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XAFS Characterization of Copper in Model Aqueous Systems of Humic Acid and Illite

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Abstract. Adsorption of heavy metals at mineral surfaces and complexation with reactive organic-matter functional groups are important processes regulating the solubility and fate of soil contaminants. To determine the nature of Cu(II) bonding in complex clay-organic systems, XAFS analyses were conducted on aqueous suspensions containing Cu(II) in various forms: (i) complexed with soil humic acid (HA) at various HA:Cu ratios, (ii) bound to illite, or (iii) bound in a mixture of illite and HA. Spectral features for Cu bound to HA did not depend significantly on the HA:Cu ratio, and average first-shell Cu-O bond lengths were consistently shorter than for the Cu-illite systems. In the mixed clay-organic suspension, Cu bonding was more characteristic to that of Cu bound with HA.

1. INTRODUCTION

Soils and other complex matrices of environmental significance contain mixtures of minerals and organic matter that bind heavy metals. Although XAFS has revealed much about the molecular-scale nature of metal binding to mineral surfaces [1], its application to structurally more heterogeneous organic matter, clay-organic mixtures, and soils has been limited [2]. Using XAFS spectroscopy to characterize adsorbed heavy metals in heterogeneous systems such as soils is complicated by a preponderance of oxygen in the first coordination shell and often weak x-ray backscatters (Si, Al, C, and H) in higher shells. The objective of this study was to determine spectroscopic features that distinguish Cu(II) bonding to soil humic acid (HA) from bonding on an aluminosilicate mineral surface, and to characterize bonding in a mixed clay-organic system.

2. MATERIALS AND METHODS

The HA used in this study was extracted [3] from a Portsmouth surface soil sample (fine-loamy over sandy or sandy-skeletal, mixed, thermic Typic Umbraquils), HF washed to reduce its ash content [4], then fractionated using a nonionic (XAD8) exchange resin [5]. The HA contained no detectable sulfur. Silver Hill illite from the Source Clays Repository of the Clay Minerals Society was acid-washed and prepared as a stock suspension of < 1- μ m particle size. Samples at pH 5.6 or 7.3 were prepared in NaClO₄ background solutions containing between 5 and 10 mM Na. Suspensions initially containing 2.5 mmol Cu(II)/kg and HA at concentrations ranging from 300 to 2400 mg organic carbon (OC) per kg suspension at pH 5.6 were equilibrated, gravity settled to concentrate the HA fraction, then analyzed. These concentrated samples contained between 5 and 9 mmol Cu(II)/kg, with <15% occurring as aqueous Cu in all but the two samples of lowest OC content. Suspensions containing 2.5 mmol Cu(II)/kg and (i) illite at a concentration of 26 g/kg, (ii) illite (26 g/kg) + HA (12.5 or 25 mg OC/kg), or (iii) HA only (300 mg OC/kg - pH 7.3 sample) were analyzed while stirring in a tetrafluoroethylene sample holder. XAFS analyses were done at Beamline X-11A, National Synchrotron Light Source, Brookhaven National Laboratory. Samples were analyzed in fluorescence mode at the Cu K-edge (8,979 eV) using a multielement detector. Dissolved Cu-acetate was used as a standard representing aqueous Cu(II) octahedrally coordinated to oxygen. Fourier transforms were done on EXAFS spectra over the wavevector range $k = 2.3$ - $11.5 \text{ \AA}^{-1}$, and model fitting was done over the radial distance range $R = 0.9$ - $1.9 \text{ \AA}$.

3. RESULTS AND DISCUSSION

Figure 1 shows radial structure functions for Cu(II) in selected samples, and Table 1 contains EXAFS fitting results for all samples. The highest amplitude peak in Fig. 1 corresponds to first-shell Cu-O bonding, and shows a detectable shift to higher radial distance between the HA, illite + HA, and illite samples. The positions of weak, higher-shell peaks between 2 and 4 $\text{\AA}$ for the mixed clay-organic suspension were more consistent with peaks for the HA suspension than for the illite suspension.

Table 1 shows that for both pH levels, the average first-shell Cu-O bond lengths in the HA suspensions were consistently shorter than those of Cu-O in the illite suspensions (1.92 to 1.93 $\text{\AA}$ versus 1.95 $\text{\AA}$, respectively). The average Cu-O bond length in the mixed illite-HA suspensions (1.94 $\text{\AA}$) was intermediate between those of the single adsorbent systems at pH 5.6, and equal to that of Cu(II) in HA at pH 7.2 (1.93 $\text{\AA}$) (Table 1). Average coordination numbers (N) and Debye-Waller factors (DW) (bonding disorder) tended to be higher in the illite suspensions compared with the HA suspensions. Although N also tended to be higher in the mixed suspensions compared with HA alone, no consistent trend in DW was observed. In comparing the data for the HA suspensions at pH 5.6, there appeared to be little effect of HA:Cu ratio on EXAFS results (Table 1).

Figure 1: Radial structure functions for Cu(II) in selected suspensions of humic acid (HA), illite, or mixed illite-HA at pH 5.6. Data are not corrected for phase shift; therefore, peaks do not represent exact bond lengths.

Table 1: First-shell EXAFS fitting results for Cu in humic acid (HA), illite, and mixed illite-HA suspensions using a 5 mM Cu-acetate suspension as a standard (N = coordination number, R = 1st-shell bond length, and DW = Debye-Waller factor). Numbers in parentheses are parameter standard deviations given as output from the University of Washington FEFF fitting program.

Sample	$N (\pm 0.5)$	$R (\text{\AA}) (\pm 0.01)$	$DW (\text{\AA}^2) (\pm 0.0004)$
Cu-acetate standard	6.0	1.95	0.0000
HA = 300 mg OC/kg, pH 5.6	5.4	1.93	0.0005
HA = 600 mg OC/kg, pH 5.6	5.8	1.93	0.0008
HA = 1200 mg OC/kg, pH 5.6	5.8	1.93	0.0009
HA = 1800 mg OC/kg, pH 5.6	5.4	1.93	0.0005
HA = 2400 mg OC/kg, pH 5.6	5.7	1.92	0.0005
illite + HA - 12.5 mg OC/kg, pH 5.6	5.9	1.94	-0.0004
illite + HA - 25 mg OC/kg, pH 5.6	6.4	1.94	0.0010
illite, pH 5.6	6.6	1.95	0.0010
HA = 300 mg OC/kg, pH 7.3	6.5	1.93	0.0011
illite + HA - 12.5 mg OC/kg, pH 7.3	6.5	1.93	0.0003
illite, pH 7.3	6.9	1.95	0.0016

Copper has a higher affinity for soil organic matter than many other heavy metals [6]. Also, the binding affinity of Cu(II) by the humic substance fulvic acid increases with increasing pH and decreasing Cu/OC ratio [7]. The effect of Cu/OC ratio has been attributed to preferential binding to high energy sites at low Cu/OC. Although we found that dissolved Cu decreased with decreasing Cu/OC ratio at pH 5.6 (data not shown), XAFS results for all of these samples were similar (Table 1). Our results did indicate that the addition of relatively low levels of HA to illite suspensions had a significant effect on average local bonding structure, and at pH 7.3, calculated bonding parameters for the mixed suspension were closer to those for HA than for illite.

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