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# A Method for Removing Copper from Charcoal of Waste Wood Using an Electrical Current

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**Abstract** The reclamation of resources from wastes, through such activities as recycling various kinds of wastes and finding more ways to use them, is an important part of changing to a sustainable society. It is also important to ensure the safety of products by, for example, removing hazardous substances from recycled items. Wood is a type of demolition waste. The reuse and recycling of wood from demolition have not progressed much. To increase the number of ways of using wood wastes we have examined methods of making carbonized materials from them and using these carbonized materials to control indoor air pollution (Shibano et al., 2002). Research currently underway on ensuring the safety of recycled items includes investigating the behavior and other characteristics of hazardous substances that are, or may very well be, found in recycled items. It is known that the smoke arising from the process of carbonizing wood wastes is mutagenic. However, such mutagenic components become smoke and separate from carbonized materials, and, especially at temperatures of 800°C and higher, they hardly remain in carbonized materials at all (Nakajima et al., 2003, 2004). In the carbonization of wood wastes containing hazardous metals such as CCA (Cr, Cu, As)-treated wood, substances that readily vaporize separate from the carbonized materials. One cannot expect, however, the same removal effect on metals that vaporize with difficulty, such as Cu, making it likely that they remain in the carbonized material (Takahashi et al., 2004). To examine methods of removing hazardous metals which may well remain in carbonized wood wastes, we investigated the removal and recovery of copper from charcoal with a high copper content by applying electricity (direct current) to it.

## Materials and Methods

For our research we purchased commercially available alkaline copper quat (ACQ)-treated wood (Tanaka, 2004, products that were somewhat aquamarine in color) that was assumed to have been pressure-treated with preservatives

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containing copper (compounds of copper and quaternary ammonium). We used color as an indicator to visually confirm that the preservative had deeply permeated the wood. We made pieces 1-cm wide (about 10 × 10 × 60 mm, weighing about 3 g, and about 10 × 10 × 20 mm, weighing about 1 g) and carbonized them. To measure the electrical resistance of the carbonized wood, we dried Japanese cypress grown in Ibaraki Prefecture, cut it into flat pieces 1-cm wide, and carbonized them. Charcoal was prepared as reported previously (Nakajima et al., 2003). The test sticks of wood were put in a porcelain crucible and carbonized in a muffle furnace (F0100, Yamato, Tokyo, Japan) with a nitrogen atmosphere while maintaining the temperature at 800°C for 1 h. As reported previously (Nakajima et al., 2003), cypress was also carbonized for 1 h at 200, 300, 400, 600, 800, and 1000°C, and used to measure electrical resistance. Electrical conductivity was measured with an off-the-shelf tester at 2-cm intervals on the surface of carbonized materials. The charcoal sticks obtained by carbonization were kept in a desiccator until they were used in tests.

For the copper removal and recovery test we put 200 mL of 0.5 mol/L dilute sulfuric acid in a 300-mL beaker and placed the electrodes in the beaker. A charcoal stick was used as the anode and a platinum plate as the cathode. A Takasago LX010-35B, which can control both current and voltage, was used as the DC power supply to apply the current at various voltages. After finishing the copper removal and recovery test, we took the platinum plate out of the dilute sulfuric acid while continuing to apply voltage, and washed it in distilled water. After wiping off the water, we weighed the platinum plate on a precision scale and estimated the weight of precipitated copper from the difference with the pre-test weight. After weighing, the reddish-brown precipitated copper was re-dissolved in 2 mL of 1 N nitric acid. A UV spectrophotometer (UV-1600, Shimadzu) was used to measure the resulting copper solution's absorbance at 814 nm. The spectrophotometer was calibrated via the external standard method. The copper content of the samples used in this test was measured with a flame atomic-absorption spectrophotometer (Z8100, Hitachi). Wood sticks or carbonized sticks were put into a platinum crucible and ashed for 3 h at 800°C in a muffle furnace, after which 2 to 3 mL nitric acid was added. This was heated and dissolved on a hot plate. The solution was put in a volumetric flask and filled to volume, and then analyzed by atomic-absorption spectrometry. We used a field-emission scanning electron microscope (S-4700 Type II, Hitachi) to make observations at 1 kV and ultra-high magnification mode of the surfaces and cross-sections of the carbonized sticks made according to various carbonization conditions, which allowed us to determine the ash on the surface and the precipitation of copper compounds in the cross-section. Elemental analysis by energy-dispersive X-ray (EDX) spectroscopy (E-MAX7000, Horiba) was conducted to confirm the elements of the copper compounds on the surfaces and cross-sections. When doing so, point analysis was used to measure the surfaces of carbonized sticks with and without precipitate thought to be copper compounds. Because it was anticipated that copper compounds would precipitate differently on surfaces (where there was contact with ambient gas) compared to interiors (where ambient gas has little effect), we used x-ray diffraction [XRD (RINT 2500, Rigaku)] to measure the surface and interior crystal structure of the carbonized sticks.

## Results and Discussion

In conducting the copper removal and recovery test, we started by checking whether the carbonized sticks we made could be used as electrodes. This was done by carbonizing pieces of cypress at various temperatures and measuring their electrical resistance. We found that charcoal made by carbonizing at comparatively high temperatures (800 and 1000°C) allowed a current to pass with little resistance, but charcoal produced at low temperatures (400 and 600°C) had infinite resistance and did not conduct electricity. We therefore decided to investigate copper-containing wood by performing the copper removal and recovery test using charcoal made at 800°C.

We used five charcoal samples made from ACQ-treated wood (about 10 × 10 × 60 mm) by heating for 1 h at 800°C to test copper recovery from those carbonized sticks onto a platinum plate. The test was run for 2 h at each of six voltages: 0, 1.0, 3.0, 3.5, 4.0, and 8.0 V. The weight of the precipitated copper was determined from the copper plate's weight change and from the change in absorbance at 814

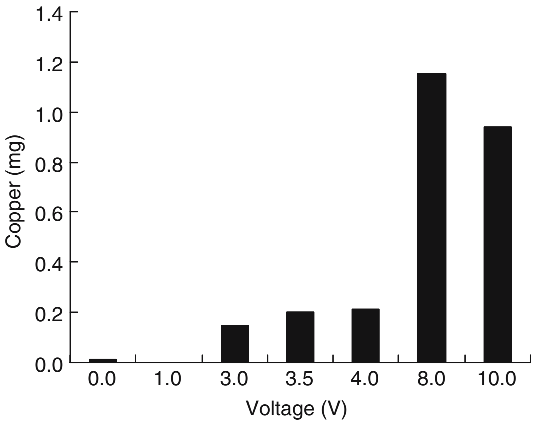

**Fig. 1** Relationship between voltage and amount of copper recovered from copper-containing carbonized sticks

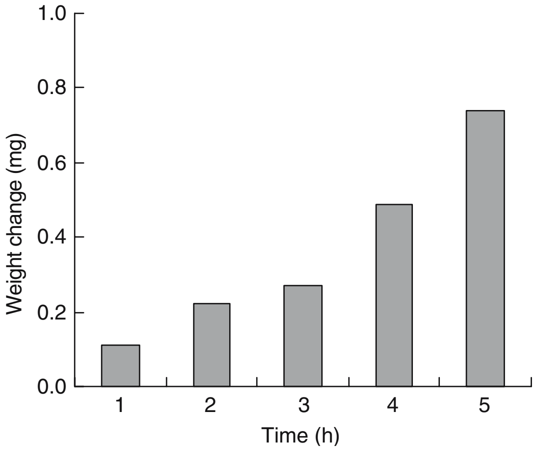

**Fig. 2** Relationship between copper recovery amount and duration of electrical current

**Table 1** Copper content of wood and carbonized sticks

| Sample | Sample weight (g) | Total Cu (μg/sample) | Cu in sample (mg/g wood) |
|---|---|---|---|
| Wood tip 1 | 0.5791 | 2178.0 | 3.76 |
| Wood tip 2 | 0.5641 | 2990.0 | 5.30 |
| Wood tip 3 | 0.5793 | 1784.5 | 3.08 |
| Wood tip 4 | 0.5886 | 2403.0 | 4.08 |
| Wood tip 5 | 0.6014 | 2494.5 | 4.15 |
| Wood tip 6 | 0.5511 | 2473.0 | 4.49 |
| Average | | 2387.2 | 4.14 ± 0.74 |
| | | | (mg/g char) |
| Charcoal tip 1 | 0.0802 | 2092.5 | 26.1 |
| Charcoal tip 2 | 0.0896 | 2316.0 | 25.8 |
| Charcoal tip 3 | 0.0829 | 1862.0 | 22.4 |
| Charcoal tip 4 | 0.0939 | 2364.0 | 25.2 |
| Charcoal tip 5 | 0.0881 | 2608.0 | 29.6 |
| Charcoal tip 6 | 0.0990 | 3633.0 | 36.7 |
| Average | | 2479.3 | 27.6 ± 4.99 |

nm of the nitric acid solution (Fig. 1). The weight of copper precipitated on the platinum plate was higher when the voltage was between 3.0 and 4.0 V than when it was between 0 and 1.0 V, and at 8.0 V it increased substantially. The measured change in weight was actually not very large, but it exhibited roughly the same trend as the changes in light absorbance by copper dissolved in nitric acid. Additionally, even in the 8.0-V experiment we obtained precipitated copper (1.2 mg). However, we observed heating of the carbonized wood at 8 V.

We were able to confirm that when using this experimental apparatus, copper in the carbonized sticks was recovered, and that the amount was affected by voltage.

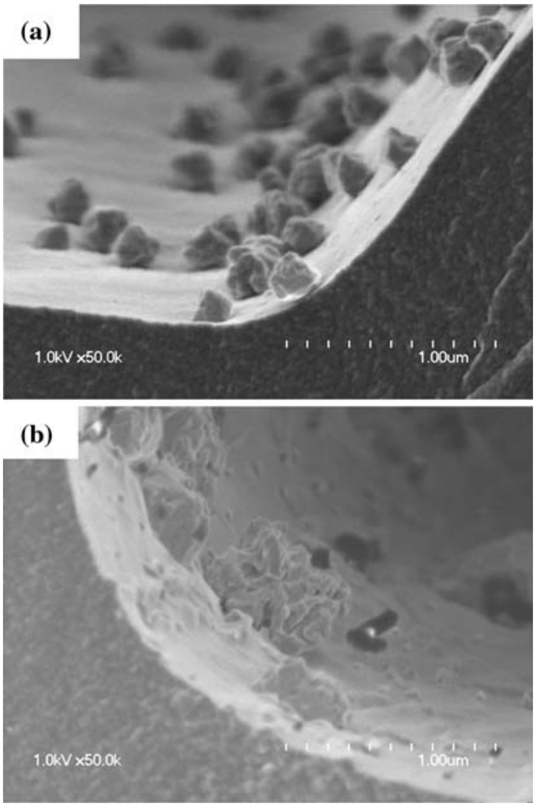

**Fig. 3** Cross-sectional view of charcoals observed by SEM Carbonized temperature at (a) 800°C (b) 1000°C

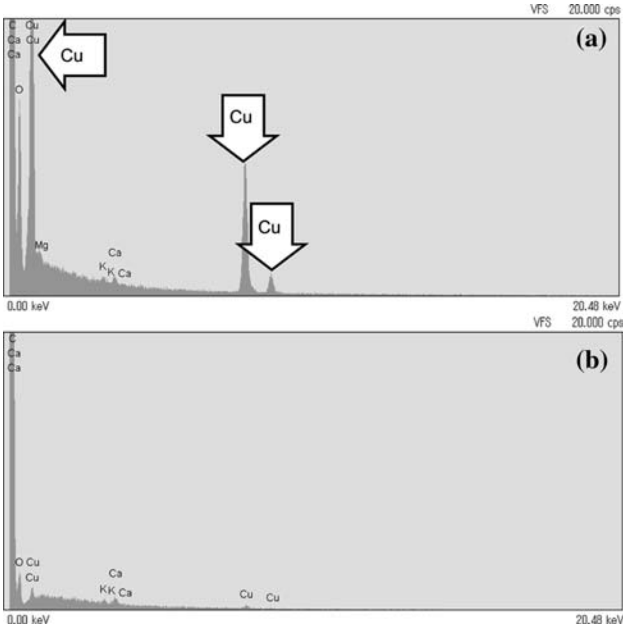

**Fig. 4** EDX analysis of nodules on surfaces of carbonized sticks. (a) Nodules, (b) carbonized stick surface

For that reason we investigated the effect of the length of time a current is applied at a constant voltage (4 V). In this test we took the electrodes out of the solution once an hour (for about 5 min), measured the weight of the platinum electrode, and determined its weight change over five

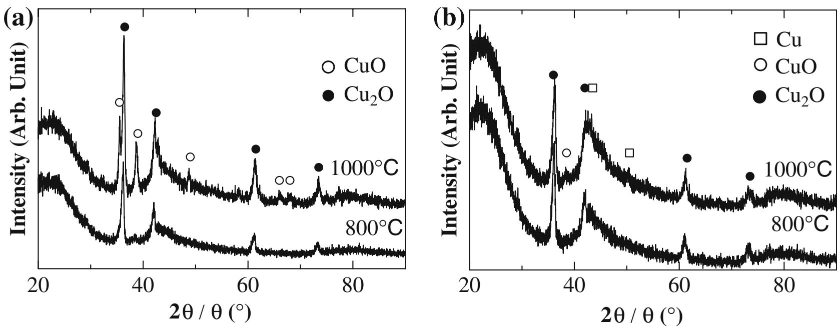

**Fig. 5** XRD patterns of charcoal with ACQ treatment. (a) Surface, (b) inside

hours (Fig. 2). The platinum electrode weight increased with current duration. These results indicate that as copper in the copper-containing carbonized sticks dissolved into the solution, it continuously precipitated onto the platinum electrode. We also found that even when this carbonized material (electrode) was taken out of the solution and a new platinum electrode was put in the solution, precipitation of copper from the solution onto the platinum electrode continued (about 4 h, data not shown). This demonstrated that the dissolution and recovery of copper from carbonized sticks also works effectively by applying a direct current and recovering the copper with a different electrode.

To find the copper recovery rate in this test we used flame atomic-absorption spectrophotometry to measure the copper content in pre-carbonized wood and in carbonized sticks. Results appear in Table 1. ACQ-treated wood had a copper content of 4.1 mg/g, which corresponds to about 12 mg in each carbonized piece. Applying 10 V for 8 h recovered about 4 mg of copper, while 5 V for 12 h recovered about 6 mg, indicating that about 45% can be recovered. On this occasion the experiment was conducted with about one-sixth of the carbonized material immersed in dilute sulfuric acid, and it is conceivable that copper migrated due to acid permeation of the charcoal. Therefore the figures obtained for the recovery rate can not be considered very accurate. A higher recovery rate is likely possible by apparatus improvements and other means.

We used SEM observations to see how copper and quaternary ammonium compounds in ACQ-treated wood changed in the carbonization process, and XRD to investigate the chemical forms of copper components on the surfaces and interiors of carbonized sticks. Figure 3 shows 50,000 magnification SEM photomicrographs of carbonized stick cross-sections made at 800 and 1,000°C. We observed many nodules about 200 nm in diameter of what appeared to be Cu or Cu compounds on cell walls inside the wood (Fig. 3a). In a carbonized sample that had been heated at 1,000°C (Fig. 3b), we observed the growth of nodules which were larger than those seen at 800°C. Cu was observed in the nodules (Fig. 4), indicating that this substance is a copper-containing compound. We therefore analyzed the surface of this carbonized material with XRD. XRD peaks for Cu, $Cu_2O$, and CuO, which were not visible in ACQ-treated wood, emerged due to carbonization (Fig. 5). The peak for $Cu_2O$ was found on both the surface and interior when the carbonization temperature was 800°C. When carbonization was done at 1,000°C, we found the CuO peak on the surface, and the Cu peak in the interior.

It appears that copper was thus reduced, changing to the forms $Cu_2O$ and Cu, thereby facilitating its electrochemical recovery. It further appears that the conductivity of carbonized materials also helped raise the copper recovery rate.

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