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Electrochemical Remediation of Copper-Contaminated Soils Enhanced by Ethylenediaminetetraacetic Acid: an in-situ X-ray Absorption Spectroscopic Study

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Speciation of copper with ethylenediaminetetraacetic acid (EDTA) during electrotreatments of a contaminated soil nearby printed circuit board recycling plants has been studied by in-situ extended X-ray absorption fine structural (EXAFS) and X-ray absorption near edge structural (XANES) spectroscopies. The least-square fits of the copper XANES spectra indicated that the main copper species in the contaminated soil were $CuCO_3$ (41%), CuO (40%) and adsorbed copper (Cu/SiO_2) (19%). By EXAFS studies, it was found that the bond distance of Cu-(O)-Si was 3.25 Å with a coordination number (CN) of 1.0 in the second shells, suggesting a chemical interaction between copper and the soil surfaces. In the presence of EDTA (0.05 M), a Cu-EDTA complex having the equatorial and axial Cu-O bond distances of 1.96 Å and 2.21 Å, respectively was observed. Interestingly, after 180 min of the electrotreatments, the axial Cu-O bond distance was increased by 0.1 Å. The perturbation might be attributed to the possibility that the weak-field carboxylic acid groups of EDTA in the equatorial plane of Cu(II) were replaced by the strong-field water molecules. In addition, about 36% of total copper in the soil was dissolved into the aqueous phase and 67% (or 24% of total copper) of which were migrated to the cathode under the electric field (5 V/cm). This work demonstrates the utilization of in-situ X-ray absorption spectroscopy for tracking and revealing speciation and possible reaction pathways of copper with EDTA in the contaminated soil under an electric field.

Keywords: Heavy metals; EDTA; XANES; EXAFS; Electrokinetic; Contaminated Soils.

1. INTRODUCTION

Toxic metals that contaminated soils may cause negative impacts to human beings and ecological cycles via many physical and chemical processes [1]. In Taiwan, over 170 heavy metal contaminated sites have been found [2]. About 5000 hazardous waste contaminated sites, which might be leaking toxic chemicals into soil and then to the ground water, have been reported [3]. Electrotreatment is one of the feasible methods for in-situ soil decontamination [4-8]. The electrotreatment that is very applicable in decontamination of heterogeneous and low-permeability soils has been used successfully in removal of toxic metals (copper, cadmium, cobalt, chromium, arsenic, mercury, nickel, manganese, lead, antimony and zinc) from clay, kaolinite, montmorillonite, argillaceous sands, mine tailings and soils [9-17].

The major scientific issues relating to chemical forms (or speciation) of toxic contaminants eventually depend on their molecule-scale structures. Basic understanding at this scale is crucial in the management of environmental contaminants that may be useful in the development of effective methods for remediation. X-ray absorption near-edge structural (XANES) spectra can offer data of oxidation states of an excited atom, the coordination geometry, and the bonding of its local environment in environmental solids. X-ray absorption fine structural (EXAFS) spectroscopy also can be used to determine speciation data such as bond distance, coordination number (CN) and chemical identity of elements in the complex matrix. In our previous studies, the nature of active sites in the well-alloyed PtCo [18], PtRu [19] and Fe [20] electrocatalysts was examined by XANES and EXAFS during oxygen reduction reaction and methanol oxidation, respectively. Speciation of Cu-humic substances in the electrokinetic remediation process has also been investigated by in-situ EXAFS spectroscopy [21]. These EXAFS data turn out to be very practical in revealing speciation of target metals and possible reaction pathways during catalytic or electrokinetic process.

Precipitation and sorption may reduce the mobility of toxic metals in soils that limits the efficiency of the in-situ electrokinetic process. Dissolution of toxic metals in soils may be enhanced in the presence of chelating agents during electrotreatments [22-24]. Ethylenediaminetetraacetic acid (EDTA), a widely used non-toxic chelating agent, has been added to improve the effectiveness of electrokinetic treatments [25-29]. Although the EDTA-enhanced electrokinetic treatments has been proven to be feasible in the laboratory-scale experiments [25,30,31], nature of toxic metals during the electrotreatments is not well understood. Thus, the main objective of the present study was to study fates of copper in the contaminated soil in the presence of EDTA during the electrokinetic treatments by in-situ EXAFS and XANES. An in-situ EXAFS cell was utilized to track the structural changes of copper during electrotreatments.

2. EXPERIMENTAL

The Cu-contaminated soil was sampled at a depth of 0-20 cm from a site nearby printed circuit board waste recycling plants in the Tainan city, Taiwan. The soil samples were dried in air at room temperature for three days, followed by grinding with a mortar and sieving with a 2-mm screen. The composition of clay minerals in soil was identified by X-ray powder diffraction (XRD) (Rigaku, Model D/MAX III-V) spectroscopy with monochromatic CuK_α radiation. Organic matters, copper contents and pH values of the soil (see Table 1) were determined by the general methods described earlier [32]**.** FTIR spectra of the soil-KBr pellets (wt. ratio of 1/25) were recorded on a Diglab FT-IR spectrometer (FTS-40) with fully computerized data storage and data handling capability. A 32-scan data accumulation was carried out at a resolution of 4 cm^{-1}.

Table 1. Chemical and mineralogical properties of the contaminated soil

Major mineral composition	Quartz, Kaolinite
pH	7.2
Organic matter content (%)	0.8
Total copper content (g/kg)	10.1

The electrokinetic experiments were carried out in a home-made in-situ EXAFS cell (see Fig. S1 in the supplementary material) which contained two Ru electrodes, two electrode reservoirs, a power supply, a cation-selective membrane (Nafion® 417, Aldrich) (to prevent precipitation of copper hydroxides on the electrode) and filters [33,34]. The soil sample (ca. 60 g) was filled uniformly in the cell and saturated with an aqueous solution of 0.01 M potassium nitrate and 0.05 M EDTA (Aldrich) as a conductive solution and chelating agent, respectively. A DC voltage of 100 volts was continuously applied to the electrodes. After 180 min of the electrokinetic treatments, the soil in the cell was separated into 10 portions of equal length immediately. Copper contents in each portion were performed with an acid digestion procedure [32] and determined by a flame atomic absorption spectrometry (Perkin Elmer, model 5100).

The in-situ EXAFS cell could be moved accurately to attain a similar optical path for each sample point during X-ray absorption measurements. In this study, the X-ray beam was fixed at the point which was 1.5 cm from the anode section. The Cu K-edge XANES and EXAFS spectra of the copper-contaminated soil were collected in the fluorescence mode on the Wiggler beamline at the Taiwan National Synchrotron Radiation Research Center (NSRRC). The electron storage ring operated at an energy intensity of 1.5 GeV. A Si(111) double-crystal monochromator was used to detune energy with an energy resolution of 1.9×10^{-4} (eV/eV). The energy of the X-ray beam was calibrated against the absorption edge of a copper foil at 8979 eV. Room-temperature Cu K edge spectra were collected with a Lytle fluorescence detector. The standard deviation calculated from the averaged spectra was used to evaluate the statistical noise and error associated with each structural parameter. The EXAFS data were analyzed by using the UWXAFS 3.0 and FEFF 8.0 programs [35]. The isolated EXAFS data was normalized to the edge jump and then converted to the wavenumber scale. The Fourier transform was performed on k^2-weighted EXAFS oscillations in the range of 3.5-10.5 $Å^{-1}$. To reduce the number of fit variables, the many-body factor (S_0^2) was fixed at 0.9.

The absorption edge was verified at the half-height (precisely determined by the derivative) of the XANES spectra after pre-edge baseline subtraction and normalization to the maximum post-edge intensity. Principal component analysis (PCA) and least-squares fitting (LSF) were carried out to optimize the quantitative extraction of relative concentrations of copper species [36] in the data treatment. Analyses were done qualitatively by comparing spectra from model compounds (such as the

Cu-EDTA, Cu/SiO_2, aqueous Cu^{2+}, CuO, $CuCO_3$, $CuSO_4$, $CuCl_2$, $Cu(OH)_2$, Cu_2O, CuCl and Cu foil) with those from the in-situ spectra. Semi-quantitative analyses of the edge spectra were conducted by the LSF of linear combinations of model compound spectra to the spectrum of the sample.

3. RESULTS AND DISCUSSION

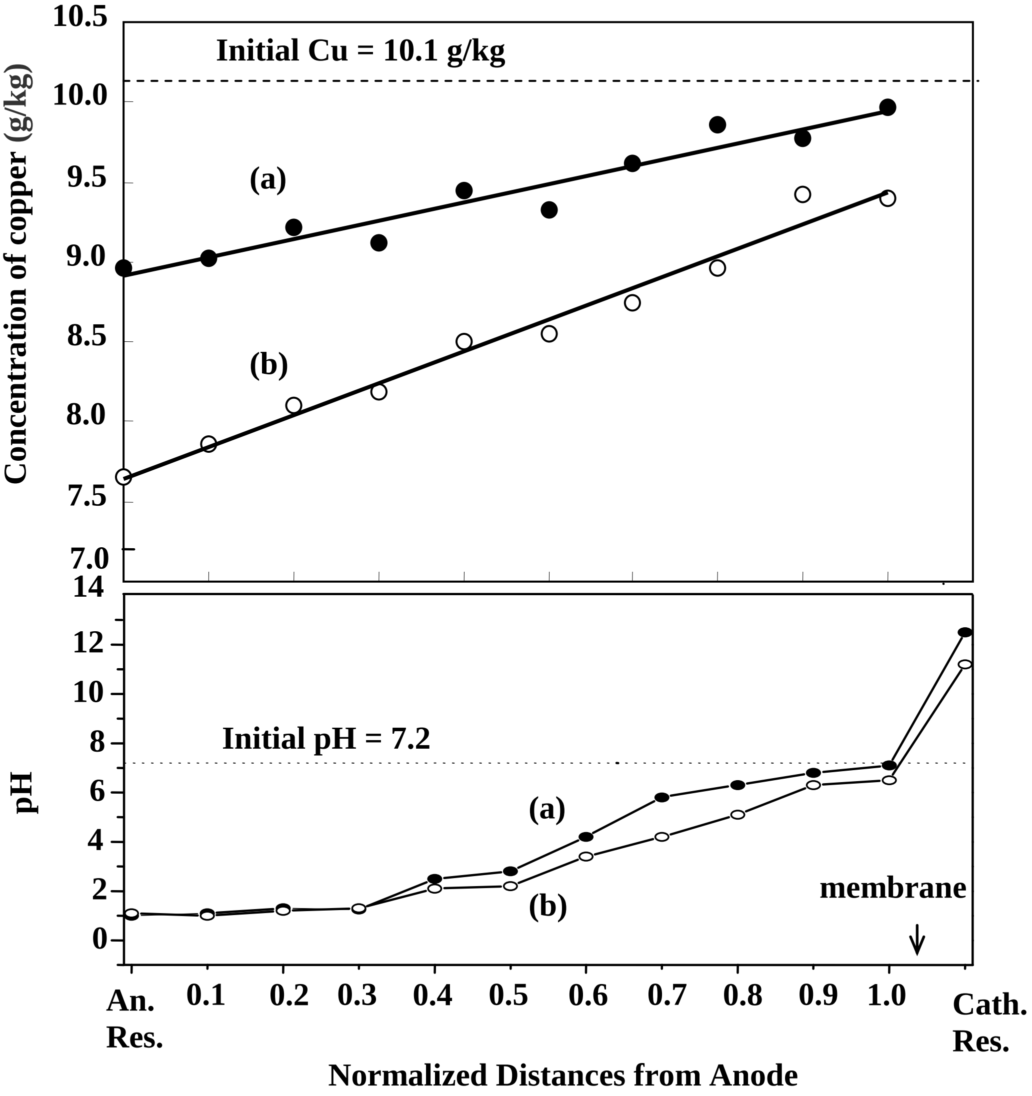

Figure 1. Concentrations of copper in the contaminated soil and pH values in the electrolyte between electrodes after 180 min of the electrotreatments (a) without and (b) with EDTA (0.05 M).

Figure 1 shows concentration profile of copper in the contaminated soil between anode and cathode after 180 min of electrotreatments. Corresponding pH value changes across the soil in the EXAFS cell are also shown in Figure 1. It is clear that dissolution of copper into the electrolyte phase near the anode could be attributed, to some extent, to the acid extraction in the high H^+ concentration environment. It was estimated ca. 23% of copper in the soil was dissolved into aqueous electrolyte. In the presence of EDTA (0.05 M), dissolution of copper from the soil was enhanced by 8-12% at a wide range of pH values (1.8-12.8).

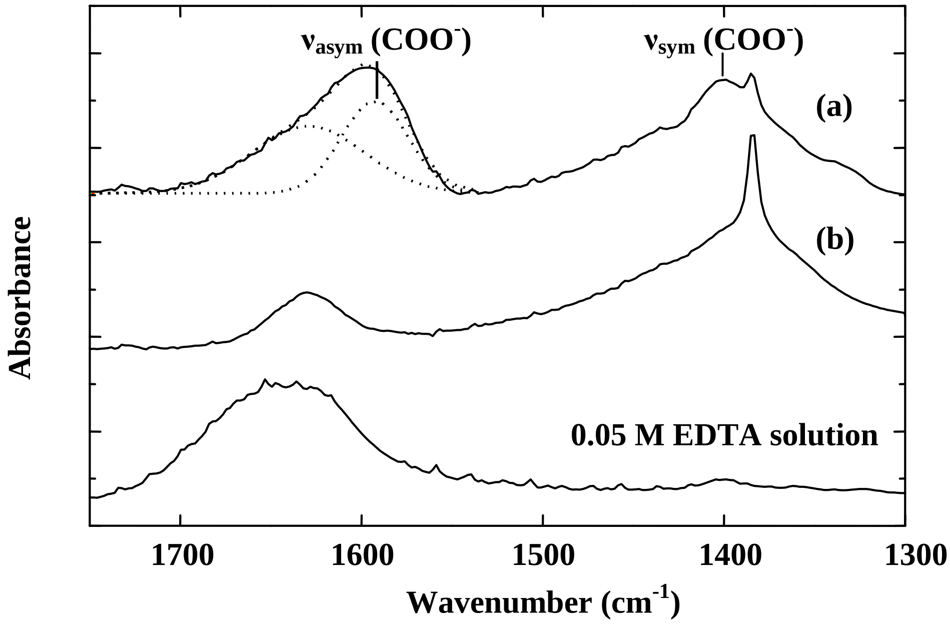

Figure 2. FTIR spectra of the Cu-contaminated soil in the presence of EDTA (0.05 M) (a) before and (b) after (180 min) the electrotreatments.

To study the interactions of EDTA with copper in the soil during the electrotreatments, their FTIR spectra were determined (see Figure 2). The C-O stretching of the carboxylate groups (1300-1700 cm^{-1}) are generally very sensitive to the ionization and coordination states of the EDTA complexes. The features centered at 1591 and 1400 cm^{-1} for copper with EDTA in the soil were assigned to carboxylate (COO$^-$) asymmetric (ν_{asym}) and symmetric (ν_{sym}) stretchings, respectively. In Figure 2, the uncomplexed EDTA (H_2EDTA^{2-}) can be observed at 1630 cm^{-1}. The absorption at 1385 cm^{-1} was attributed to the ionic nitrate in the presence of conductive electrolyte solution (KNO_3). It is worthy to note that the decreases in the absorbance of the features at 1591 and 1400 cm^{-1} suggested that the amount of Cu-EDTA complexes on the soil surfaces was decreased after 180 min of the electrotreatments. Nakamoto et al. [37] also reported that the absorbance of the asymmetric COO$^-$ species was generally proportional to the number of EDTA carboxylate groups bonded to copper ions.

In order to understand the structural changes of copper with EDTA during the electrotreatments, oxidation state, bond distance and coordinate number of copper were also studied by in-situ EXAFS and XANES. The in-situ Cu K-edge XANES spectra and their first derivatives of the contaminated soil during the electro treatments are shown in Figure 3. The pre-edge XANES spectra of copper in the contaminated soil exhibit a very weak 1s-to-3d transition (8977 eV) that is forbidden by the selection rule in the perfect octahedral symmetry [38,39]. A shoulder at 8986 eV and an intense band at 8992 eV may be attributed to the 1s-to-4p transition that indicates the existence of Cu(II) in the soil.The XANES spectra were also expressed mathematically in a LC XANES fit vectors, using the absorption data within the energy range of 8970-9020 eV. XANES spectra of model compounds such as Cu-EDTA, Cu/SiO_2, aqueous Cu^{2+}, CuO, $CuCO_3$, $CuSO_4$, $CuCl_2$, $Cu(OH)_2$, Cu_2O, CuCl and Cu foil were also measured on the Wiggler beamline. Relative contents of the copper species in the presence of EDTA during the electrokinetic treatments with an over 90% reliability in the fitting process are shown in Figure 3. It was found that $CuCO_3$ (41%), CuO (40%) and adsorbed copper (Cu/SiO_2) (19%) were the main copper species in the contaminated soil. About 20% of copper species in the soil were chelated with EDTA (0.05 M) in a short contact time (<5 min). It seems that the adsorbed copper species (Cu/SiO_2) were chelated with EDTA while CuO or $CuCO_3$ was little perturbed. The concentration of Cu-EDTA complexes in the soil was decreased by 8% in the first 90 min of the electrotreatments. After 180 min of treatments, the Cu-EDTA complexes in the soil were dissolved into the aqueous phase. The Cu-EDTA complexes in the aqueous phase during electrotreatments might involve in the ligand exchange with the high electron field H_2O and possibly formed $[Cu(H_2O)_6]^{2+}$. About 36% of the Cu(II) species were dissolved into the aqueous phase and 24% of which were migrated to the cathode after 180 min of the electrotreatments. The time dependence for dissolution, ligand exchange or migration of copper during the electrotreatments is shown in Figure 4. About 20% of the adsorbed copper species were chelated with EDTA for the contact time of 5 min. Nevertheless, a small amount of the low solubility compounds such as $CuCO_3$ and CuO in the soil were dissolved at a low pH value of 1.8 after 180 min of the electrotreatments. The dissolution curve reached a plateau after 60 min of the electrotreatments. Under the high electric field (5 V/cm), migration of copper to the cathode was very effective. In the first 180 min of the electrotreatments, an averaged electromigration rate of copper ions in the electrolyte was 0.8 mmol/hr.

In order to further understand the chemical structure of the species involved in the dissolution, ligand exchange and electromigration, in-situ EXAFS spectra of copper with EDTA during the electrotreatments was also determined. The experimental and fitted EXAFS data of copper in the presence of EDTA during electrotreatments is shown in Figure 5. The in-situ EXAFS spectra were recorded and analyzed in the k range of 3.3-10.5 $Å^{-1}$. Due to the axial distortion of the CuO_6 octahedron caused by the Jahn-Teller effect, the distances between copper and the equatorial and axial oxygens were not identical. The feature centered at about 1.60 Å was arisen from the equatorial Cu-O bonding while a small feature between 2.18 and 2.65 Å represented the scattering from additional oxygen atoms in the first shells of the axial Cu-O. In addition, a feature between 2.81 and 3.40 Å was found in the soil, which might be due to the contribution from Si atoms in the second shells. The bond distances of the axial and equatorial Cu-O as well as Cu-(O)-Si and their Debye-Waller factors (σ^2) for electrotreatments of the soil are also shown in Table 2. With the phase shift correction, copper in the contaminated soil possessed the equatorial and axial Cu-O bond distances of 1.96 Å and 2.20 Å with coordination numbers (CNs) of 4.2 and 2.1, respectively. In the second shells, the bond distance of Cu-(O)-Si for copper in the soil was 3.25 Å with a CN of 1.0. Cheah et al. also found that copper was bonded to a SiO_4 tetrhrdron in a monodentate mode with a Cu-(O)-Si bond distance of 2.6-3.5 Å [40].

A fast abstraction of the adsorbed surface copper (Cu/SiO_2) by EDTA was observed by XANES (see Figure 3 and 4) as well as the fact of the disappearance of the Cu-(O)-Si bonding (see Table 2).

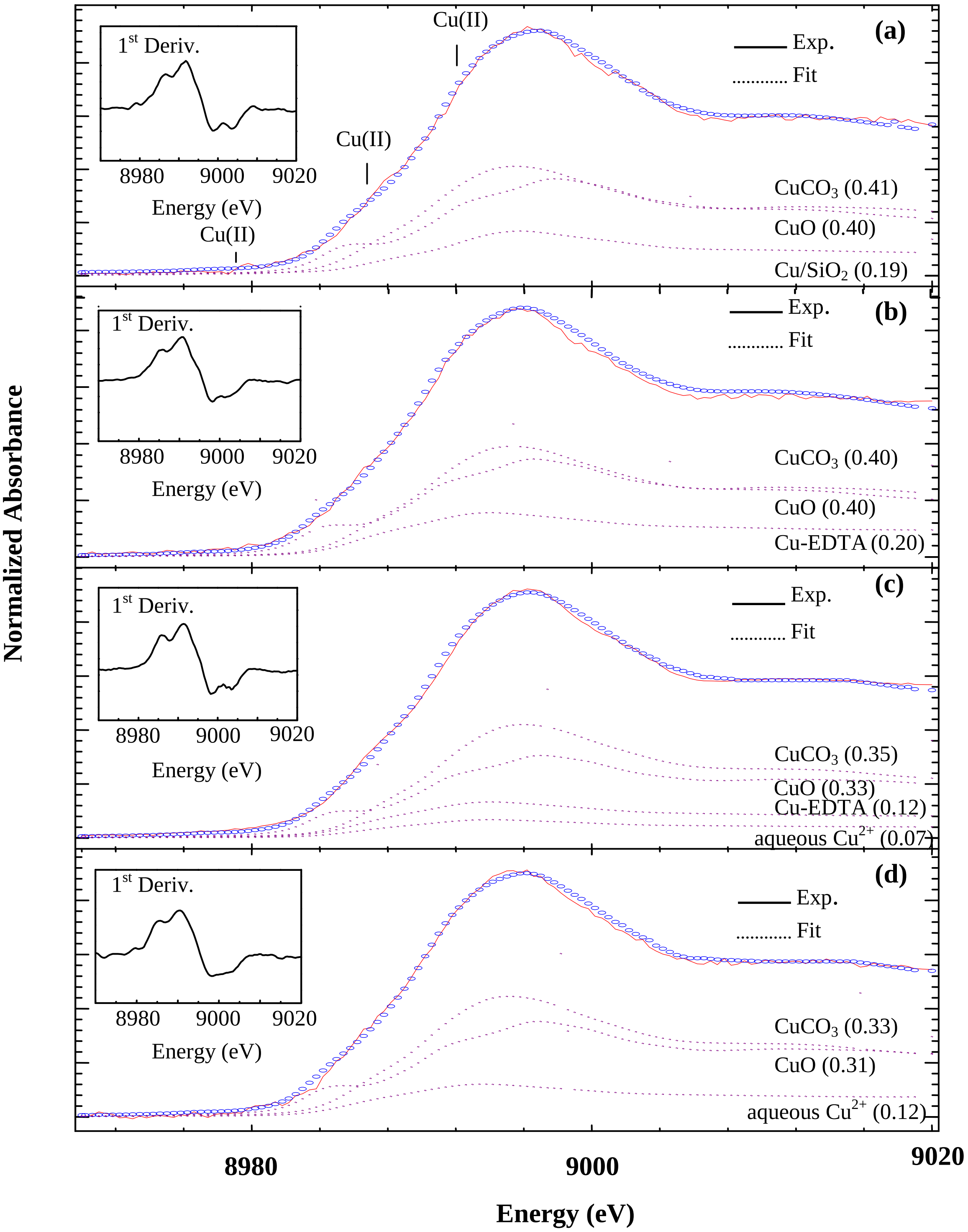

Figure 3. In-situ XANES spectra and their first derivative of the Cu-contaminated soil (a) without and (b) with EDTA (0.05 M) for the electrotreatments of (c) 90 and (d) 180 minutes. Solid lines and circles represent experimental data and the least-square fits, respectively. Dotted lines denote fractional contributions of the four main components ($Cu(OH)_2$, $CuCl_2$, Cu-EDTA and aqueous Cu^{2+}) making up the fitted spectra.

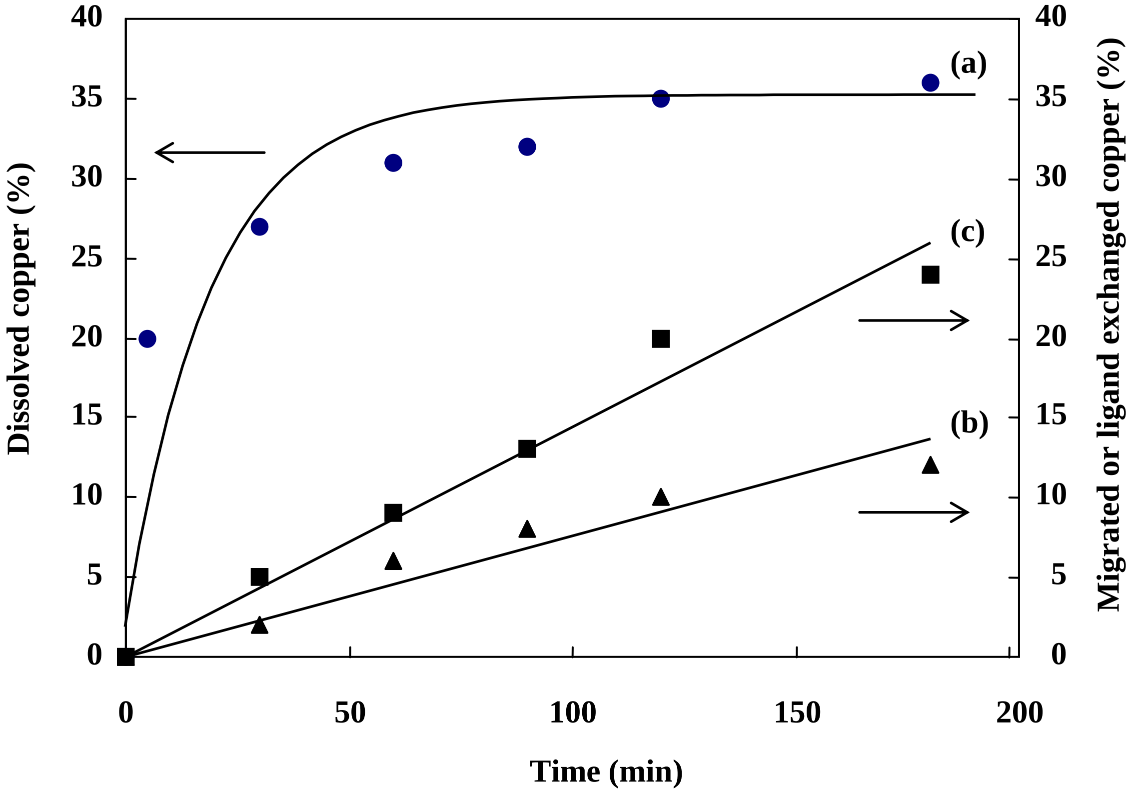

Figure 4. Time dependence for (a) dissolution, (b) ligand exchange and (c) electromigration of copper during the electrotreatments.

The Cu-EDTA complexes in the contaminated soil had equatorial and axial Cu-O bond distances of 1.96 Å and 2.21 Å with CNs of 4.5 and 2.3, respectively. Interestingly, the equatorial and axial Cu-O bond distances were increased by 0.01-0.11 Å in the electrokinetic process.

For the d^9 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_{z^2} and $d_{x^2-y^2}$) is removed, one of the two orbitals can be stabilized by lengthening either two axial or four equatorial metal ligand bonds [41]. Weak-field equatorial ligands of Cu-EDTA complexes might be replaced by stronger ligands (such as H_2O). An increase in the axial Cu-O bond distances (from 2.20 to 2.31 Å) was found, which might be due to the ligand exchange of the Cu-EDTA complexes with H_2O in the aqueous phase. Prolonging the contact time to about 180 min, little Cu-EDTA complexes were found in the soil.

A possible reaction path for Cu involved in the EDTA-enhanced EKR process is also shown in Scheme 1. Copper in the contaminated soil had equatorial and axial Cu-O bond distances of 1.96 and 2.20 Å with CNs of 4.2 and 2.1, respectively. In the second shells, Cu-(O)-Si (3.25 Å with a CN of 1.0) was found. However, in the presence of EDTA, dissolution of the adsorbed copper (Cu/SiO_2) (20%) was enhanced (1.2 mmole/hr). The Cu-EDTA complexes, coordinated in a square-planar arrangement with four oxygen-containing groups of EDTA, possessed equatorial and axial Cu-O bond distances of 1.96 Å and 2.21 Å with CNs of 4.5 and 2.3, respectively. After 180 min of the electrotreatments, the Cu-EDTA complexes were perturbed to a great extent in the presence of the electric field and the high concentration of H^+ (pH = 1.8).

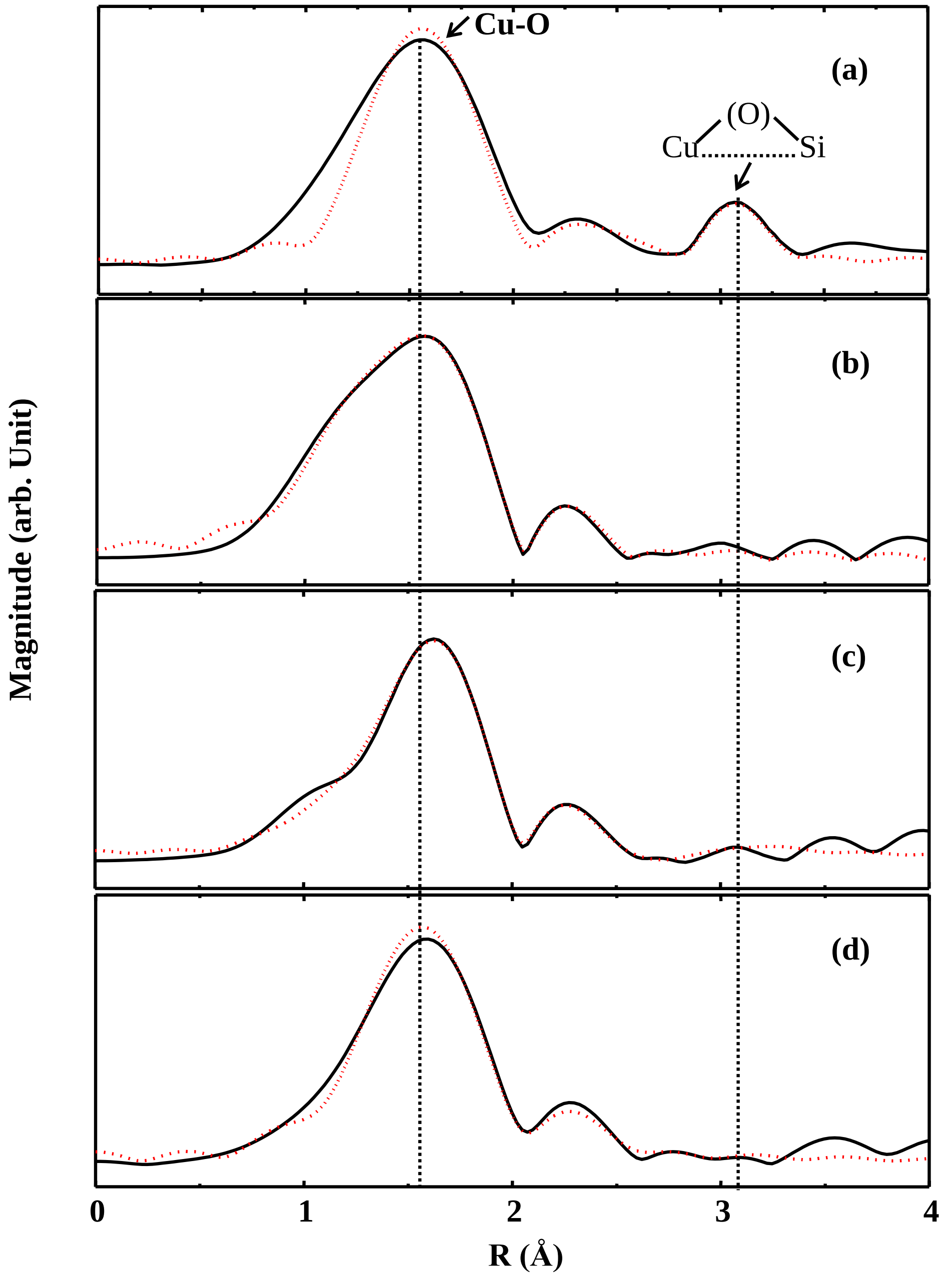

Figure 5. In-situ Fourier transformed Cu K edge EXAFS of Cu-contaminated soils (a) without and (b) with EDTA (0.05 M) for the electrotreatments of (c) 90 and (d) 180 min. The dotted curves denote the best fitting of the EXAFS spectra.

Table 2. Speciation of copper in the contaminated soil in the presence of EDTA (0.05 M) during the electrotreatments

status	shell	R (Å)	CN	σ^2 (Å^2)
Before electrotreatments	Cu-O$_{eq}$	1.96	4.2	0.005
(without EDTA)	Cu-O$_{ax}$	2.20	2.1	0.010
	Cu-(O)-Si	3.25	1.0	0.012
Before electrotreatments	Cu-O$_{eq}$	1.96	4.5	0.005
(+0.05 M EDTA)	Cu-O$_{ax}$	2.21	2.3	0.010
Electrotreatments for 90 min	Cu-O$_{eq}$	1.96	3.2	0.005
(+0.05 M EDTA)	Cu-O$_{ax}$	2.24	1.4	0.010
Electrotreatments for 180 min	Cu-O$_{eq}$	1.97	3.6	0.006
(+0.05 M EDTA)	Cu-O$_{ax}$	2.31	1.6	0.010

R: Bond distance; CN: Coordination number; σ^2: Debye-Waller factor.

The observation of in-situ XANES, EXAFS, and FTIR suggested that the Cu-EDTA complexes were ligand exchanged with H_2O at a rate of 0.4 mmol/hr during electrotreatments. About 24% of copper ($[Cu(H_2O)_6]^{2+}$) was migrated to the cathode under the electric field (0.8 mmol/hr).

4. CONCLUSIONS

This work has showed the utilization of in-situ EXAFS and XANES for revealing speciation of copper with EDTA in a contaminated soil during the electrotreatments. By the least-square fits of the XANES spectra, main copper species such as $CuCO_3$ (41%), CuO (40%) and adsorbed copper (19%) were found in the contaminated soil. The in-situ EXAFS data showed that the bond distance of Cu-(O)-Si was 3.25 Å with a CN of 1.0, which suggested an interaction of copper with the soil surfaces. In the presence of EDTA, dissolution of copper in the soil was enhanced by 8-12%. About 20% of copper in the soil was chelated with EDTA in a short contact time (5 min). A high selectivity for chelation of EDTA with the adsorbed copper species was also observed while other copper species such as CuO or $CuCO_3$ was the little perturbed. Note that weak-field carboxylic acid groups in the equatorial plane of Cu-EDTA were replaced with the strong-field water molecules. After 180 min of the electrotreatments, about 36% of total copper in the soil was dissolved into the aqueous phase and 67% (or 24% of total copper in the soil) of which was migrated to the cathode under the electric field (5 V/cm).

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