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Characterization of Copper Sorbed by a Compost

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Cu compounds have two common oxidation states: 1+ and 2+. If not properly treated before discharge, Cu-containing plating water will contaminate the soil and underground water systems, thereby damaging the food chain and eventually endangering human life. Bioaccumulation of Cu compounds has an adverse effect on crop growth (Marshall 1976). The solubility of copper can be considerably reduced with a pH increase; therefore formation of Cu precipitate in alkaline conditions followed by its removal is a generally acceptable means to reduce copper ion concentration in waste water. However, such a method requires the addition of inorganic chemicals in a few processes in series. Another method to remove copper from liquid by using organic substance such as plants, humic substances, etc. has recently been studied (Salt et al. 1997; Polette et al. 1998; Gardea-Torresdey et a. 1997; Gardea-Torresdey et al. 2001; Reddad et al. 2002; Kapoor and Viraragharan, 1997; Frankel et al. 2000; Kogut et al. 2001; Lu et al. 1997; Korshin et al. 1998; Xia et al. 1997; Hsu et al. 2001; Chang and Chen 1995). Various functional groups such as alcohols, ketones, carboxylic acid, and phenolic hydroxides have been recognized to be responsible for the sorption of heavy metals. Plants like Indian mustard (*Brassica juncea*), creosote bush (*Larrea tridentate*), and alfalfa (*Medicago sativa*) have proven to be good sorbents for heavy metals (Salt et al. 1997; Polette et al. 1998; Gardea-Torresdey et al. 1997&2001; Kapoor and Viraraghavan. 1997). Sugar beet pulp was used to remove Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Ni^{2+} from water through an ion exchange mechanism (Reddad et al, 2002). It was reported that the removal rate was in the following decreasing order: $Pb^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+} > Ni^{2+}$ (Reddad et al. 2002). Humic substances were also found to be effective in sorbing various heavy metals (Frenbel et al. 2000; Kogut et al. 2001; Lu et al. 1997; Korshin et al. 1998, Xia et al, 1997). A compost product derived from swine manure was applied to soil and was found to be capable of retaining heavy metals such as Cd, Pb, Cu, Zn, Cr, and Ni (Hsu et al. 2001). Composts made of cellulosic materials including corn cob, rice straw, and saw dust were used to sorb Cu, Pb, Zn, Cd, Cr, and Ni from water (Chang and Chen 1995) and it was reported that compost made from rice straw was the most effective one due to its high content of various functional groups (Chang and Chen 1995). Compost made of sawdust was the least effective one (Chang and Chen 1995) because of the least content of the functional groups.

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X-ray absorption spectroscopy (XAS) is a non-destructive tool to probe the molecular environment. It benefits studies related to chemical speciation without the intrusive interference caused by wet-chemistry measurements. Some studies have reported the results of heavy metal sorption onto organic substances (Salt et al. 1997; Frenkel et al. 2002; Korshin et al. 1998; Xia et al. 1997) using XAS technique. They proved that Cu^{2+} was sorbed by the acidic functional groups. Composting has emerged as a desirable means to treat organic wastes due to its capability to recycle humic substances into the natural environment. The growing amount of compost stimulates various practical applications. The objective of this study was to use compost derived from kitchen waste as a sorbent to remove Cu^{2+} from waste water. XAS and solid state nuclear magnetic resonance (^{13}C-NMR) spectroscopy were used to obtain a better understanding of Cu^{2+} removal by kitchen compost.

MATERIAL AND METHODS

The kitchen compost used in this study was prepared by the Feng-Yuan City Government of Taiwan. It has a moisture content of 16%, an ash content of 8.4%, and a combustible content of 75.6%. The elemental analysis gave the following composition: 37% C, 5.9% H, 4.2% N, 0.7% S, 0.1% Cl, and 27.8% oxygen (by difference). The pH of the kitchen compost was 5.0, as determined according to US EPA SW-846 Method 9045C.

Experiments on Cu^{2+} adsorption onto the compost were carried out as follows. 100 ml $Cu(NO_3)_2$ with the Cu^{2+} concentrations of 50, 100, 200, 500, 1000, 2000, and 4000 mg Cu^{2+}/L were end-to-end mixed with 5g compost in a 100-ml PE bottle at a rotating speed of 30 rev/min. The mixing time was 0.5, 1, 3, 6, 12, and 48 hr. After the sorption mixing, solid and liquid phases of the mixture were separated through an N_2-pressurized filtration process. Cu^{2+} concentration in the liquid phase was determined using a flame atomic absorbency spectrometer (FAAS); while the solid phase was de-moisturized (dried) at 30±5℃ till a constant weight was reached. These dried Cu^{2+}-sorbed composts were then studied using (i) ^{13}C-NMR (DSX 400W, Bruker, Germany) with cross polarization magic angle spinning, operated at 100.46 MHz for the ^{13}C nucleus with a contact time of 1500 μsec; (ii) XAS (Wiggler BL 17C, Synchrotron Radiation Research Facility, Taiwan) with a beam energy of 1.5 GeV, and a beam current of 120—200 mA; and (iii) scanning electron microscopy (SEM, JXA-840, JEOL, Japan). XAS spectra for reference compounds were collected in the transmittance mode; while those for Cu^{2+}-sorbed composts used the fluorescence mode. Data collected from XAS experiments were analyzed using commercially available software—WinXAS 2.0 (Ressler 1998).

Quality assurance (QA) and quality control (QC) approaches for the analysis of Cu^{2+} in the liquid phase are described as follows. Cu^{2+} stock solution (1000mg Cu^{2+}/L, Merck) was diluted to various concentrations, followed by the measurement of Cu^{2+} with the FAAS to generate calibration curves. The calibration curves covered six different Cu^{2+} concentrations (range: 0.5—8.0

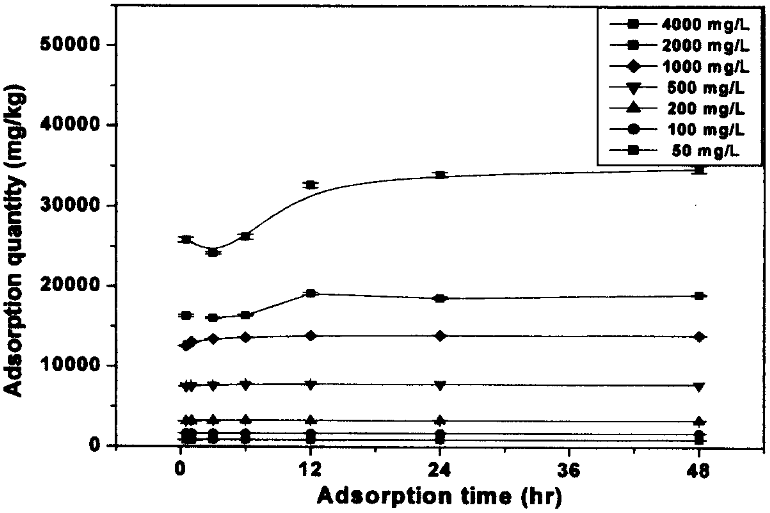


Figure 1. Adsorption quantity of Cu(II) vs. adsorption time from solutions of different Cu(II) concentration.

mg/L). Three replicates were carried out for the Cu^{2+} measurement at each concentration. The minimum requirement for the correlation coefficient (r^2) was 0.995. For each batch of 20 measured samples, a QC standard solution of known Cu concentration was measured with the FAAS to check the validity of the calibration curve. If the recovery yield fell outside the 80—120% range, a new calibration curve was constructed and the last 20 measured samples were re-measured for their Cu concentration. The method detection limit (MDL) was obtained as follows. One of the unknown sample solutions was diluted to a level where the FAAS' signal-to-noise ratio was just greater than three, followed by the FAAS measurement for Cu^{2+} in 12 replicates. Three times the standard deviation was considered as the absorbency for the MDL. The MDL for Cu^{2+} was determined to be 0.018 mg Cu^{2+}/L, which was equivalent to 0.36 mg Cu^{2+} (kg compost)$^{-1}$.

RESULTS AND DISCUSSION

Figure 1 shows the Cu^{2+} sorption quantity from the solutions containing 50, 100, 200, 500, 1000, 2000, and 4000 mg Cu/L versus varying sorption times. It shows that as the copper concentration increases, the sorption quantity increases. The Cu^{2+} sorption quantity reaches an almost constant value after sorption for 24—48 hr, at which Cu^{2+} solid-liquid equilibrium was reached. Percent Cu^{2+} removed from the 50-mg/L solution was 99%, while it dropped to 42% for sorption in the 4000 mg/L solution for 48 hr. The Cu^{2+} sorption capacity of the compost reached ~35000 mg Cu^{2+}/kg after 48-hr sorption in the 4000 mg/L solution.

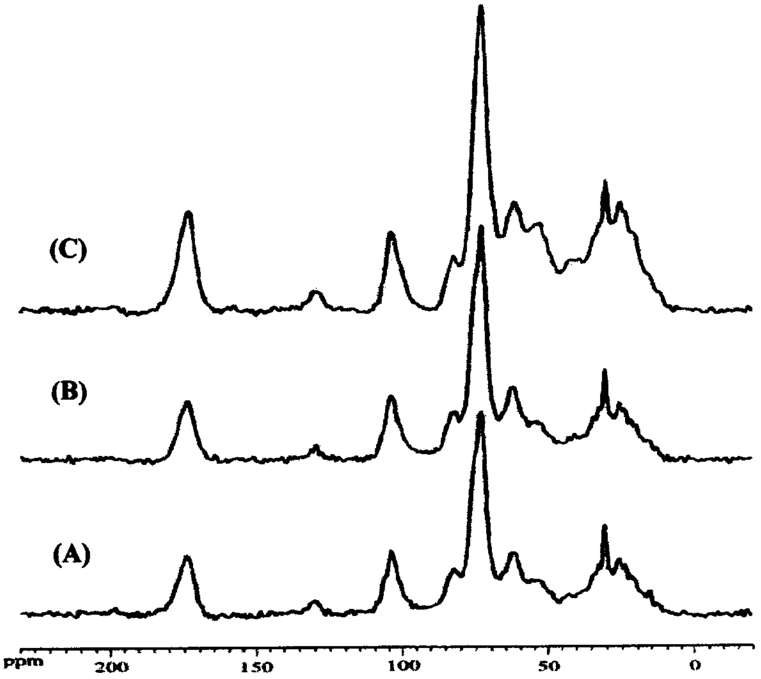
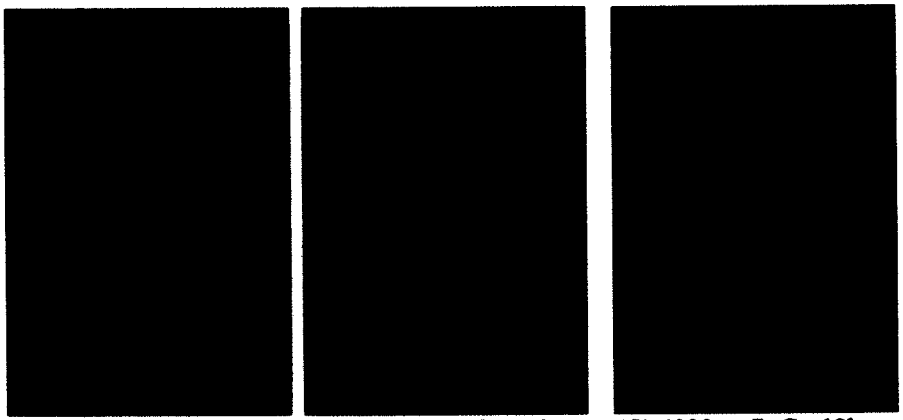


Figure 2. ^{13}C-NMR spectra of compost and Cu-sorbed compost. (A) Neat Compost, (B) Cu-sorbed de-moistured compost (after sorption of Cu from 2000 mg/L solution for 12 hr; termed as 2000 mg/L-Cu-12 hr), and (C) Cu-sorbed de-moistured compost (after sorption of Cu from 4000 mg/L solution for 12 hr; termed as 4000 mg/L-Cu-12 hr).

Both Langmuir and Freundlich equations were used to explain the sorption data. The Langmuir isotherm was unable to fit our sorption data satisfactorily. However, the Freundlich isotherm can explain the data quite well ($n = 0.29$, $k = 879$, and $r^2 = 0.965$). Results of the fitting indicate that Cu^{2+} sorption onto compost was not through a mono-layer sorption.

The ^{13}C-NMR spectra for the neat compost and two Cu^{2+}-sorbed composts are shown in Figure 2. The ^{13}C-NMR spectrum of the sample can be classified into five regions (Marcolm 1989): (i) 0—50 ppm for aliphatic C-C; (ii) 50—90 ppm for carbohydrate not including polysaccharides; (iii) 90—110 ppm for polysaccharides; (iv) 110—160 ppm for aromatic C-C; and (v) 160—220 ppm for carboxyl carbon. To study the change of the area of each region incurred by the Cu^{2+} sorption, each region of the spectra for neat compost and Cu^{2+}-sorbed compost was integrated. The peak area at the 160—200 ppm region for the neat compost was set to be 100, which served as a reference basis for



(A) Neat compost (B) 2000mg/L-Cu-12hr (C) 4000mg/L-Cu-12hr

Figure 3. Morphologies (×3000) of compost and Cu-sorbed compost by SEM

Table 1. Variation of peak area for each region of the ^{13}C-NMR spectra

sample	peak area for each region				
	200—160 ppm carboxy C	160—110 ppm aromatic C	110—90 ppm polysaccharides	90—50 ppm carbohydrate	50—0 ppm aliphatic C
(A)	100.0	21.53	59.41	420.52	274.64
(B)	69.75	--	58.06	297.17	153.36
(C)	61.78	--	53.47	260.82	143.18

determining the area of all other regions for all samples. The results are presented in Table 1. Clearly, sorption of Cu^{2+} caused a decrease in peak area for all regions, although the reduction in peak area for the 90—110 ppm region (i.e., polysaccharides) was not too obvious. It is inferred that, since Cu^{2+} is not an oxidant, the partial destruction of the compost upon Cu^{2+} sorption may have been due to the acidic hydrolysis. It should be noted that $Cu(NO_3)_2$ converts into $Cu(OH)_2$ and NO_3 upon dissolution in water as previously observed (Wei et al. 2001).

The SEM results are presented in Figure 3. The image of the compost that sorbed Cu^{2+} for 12 hr from the 4000 mg/L solution shows some breakage in its morphological structure. This may be due to the acidic hydrolysis caused by the $Cu(NO_3)_2$ solution. This hydrolysis was less severe for the compost sorbing Cu^{2+} from the 2000 mg/L solution than that from the 4000 mg/L solution. These SEM results are supportive of the ^{13}C-NMR results.

In order to assess how strong the sorption between Cu(II) and compost was, it was necessary to gain the insight into the speciation of Cu compounds after this sorption. Studying the Cu molecular environment can provide such information.

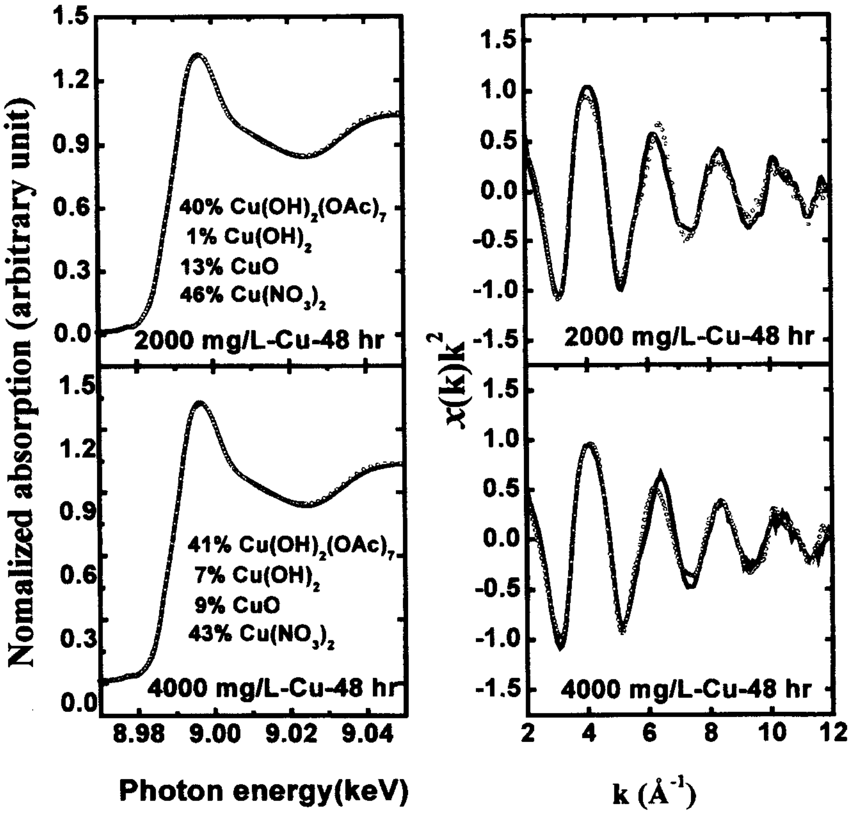


Figure 4. XANES fitting of various Cu-sorbed composts with four references(left column), and performace of fitting of the EXAFS spectra for Cu(II)-sorbed compost(right column) (——— : experimental spectrum , ○ : simulated spectrum).

The left column of Figure 4 shows the results of the determination of Cu species sorbed on the solid phase through the XANES fitting process. The left top compartment of Figure 4 is the XANES fitting results for Cu that was sorbed onto compost from 2000 mg/L solution (the sorption time was 48 hr). The left bottom compartment is the one for Cu sorption from 4000 mg/L solution. The percents of the four Cu compounds listed in each compartment were the results derived from the XANES fitting. The results in the top compartment indicate that $Cu(OH)_2(OAc)_7$ only represented 40% of the total sorbed Cu, while 46% Cu was in its original form—$Cu(NO_3)_2$. The percent for CuO was 13%, and $Cu(OH)_2$ existed in a negligible amount. The results in the bottom compartment show that there was 41% $Cu(OH)_2(OAc)$, 43% $Cu(NO_3)_2$, 9% CuO, and 7% $Cu(OH)_2$. It is noteworthy that because the acidic functional group was suggested to be the main one responsible for Cu^{2+} sorption through an ion-exchange mechanism (Reddag et al, 2002), it is therefore suggested that 40—41% Cu was ion-exchanged to the compost. The rest (~60%) of the Cu compounds was sorbed by the compost simply through a precipitation process. The right column of Figure 4 presents the simulation of the corresponding EXAFS spectra for the Cu^{2+}-sorbed compost using the linear combination of the set of reference compounds based on the weight percents resulting from their corresponding XANES fitting. The results of the simulation are satisfactorily; they are consistent with the fitting of the XANES spectrum.

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