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# Removal of Copper from Water by Activated Carbon

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Activated carbon is characterized by high surface area and strong sorption capacity toward various sorbates. The preparation of activated carbon having different pore structure and surface area generally includes pyrolysis and activation of peat, lignite, wood, polymers, and wastes etc. (Lua and Guo 2000; Yun et al. 2001). Waste tires contain a high percentage of carbon additive (Helleur et al. 2001), and activated carbon can be derived from the pyrolysis of waste tires (Roy et al. 1995). Chen et al. (1996) studied the adsorption kinetics and equilibrium of Cu adsorption onto activated carbon, and found that as solution pH increased from 2.3 to 8, the Cu removal rate increased from 10% to 95%. Their theoretical model predicted that Cu ion formed surface-metal complexes with activated carbon. The surface-metal complexes were suggested to be $SOCu^+$ and SOCuOH (where "S" represents the activated carbon sorbent) (Chen et al. 1996; Chen and Lin 2001). Park et al. (1997) studied $CuCO_3$- and $ZnCO_3$-impregnated activated carbon with X-ray photoelectron spectroscopy (XPS) and scanning auger microscopy (SAM), and they proposed $Cu(OH)_2$ and $CuCO_3$ as the main copper species sorbed on the surface of activated carbon; while the $Zn^{2+}$ appeared to be the main Zn species based on their XPS and SAM data. They also reported that organic functional groups such as C=O, C-O, C-O-C, OH, CH, $CH_2$, and $CH_3$ were only found on the surface of the exterior portion of the metal loaded samples (Park et al. 1997). Biniak et al. (1999) investigated the sorption properties of a modified activated carbon, containing various oxygen- and/or nitrogen-containing functional groups in $CuSO_4$ solution, using techniques of XPS and Fourier transform infrared spectroscopy (FTIR). They concluded that the amount of sorbed ions depended on the quantity and nature of surface acid-base functionality and on the pH in solution (Biniak et al. 1999).

An ion-exchange process with the strong acid surface group was considered as the possible dominant interaction between heavy metals and the carbon surface (Biniak et al. 1999). The formation of surface complexes with N- and/or O-containing surface groups might also be important in some sorption cases (Biniak et al. 1999). Kadirvelu et al. (2000) used activated carbon cloths to sorb heavy metals from aqueous solution and suggested that the sorption mechanism involved ion-exchange, especially on the carboxylic group, and precipitation. Goyal et al. (2001) determined the sorption of Cu onto activated carbon as type I of the BET classification that represents a rapid sorption in the early stage

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followed by a slow sorption reaching a plateau maximum. It was observed that oxidation of activated carbon could increase its sorption capacity for Cu due to the transformation of the C=C bond into carbon-oxygen acidic surface groups such as carbonyls and lactones (Goyal et al. 2001). Negatively charged $-COO^-$ sites were generated through the hydrolysis of the acidic surface groups (Goyal et al. 2001). Activated carbon generated from walnut shell was found to sorb Cu according to the Freundlich isotherm (Kim et al. 2001). Jia et al. (2002) studied Cu sorption with activated carbon containing N-containing surface functional groups, and their results suggested that pyridinic surface groups in the activated carbons sorbed Cu ion through a coordination mechanism. Dastgheib et al. (2002) used activated carbon made from pecan shells to sorb metal ion solutes. They found that the Langmuir isotherm was unable to describe their sorption data, while slips and Freundlich equations fitted the data successfully. Higher electronegativities and stability constants generally corresponded to a higher adsorption level of metal ions onto the activated carbon (Dastgheib et al. 2002). It was suggested that at low concentrations, the adsorption mechanism was the ion exchange of one proton with one equivalent metal ion; while at high concentrations, the surface complexation reactions should be included. The objective of this work was to study the sorption isotherm of copper on an activated carbon that was generated from a pyrolysis process designed for waste tires and to speciate the copper sorbed on the activated carbon.

## MATERIAL AND METHODS

The ready-for-use activated carbon donated by a waste tire prolysis company in Taiwan was pre-treated prior to the sorption study in our laboratory as follows. Activated carbon (BET area: 560 $m^2/g$) from waste tire pyrolysis was oven-dried at 105±5℃ until it reached a constant weight (i.e., requiring 1—2 days), ground, passed through a 100-mesh sieve, and re-dried again. It was then stored in a PE bottle. Batch sorption experiments were described as follows.

Each of five 100 mL $Cu(NO_3)_2$ solutions with $Cu^{2+}$ concentration of 200, 500, 1000, 2000, and 4000 mg Cu/L was end-to-end mixed with 5 grams activated carbon in a 100 mL PE bottle at a rotating speed of 30 rpm. The mixing time was 0.5, 1, 2, 3, 6, 12, 24, and 48 hr. After the sorption, the liquid and solid phases of the mixture were separated using an $N_2$-pressurized filtration process. A flame atomic absorbance spectrometer (FAAS)(Z-6100, Hitachi, Japan) was used to measure Cu concentration in the liquid phase. The solid phase was dried at 30±5℃ until it reached a constant weight. These solid samples were then studied with (i) scanning electron microscopy (SEM, JXA-840, JEOL, Japan), (ii) Fourier transform infrared spectrometer (FTIR) (FTS-40, BIO-RAD, USA), (iii) $^{13}C$-solid state nuclear magnetic resonance spectrometer with cross polarization magic angle spinning (CPMAS-$^{13}C$-NMR) (AVANCE 400, BRUKER, Germany), and (iv) X-ray absorption spectroscopy (XAS) to reveal Cu speciation (Wiggler BL 17C, Synchrotron Radiation Research Facility, Taiwan).

An XAS spectrum contains three parts: Pre-edge region, X-ray absorption near-edge structure (XANES), and extended X-ray absorption fine structure (EXAFS). The XANES contains information on the electronic state (e.g., oxidation state, extent of d-orbital occupation, etc) of the target element—Cu in this study; while EXAFS reveals the coordination environment around the target element. Spectra recorded were analyzed using WinXAS 2.0 software (Ressler 1998).

The quality control (QC) approach for the measurement of Cu in the liquid phase is described as follows. Cu(II) stock solution (1000 mg/L, Merck) was diluted with de-ionized water to six different concentrations. Each of them was measured with the FAAS in triplicate to construct a calibration curve in the range of 0.5—8.0 mg/L. The acceptable correlation coefficient ($r^2$) of the calibration curve was set to be > 0.995. For each batch of 20 measured samples, a QC copper standard solution was measured with the FAAS to check the validity of the calibration curve. The acceptable recovery yield was set to be 80—120%. If the recovery yield was outside this region, a new calibration curve ($r^2 > 0.995$) was re-constructed, and the last 20 samples were re-measured for their Cu concentration. To determine the method detection limit (MDL), an unknown sample was diluted to a level at which the FAAS signal-to-noise ratio was just greater than three, and its Cu concentration was measured by the FAAS in 12 replicates. Three times the standard deviation of the 12 replicate measurements was used as the absorbency to calculate the MDL. The Cu MDL in this study was determined to be 0.36 mg Cu (kg solid sample)$^{-1}$.

## RESULTS AND DISCUSSION

Figure 1 presents the amount of Cu sorbed by the activated carbon versus the sorption time in solutions of different Cu concentrations. Clearly after sorption for 24—48 hr, the sorption quantity of copper on the activated carbon reached a plateau which suggested that a solid-liquid equilibrium of Cu was obtained. For most runs, the sorption rate was rapid and the equilibrium was reached during the first hour. This observation is consistent with the behavior of type I of BET classification (Goyal et al. 2001). Both Langmuir and Freundlich equations were used to explain the data; however, the Langmuir equation failed to fit the sorption data satisfactorily and the constants derived from this fitting are not presented here. The general form of the Freundlich equation is expressed as:

$$q_e = KC_e^{1/n}$$

where $q_e$ is the amount of adsorbate sorbed by per unit mass of adsorbent (mg/kg), K the adsorption capacity (L/kg), $C_e$ the equilibrium concentration of adsorbate in solution (mg/L), and n the adsorption intensity. The correlation coefficient ($r^2$) for the Freundlich fitting in this study was 0.99, the n value 5.1, and the K value 9714 L/kg. For the Freundlich isotherm fitting, only the 48-hr sorption data were used.

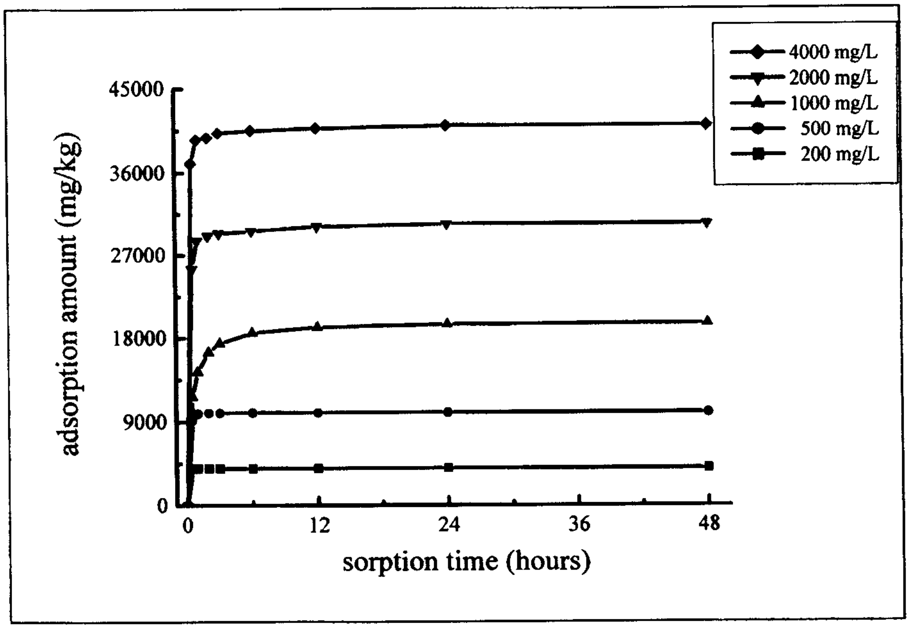
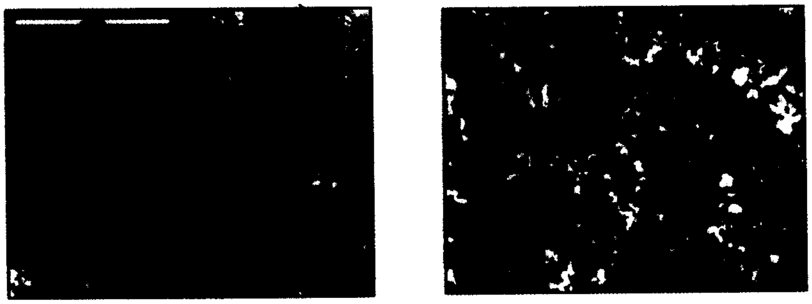


**Figure 1.** Adsorption amount of Cu(II) onto activated carbon vs. sorption time from solutions of different Cu concentrations.

The SEM results show that there is no obvious change in the morphology of the activated carbon prior to and after Cu sorption (Figure 2). Our FTIR spectrum (not included here) for the activated carbon indicated that various functional groups such as C=O (1640—1500 $cm^{-1}$), quinone (1660 $cm^{-1}$), conjugated ketone (1660 $cm^{-1}$), lactone (1740 $cm^{-1}$), aromatic C=C (1400—1380 $cm^{-1}$), and carboxyl-carbonate (1400—1380 $cm^{-1}$) on the activated carbon were observed. In addition, Zn-O at 430 $cm^{-1}$ (Mokili et al. 1996) also appear in our FTIR spectrum. ZnO is usually used as an additive during the tire manufacturing process (Darmstadt et al. 2000). The $^{13}$C-NMR result (obtained by an overnight running) only show the existence of the carboxylic group. All other organic functional groups were un-detectable.

Figure 3 shows the experimental XANES spectrum (the solid line) for Cu sorbed on the activated carbon. The fitting curve (open circles) represents a linear combination (least square fit) of the XANES spectra of the reference compounds: $Cu(NO_3)_2$, $Cu(OH)_2$, and $Cu(CH_3COO)_2$. The percent contribution of each reference compound in the unknown sample is shown in Figure 3. The reason for using these three reference compounds is as follows. $Cu(NO_3)_2$ was originally loaded to the activated carbon, and believed to exist in the dried solid phase after solid-liquid separation. $Cu(OH)_2$ was selected because a previous study identified it in the Cu-sorbed activated carbon with XPS, but without revealing its percentage (Park et al. 1997). The reason for selecting $Cu(CH_3COO)_2$ is because it



activated carbon

Cu-sorbed activated carbon

**Figure 2.** Morphologies (×5000) of activated carbon and Cu-sorbed activated carbon.

was previously shown that Cu could be sorbed through the ion-exchange mechanism (Dastgheib et al. 2002), and because both our FTIR and $^{13}$C-NMR results indicated that the carboxylic group was an important organic functional group on the activated carbon. Note that an effort to search for other appropriate organic Cu compounds was made during this study, but such copper compounds seemed to be commercially unavailable.

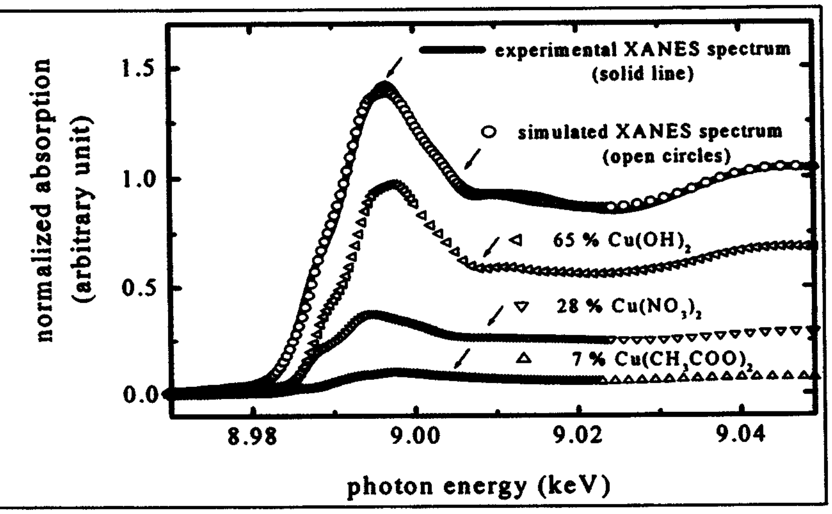


**Figure 3.** Fitting of XANES spectrum for Cu-sorbed activated carbon with three references.

The XANES fitting results (Figure 3) indicate that $Cu(OH)_2$ was the main Cu species sorbed by the activated carbon; while $Cu(CH_3COO)_2$ only represented 7%. A previous study used the XAS technique to investigate the copper speciation (Wei et al. 2001). They doped $Cu(NO_3)_2$ into kaolin and silica aqueous solution, followed by oven-drying the mixed slurries at 105 ℃ for 3 days. The main copper species in the oven-dried mixtures was found to be $Cu(OH)_2$ that represented 69.9 and 81.4% of the total doped copper for the silica and kaolin mixtures, respectively (Wei et al. 2001). The result in this study that only 7% of the total doped copper was sorbed by the activated carbon via the ion-exchange mechanism can be explained as follows. The activated carbon in this study was used as-received without further oxidation which is usually carried out to increase the carboxylic and carbonyl functional groups on the carbon surface to improve its sorption toward cations. In conclusion, it is suggested that Cu sorbed onto the non-oxidized activated carbon in this study was mainly through precipitation, rather than through ion exchange with hydrogen ions.

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