structure in the region halfway up the edge due to $1s-4p$ transitions. Meanwhile, 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 tetragonally-distorted octahedral.

The EXAFS oscillations with k^3 weighting for six representative samples are shown in Fig. 2. At an equilibrated pH of suspension below 5.63, samples A and E both exhibit similar amplitude, frequency, and phase in EXAFS oscillations. This evidence indicates that the local chemical environment of Cu(II) on these two samples is similar to each other even though the type and concentration of the

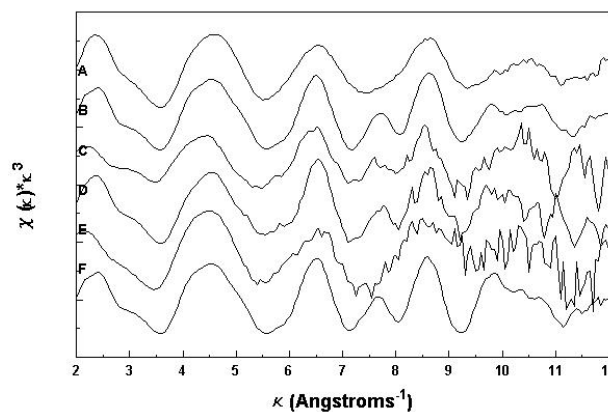


Fig. 2: k^3 -weighted EXAFS spectra of (A) 2 g L^{-1} $\text{Al}(\text{OH})_3$, pH 5.32, (B) 5 g L^{-1} $\text{Al}(\text{OH})_3$, pH 6.22, (C) 2 g L^{-1} MnO_2 , pH 5.63, (D) 2 g L^{-1} MnO_2 , pH 8.86, (E) 5 g L^{-1} SiO_2 , pH 5.54, and (F) 2 g L^{-1} SiO_2 , pH 6.25.

sorbent are different. On the other hand, at a pH above 5.63, samples B, C, D, and F all show strong similarities in their EXAFS spectra, but with an extra peak at $k = 7.6 - 7.8$ being distinguished from samples A and E. Accordingly, the local structural environments surrounding Cu are different at equilibrated pH of suspension below or above 5.63. Figure 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 5.70 (gibbsite system), 5.63 (pyrolusite system), or 5.87 (amorphous silica system). Therefore, $\text{Cu}(\text{OH})_2$ may exist as the main sorbed species for solutions with pH greater than 5.63.

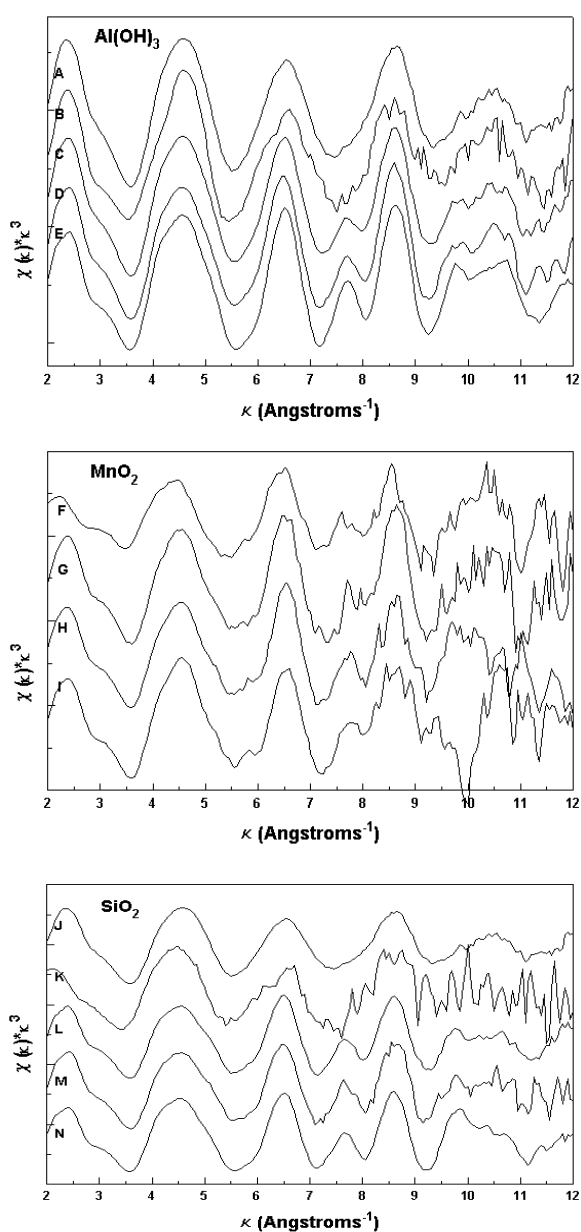


Fig. 3: Effect of pH on EXAFS spectra of Cu(II) sorbed on $\text{Al}(\text{OH})_3$ at (A) pH 5.32, (B) pH 5.48, (C) pH 5.70, (D) pH 6.54, (E) pH 6.54; on MnO_2 at (F) pH 5.63, (G) pH 7.60, (H) pH 8.86, (I) pH 9.12; and on SiO_2 at (J) pH 5.54, (K) pH 5.60, (L) pH 5.87, (M) pH 5.98, (N) pH 6.25.

The radial structure function of Cu(II) sorbed by three sorbents, together with the best fit, at different pH and sorbent concentrations are shown in Fig. 4. At equilibrium pH below 5.63, the Cu atom on both gibbsite and amorphous silica samples was surrounded by four nearest O atoms at the distance of 1.95 Å. The second shell has a distance of 2.65 Å, which is consistent with previous reports of 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, $\text{Cu}_5(\text{SiO}_3)_4(\text{OH})_2$. The Cu on this shell is bridged by two oxygen atoms to

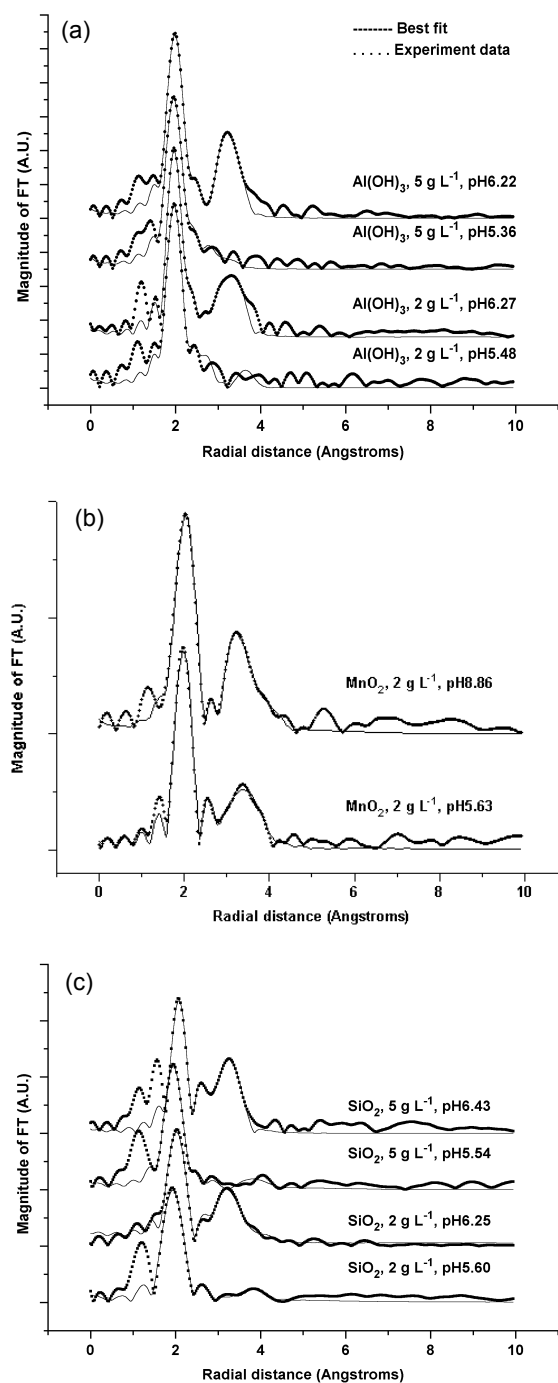


Fig. 4: Radial structure function of Cu(II) sorbed on (A) $\text{Al}(\text{OH})_3$, (B) MnO_2 , and (C) SiO_2 , along with the best fit.

form "ribbons" of oxygen-bridged chains and the Cu-Cu distance is very short due to the constricted surrounding of the aluminosilicate matrix. Therefore, it may imply that there is an adsorbed Cu species on the sorbent. The third shell may be attributed to either Cu or the center atom of the sorbent (Al or Si). On the other hand, at an equilibrium pH above 5.63, $\text{Cu}(\text{OH})_2$ exists in all samples. The structural parameters are found to be the same as those for pH below 5.63; however, an extra shell, with a coordination number of 2.0 at a distance of 2.95 Å, is found. This shell is attributed to the backscattering of Cu in $\text{Cu}(\text{OH})_2$. This indicates that both adsorbed (Cu^{2+}) and precipitated ($\text{Cu}(\text{OH})_2$) Cu species exist on the sorbent at pH above 5.63.

BEAMLINE

17C1 W20/EXAFS beamline

EXPERIMENTAL STATION

XAS end station

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