

Speciation of Copper-Humic Substances in a Contaminated Soil

Electrokinetic remediation (EKR) is one of the methods for in-situ soil decontamination. Like other technologies such as bioremediation and soil flushing, EKR has advantages in avoiding the high cost and human health risks of excavation. In addition, EKR is applicable to decontamination of heterogeneous and low-permeability soils. EKR has been successfully employed in removal of more than 90% of heavy metals (copper, cadmium, cobalt, chromium, arsenic, mercury, nickel, manganese, lead, antimony and zinc) from clay, kaolinite, montmorillonite and argillaceous sands.

Although EKR has been proven to be very feasible in laboratory and bench-scale experiments as well as small-scale field tests, the complex transport phenomena and electrochemistry involved in the EKR is still not well understood. Many reactions in addition to electromigration and electroosmosis occur simultaneously when an electric field is applied to a wet soil. These reactions may include ion diffusion, ion exchange, mineral decomposition, precipitation of salts, hydrolysis, oxidation, reduction, physical and chemical sorption, and complexation with humic substances (HS).

Humic substances including humic acids, fulvic acids and humin are the most abundant groups of organic macromolecules in natural soils and water. Soil HS is a complex and heterogeneous mixture with high molecular weights of ubiquitous organic oligomers or polymers. Generally, soil HS contains several major functional groups such as carboxyl, phenolic, alcohol, and carbonyl. It is known that Cu-HS complexes play an important role in controlling the bioavailability and biogeochemical cycling of trace elements in the natural ecosystems. Moreover, the mobility of copper is strongly influenced by HS in soils. Studies of trace metal complexation with HS usually focus on

measuring conditional stability constants and complexation capacities. Many spectroscopic methods such as IR, fluorescence, NMR and EPR have been used in revealing the chemical structure of metal-HS complexes in contaminated soils. However, the abundance of different functional groups varies depending on the origin of HS and the method of measurement.

Speciation data such as bond distance, coordination number (CN) and chemical identity of elements in the complex matrix can be determined by EXAFS spectroscopy. Besides, XANES can provide the information of oxidation state of an excited atom and the coordination symmetry. Note that the main scientific issues concerning the speciation or chemical forms of contaminants ultimately depend on their molecular-scale structure. Thus, a basic understanding at this scale is essential to the management of environmental contaminants, which may also help the development of effective methods for remediation. The main objective of this work was to investigate the speciation of copper-HS in the EKR process by EXAFS and XANES.

The EKR experiments were carried out in a home-made in-situ cell which consisted of two Ru electrodes, two electrode reservoirs, a power supply, a cation-selective membrane (Nafion 417) (to prevent precipitation of copper hydroxides on the electrode) and filters. About 60 g of the soil sample was filled uniformly in the cell and saturated with 0.01 M potassium nitrate as a conductive solution. A DC power of 100 volts was constantly applied to the electrodes. After 180 minutes of EKR experiment, the soil in the cell was sliced into ten portions of equal length immediately. Copper contents in each portion were determined via an acid digestion procedure and analyzed by means of flame atomic absorption spectroscopy. The concentrations of copper in soil

and pH values in electrolyte between anode and cathode are shown in Fig. 1. Copper was found to accumulate near the cathode. The pH values on the anode and cathode were about 1.8 and 12.8 (6.2 in the soil near the cathode), respectively. Near the anode, about 13% of copper in the soil dissolved into the aqueous electrolyte.

The Cu *K*-edge spectra of the contaminated soil were collected in the fluorescence mode. The standard deviation calculated from the averaged spectra was used to estimate the statistical noise and error associated with each structural parameter. The EXAFS data were analyzed using the UWXAFS 3.0 and FEFF 8.0 programs. On the other hand, principal component analysis (PCA) and least-squares fitting (LSF) are quantitative analytical tools for speciation of dilute and/or amorphous multicomponents. PCA was used in the data treatment to optimize the quantitative extraction of relative concentrations of copper species. Semi-quantitative analyses of the XANES spectra were conducted by the least-square fitting of linear combination (LC) of the model compound spectra to the spectrum of the soil samples.

The in-situ XANES spectra and their first derivatives of the Cu-contaminated soil during EKR are shown in Fig. 2. The XANES spectra of copper in the contaminated soil exhibit a very weak pre-edge peak corresponding to the 1s-to-3d transition that is forbidden by the selection rule in the case of perfect octahedral symmetry. The band at 8982 eV may be due to the dipole-allowed 1s-

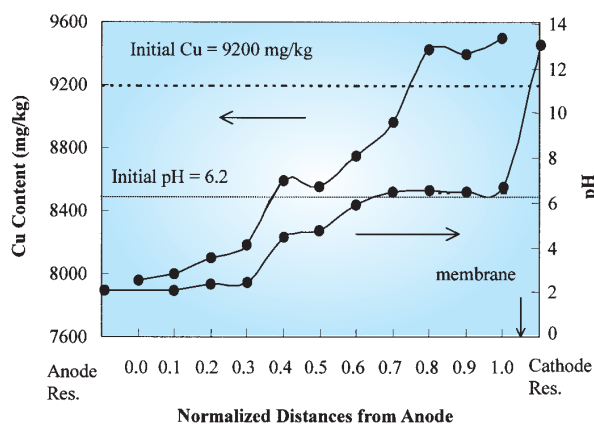


Fig. 1: Copper concentration and pH profile across soil after 180 min of the EKR.

to-4p transition of Cu(I). In the early stage of EKR (see Fig. 2 (b), for instance), the content of Cu(I) was decreased to some extent, that might be due to oxidation of copper involved in the EKR process. The first derivatives of the XANES spectra revealed two shoulders at 8986 eV (α) and 8992 eV (β). Generally, the β shoulder represents the main absorption transition (1s-to-4p) of Cu(II), while the α shoulder is influenced by the degree of bond covalency and the degree of local structural disorder. The increase in intensity of both α and β peaks indicated that Cu(II) coordination environment depended on the time of EKR. Prolonging the EKR time to 180 min, the peaks at 8986 and 8992 eV were very prominent possibly because of perturbation of the copper octahedron in the Cu-HS complexes by EKR.

The XANES spectra were also expressed mathematically in a LC fit vectors, using the absorption data within the energy range of 8970-9020 eV. XANES spectra of model compounds such as Cu-HS, CuO, CuCO₃, CuSO₄,

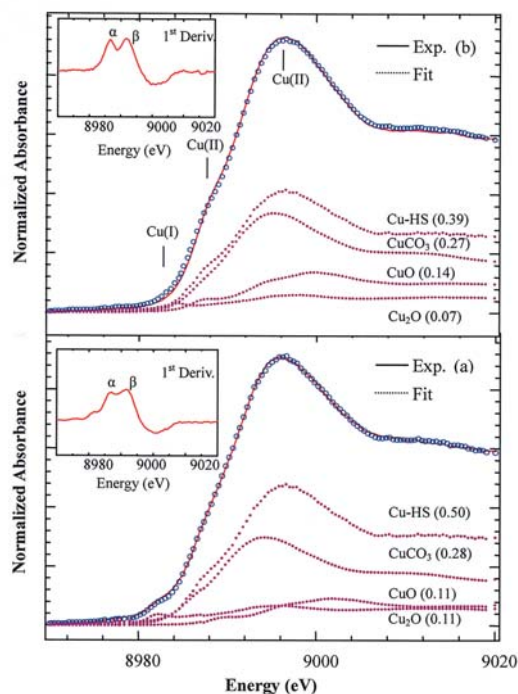


Fig. 2: Experimental data (solid line) and the least-square fits (circles) for the XANES spectra of the Cu-contaminated soil (a) before and (b) after 180 min of EKR. Dotted lines denote fractional contributions of the four main copper species making up the fitted spectra.

CuCl₂, Cu₂O, CuCl and Cu foil were considered in the fit. It was found that Cu-HS, CuCO₃, CuO and Cu₂O were the main copper species in the Cu-contaminated soil. Relative contents of the copper species in the EKR with an over 90% reliability (in the data fitting process) are shown in Fig. 2. It is clear that the perturbation and dissociation of Cu-HS complexes effected by electric field led to a decrease of about 11% of the Cu-HS species in the soil. Oxidation of Cu(I) was also observed during EKR. However, CuCO₃ was insignificantly perturbed after 180 min of the EKR treatments.

The in-situ EXAFS data were analyzed in the k range of 3.5-11.5 Å⁻¹. Due to the axial distortion of the CuO₆ octahedron caused by the Jahn-Teller effect, the distances between the copper and the equatorial and axial oxygen atoms were not identical. Structural parameters obtained from detailed data analysis are listed in Table 1, which also provides important information about the nature of the inner shells in complexation of copper with HS. Copper in the contaminated soil had equatorial and axial Cu-O bond distances of 1.94 Å and 2.17 Å with coordination numbers (CN) of 3.6 and 1.4, respectively. Interestingly, both the equatorial and axial Cu-O bond distances of the Cu-contaminated soil increased in the EKR process.

Generally, the d orbitals contain double (e_g)

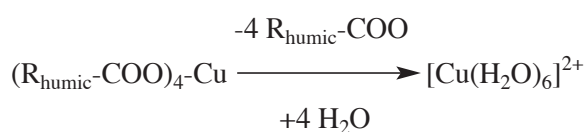
and triple (t_{2g}) degeneracies for transition metals in the octahedral field. For d⁹ metals such as Cu(II), only three electrons occupy the higher-energy e_g level. While the degeneracy of the e_g set of orbitals (d_{z²} and d_{x²-y²}) is removed, one of the two orbitals is stabilized by lengthening either two axial or four equatorial metal-ligand bonds. Weak-field equatorial ligands (such as COOH) of copper can be replaced by stronger ligands (H₂O). An increase in the axial Cu-O bond distances (from 2.17 to 2.32 Å) in the soil was found in the EKR process, which might be due to the ligand exchanges in the EKR process. Accordingly, it is thought that carboxylic ligands of HS were replaced by water molecules during EKR. With the contact time prolonged to about 180 min, about 11% of the Cu-HS complexes were dissolved in the aqueous phase.

The possible reaction pathway for Cu-HS complexes involved in the EKR process is shown below, where R_{humic} denotes the carbon at which the carboxylic group attaches to the humic molecules. Transformation of the (R_{humic}-COO)₄-Cu complexes into 4 R_{humic}-COOH and Cu(II) was observed by in-situ XANES and EXAFS spectroscopies. An increase in the axial Cu-O bond distance in the EKR process is attributable to a ligand-exchanged reaction in which carboxylic ligands of HS were replaced by the strong-field water molecules.

Table 1. Speciation changes of Cu-HS in the contaminated soil in the EKR process.

Contact Time (min)	Shell	R (Å)	CN	σ ² (Å ²)
0	Cu-O _{eq}	1.94 ± 0.01	3.6 ± 0.7	0.008
	Cu-O _{ax}	2.17 ± 0.02	1.4 ± 0.4	0.006
60	Cu-O _{eq}	1.94 ± 0.01	4.3 ± 0.8	0.007
	Cu-O _{ax}	2.18 ± 0.02	2.1 ± 0.6	0.006
120	Cu-O _{eq}	1.97 ± 0.01	4.2 ± 0.9	0.008
	Cu-O _{ax}	2.24 ± 0.02	2.3 ± 0.5	0.006
180	Cu-O _{eq}	1.96 ± 0.01	4.1 ± 0.7	0.010
	Cu-O _{ax}	2.32 ± 0.02	2.1 ± 0.3	0.006

R: Bond distance; CN: Coordination number; σ²: Debye-Waller factor.



In summary, fractions of main copper species such as Cu-HS (50%), CuCO₃ (28%), Cu₂O (11%) and CuO (11%) were found in the contaminated soil by the least-square fitting of the XANES spectra. The in-situ EXAFS data indicated an increase in the axial Cu-O bond distances of the CuO₆ octahedron during the EKR. The observations may be due to the fact that weak-field carboxylic acid groups in the equatorial plane of Cu(II) species were replaced by the strong-field water molecules. About 11% of the Cu-HS complexes were dissolved and formed [Cu(H₂O)₆]²⁺ after 180 min of the EKR. This work exemplified the utilization of in-situ EXAFS and XANES for speciation of copper with HS in the EKR process.

Beamline:

17C1 W20/XAS beamline

Experimental Station:

EXAFS end station

Authors:

S.-H. Liu and H. Paul Wang

Department of Environmental Engineering,
National Cheng Kung University, Tainan, Taiwan

Publications:

- Y.-J. Huang, H. Paul Wang, and J.-F Lee, Appl. Catal. B: Environ. **40**, 111 (2003).
- M. C. Hsiao, H. Paul Wang, and Y. W. Yang, Environ. Sci. & Technol. **35**, 2532 (2001).
- Y.-C. Chien, H. Paul Wang, and Y. W. Yang, Environ. Sci. & Technol. **35**, 3259 (2001).
- S.-H. Liu and H. Paul Wang, Langmuir (2003) (submitted).

Contact e-mail:

wanghp@mail.ncku.edu.tw