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Behavior of Cadmium and Lead Contained in Wood During the Carbonization Process

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Abstract The behavior of heavy metals in wood during its carbonization process was examined. Cadmium in wood samples was found to be volatile when the samples were carbonized at 600°C or higher, which demonstrated that removal of cadmium was feasible. Meanwhile, lead was found to be barely volatile even if the wood samples were carbonized at 1,000°C or higher, which demonstrated that lead was difficult to remove and recover. The possibility of removing/recovering lead contained in wood by energization was then examined. By examining the concentration of sulfuric acid used as an electrolyte as well as load voltage, approximately 10% of lead was found to be recoverable.

Keywords Cadmium · Lead · Charcoal · Remediation

Carbonization has recently been attracting attention as an efficient method for reusing wood. Charcoal is widely used as an adsorbing agent, soil conditioner (Nagasawa et al. 1995; Doi and Kikuchi 1987; Imamura 2000) etc., Pyroligneous acid, which is generated in the carbonization process, can also be used as a gardening material. Currently, however, the only charcoal that can be reused is charcoal generated from wood that does not contain toxic substances, because charcoal containing residual heavy metals poses a safety risk. Meanwhile, cadmium and lead are major heavy metal contaminants in the environment. The former is considered to have caused the Itai–itai disease, while the latter is known to present health risks such as hemolytic anemia, hem synthetic disorder, immune system dysfunction, and kidney problems, in addition to its genotoxicity. Heavy-metal contamination, which generally originates in mines and refineries, spreads into the entire environment through rivers, soil, and air. For example, it was reported that agricultural lands were polluted by cadmium in Dayu in China, Taoyan in Taiwan (Hata 2003), and Guangzhou in China (Li et al. 2006). The soil contaminated with lead and resulting contamination of tealeaves pose serious problems. Jin et al. (2005) measured the concentration of lead in branch, leaf of tea tree, and in deep and surface soil at that area. Phytoremediation is currently being studied as a countermeasure against contamination. One report confirmed the effect of phytoremediation in practical applications by combining it with organic fertilizers, fine coal, soil capping and discing (Peng and Yang 2005). A study using mustard was also conducted (Su and Wong 2004). Trees that grow in contaminated areas are likely to contain significant amounts of metals, which is why not only soil purification techniques but also methods of treating heavy-metal contaminants in wood must be developed. We have already

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reported on the creation of carbide that does not contain mutagenic organic compounds (Nakajima et al. 2003, 2004), and on the method of applying DC current to charcoal created from wood subjected to chemical treatment using commercially available chemical agents containing copper, thus recovering/removing the copper in reduced form (Goto et al. 2007). This method can be used to facilitate recovering metals from activated carbon, which has been used to purify water contaminated with heavy metals by adsorption, reusing activated carbon, and implementing phytoremediation of contaminated soil using woody plants. The method is also considered to be applicable to other heavy metals. This paper describes the result of our study on the removal of residual cadmium and lead in wood by carbonization and other methods.

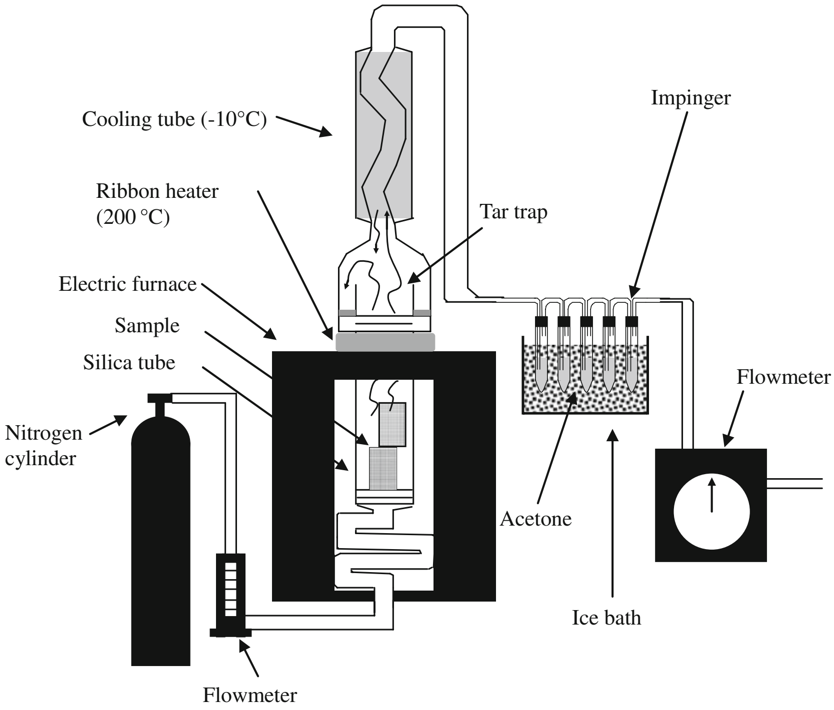
Materials and Methods

Cadmium chloride, nitrate, sulfuric acid, nitric acid, and sodium hydroxide (special-class reagents by Nakalai Tesque, Inc.,) and acetone for testing residual agricultural chemicals (Wako Pure Chemical Industries, Ltd) were used. A plate of Japanese cedar (*Cryptomeria japonica*) purchased from a wood shop was cut as required into pieces to use them for the test.

Pieces of wood containing cadmium were prepared as follows: 2% cadmium chloride solution of 500 mL was placed in a vacuum desiccator, then wood pieces measuring 1 × 1 × 6 cm and 1 × 1 × 2 cm were immersed in the solution, which was then depressurized for 5 h with a vacuum pump and dried for 15 h in an oven at 105°C. Pieces of wood containing lead were prepared in the same manner using 5% nitrate solution. Pieces of wood containing copper were prepared in the same manner using 2% sulfate pentahydrate solution. Preliminary tests were conducted and revealed that the weight increase of pieces of wood ceased after approximately 5 h, with seepage reaching the steady state, and that weight decrease ceased after 15 h of drying.

The apparatus used for our previous experiment (Nakajima et al. 2007; Fig. 1) was used to recover metals during the carbonization process. A nitrogen gas inlet was installed at the muffle furnace (FUW242PA, Toyo Engineering Works), with which the temperature rise program could be set, and the nitrogen gas tube was connected to the silica tube through a corrugated tube, which allowed nitrogen gas to stay for a long time within the furnace to prevent external nitrogen gas (99.99%) from causing the temperature of the test samples to decrease. One end of the silica tube was made to protrude from the top of the muffle furnace to outside, and a glass tar trap was placed over the protrusion. The tar trap was then connected to another corrugated tube, into which cooling water at −10°C was fed. To prevent the gas components liquefied by cooling from returning to the silica tube within the muffle furnace, they were made to fall along the wall to the bottom of the tar trap. Five impingers were connected in series to the end

Fig. 1 Carbonized gas and tarry substance collecting apparatus



of the corrugated tube for cooling. Five milliliter each of acetone was placed in the first two impingers, while 0.5 M of nitric acid was placed in the third one, distilled water in the fourth, and 1.0 M of sodium hydrate solution in the fifth.

Test samples of approximately 2 g were placed in a 20 mm-dia and 280 mm-long silica tube and heated while nitrogen gas was fed (at 10 mL/min) for carbonization (rate of temperature increase: 10°C/min) The carbonization temperature was set to 400, 600, 800, and 1,000°C. Once the set temperature was reached, the furnace was kept at that temperature for 1 h, and then allowed to cool. After the furnace had cooled down, charcoal in the silica tube was taken out for use as carbide samples. All the parts including the silica tube, from which samples had been taken out, tar trap, corrugated tube for cooling, connected tube, and the two impingers in the former stage were washed with acetone for recovery, and the recovered solution was diluted to 50 mL with acetone. The contents of the three impingers in the latter stage were collected individually, and the recovered solution was diluted to 10 mL with each solution.

Each wood sample was analyzed using a thermo gravimetry-differential thermal analysis (TG-DTA) system (WS-002 system, Bruker AXS). The sample wood was cut into 1 mm pieces, they were mixed thoroughly, and 10 mg was measured accurately and used for measurement. Helium was used as atmospheric gas, the temperature was increased at the rate of 20°C/min., and measurement was taken in the range from room temperature to 1,000°C.

The metallic elements on the surface of the samples before and after the carbonization were identified using a scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) system (SEM: JSM-5900LV, JEOL; EDS: Inca Energy IE300, Oxford). As pretreatment for SEM-EDS, carbon was deposited on the surface of the samples using a carbon vapor deposition system (JEC-530, JEOL). Deposition conditions were as follows: pressure: approximately 2 Pa, current: 100 A, voltage: 4.2 V, deposition duration: 30 s. The accelerating voltage in the SEM observation was set to 15 keV. To identify metallic elements, the surface of the samples was observed under the SEM at the magnification of 1000 times, and characteristic X-rays were detected from the 100 μm × 125 μm area. The detected characteristic X-rays were used to identify the elements on the surface of the samples.

In the experiments of collecting metals during the carbonization process, the recovered acetone solutions were diluted to 50 mL, while 0.5 M nitric acid and water, and 1.0 M sodium hydroxide solutions were diluted to 10 mL each. Ten microliter of each of these solutions were diluted to 100 times the original volume with 0.1 M nitric acid, and the concentrations of cadmium, lead, and copper contained in them were measured using an inductively coupled plasma-atomic emission spectroscopy (ICP-AES) system (ICAP-61E-Trace, Thermo Jarrell Ash). The pieces of wood and charcoal containing heavy metals were crushed into powder, which was weighed, mineralized using a microwave heating apparatus, made into a 0.1 M nitric acid solution, and quantified using another ICP-AES system (Optima 5300DV, PerkinElmer).

The 1 × 1 × 6 cm samples (pieces of wood containing each heavy metal and those not having undergone the immersion treatment process) were placed in a porcelain crucible, and nitrogen was fed into the muffle furnace (FO100, Yamato) while the furnace was heated. When 800°C was reached, the temperature was maintained for the specified period, and then the furnace was allowed to cool naturally to create carbide.

Recovery of metals remaining in charcoal was attempted using the apparatus already described (Goto et al. 2007). Platinum (Pt) was used as the cathode, while charcoal was used as the anode for energization. A 3 cm × 3 cm × 0.2 mm platinum plate was placed diagonally as an electrode, with half of the plate immersed in the electrolyte, while the charcoal electrode was set with 4 cm immersed in the electrolyte. Dilute sulfuric acid was used as electrolyte, and the recovery volume at each concentration (0.25, 0.5, 1.0, and 2.0 mol/L) and voltage (1, 2, 3, 4, and 5 V) was measured and compared. The platinum electrode was taken out, and then the power was turned off. The surface of the electrode was then washed lightly with distilled water, moisture on the surface was wiped off with KimWipes, and then the weight was measured with a scale. The difference in weight before and after the energization was regarded as the recovered volume. The metal that attached on the platinum electrode was washed with concentrated nitric acid of exactly 2 mL, of which 1 mL was measured accurately, diluted to 100 mL with distilled water, and the amount was determined by ICP spectrometry.

Results and Discussion

A thermo gravimetry-differential thermal analysis (TG-DTA) system, which measures the weight of the sample placed on a scale filled with inert gas (helium) while heating the sample, can reproduce the charcoal production process, if wood pieces were used as samples. The change of weight during the carbonization process can thus be clarified. Prior to commencing the carbonization experiment, the change of weight due to thermal decomposition of the piece of wood not impregnated with heavy metals (wood) and those impregnated with heavy metals (wood-Cu, wood-Cd, and wood-Pb) was measured with the TG-

DTA. As shown in Fig. 2, weight decrease due to carbonization began at around 400°C. The rate of weight decrease of the wood containing copper or lead was smaller than that of the wood not impregnated with heavy metals (wood). The longitudinal axis of the graph (Fig. 2) represents the weight percentage relative to that at the start of thermal decomposition as 100%. The wood containing heavy-metal salt is slightly lower in the percentage subjected to thermal decomposition than those not containing heavy-metal salt, which is why the ratio of weight decrease of the wood containing copper and lead was slightly lower. On the other hand, the wood containing cadmium exhibited larger weight loss than that of raw wood at around 800°C, which suggested that cadmium started to vaporize at that temperature.

To confirm the occurrence of volatilization suggested by TG-DTA, the surface of the wood samples was observed under an SEM before and after the carbonization. Figure 3 presents the result of measurement of elements observed under the SEM. The peak observed with cadmium before carbonization was no longer found after carbonization, which confirmed that cadmium had been volatilized.

Since the above results confirmed that cadmium had volatilized during the carbonization process, pieces of wood impregnated with cadmium were carbonized, gas components generated were recovered, and their behavior was checked. Specifically, pieces of wood impregnated with cadmium, copper, and lead were carbonized using the apparatus shown in Fig. 1, and the gas components generated were recovered, classified into tar, low-molecular organic gas, low-molecular basic gas, and low-molecular acidic gas. As a result of measuring each component by ICP-AES, copper and lead were detected only from the charcoal, irrespective of the temperature at which carbonization was performed, and neither of them was detected from gaseous components. On the other hand, cadmium was detected from the tarry substance of the

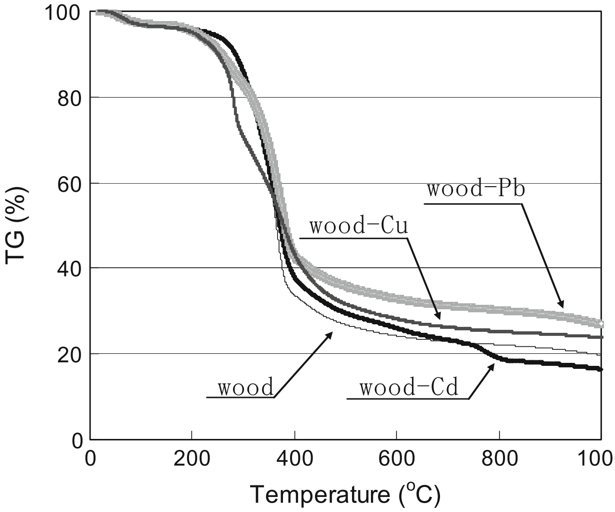


Fig. 2 TG-DTA curve of wood containing heavy metals

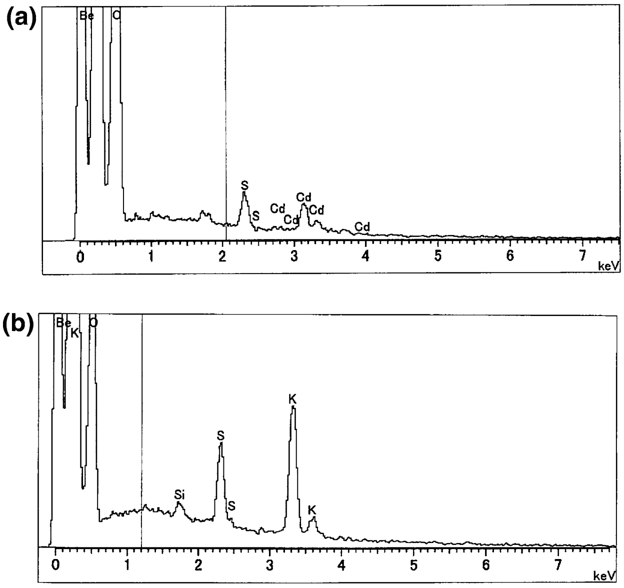


Fig. 3 SEM-DES pattern of wood containing cadmium and on the surface of its carbide: **a** Wood containing cadmium before carbonization, **b** Carbide created at 800°C from the wood containing cadmium

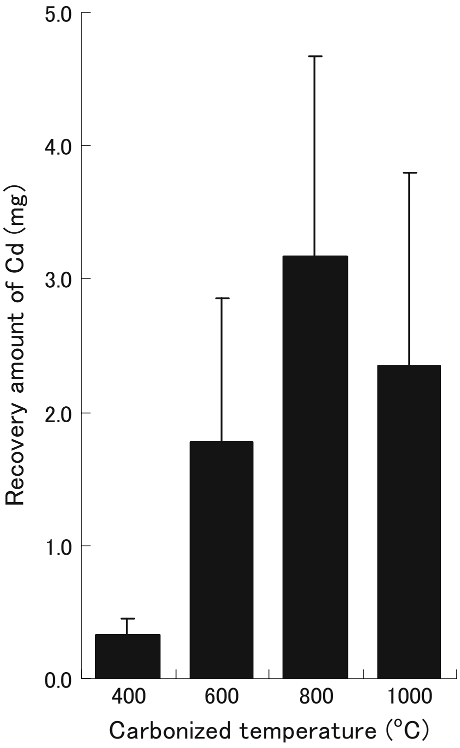


Fig. 4 Amount of cadmium in the gas component obtained when wood containing cadmium was carbonized

gaseous component. Figure 4 shows the amounts of cadmium recovered from the tarry substance at each carbonization temperature. Since the tests were conducted only three times, and the weight and heavy-metal concentrations of the wood samples impregnated with heavy metals used for carbonization varied, a significant difference was not found. However, it is clear that cadmium volatilized at higher temperature. The cadmium in the charcoal created by carbonization at 800°C was found to be lower than the limit of detection.

The above results confirmed that the cadmium in the wood samples had been removed through volatilization during the carbonization process. On the other hand, almost 100% of the copper and lead in the wood samples was found to be remaining in the charcoal at any carbonization temperature. Even when the wood samples were carbonized at 1,000°C, only several percentages of these components were detected from the tarry substance, which confirmed that it was impossible to remove these metals even by carbonization at around 1,000°C. This fact coincides with the result of the TG-DTA shown in Fig. 2, which demonstrated that the weight decrease of the wood samples containing both metals was smaller than that of the wood not containing metals.

We have reported, that approximately 45% of the residual copper in wood could be removed by energization (Goto et al. 2007), so we examined whether lead can also be removed by energization. Using charcoal containing lead produced at 800°C, load voltage and sulfuric acid concentration conditions were studied, and it was found that the highest recovery rate was obtained when the voltage was 4 V and the concentration was 1.0 mol/L. Experimental conditions were set based on the above result, and removal by energization was attempted. As shown in Fig. 5, the amount of recovery increased with longer energization.

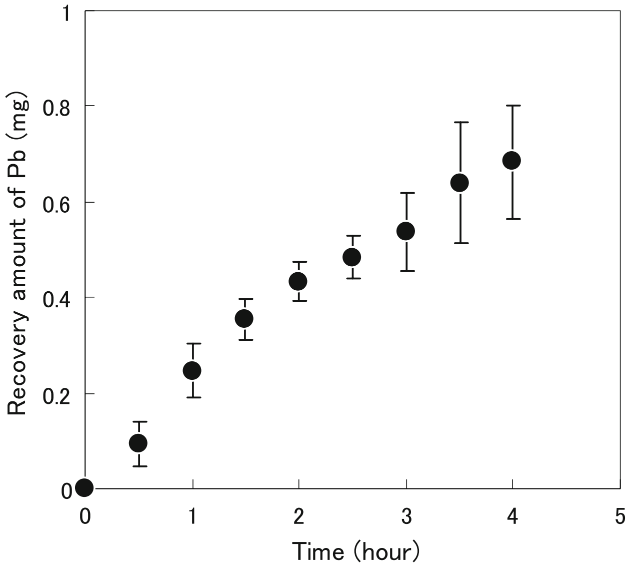


Fig. 5 Amount of lead recovered by energization from carbide containing lead (Electrolyte: 0.1 mol/L sulfuric acid, Voltage: 4.0 V)

Energization experiments were conducted four times under the above conditions, and the lead remaining in the charcoal after energization, deposited on the surface of the platinum electrode, and remaining in the electrolyte was measured with the ICP-AES to examine their distributions. When the energization duration was set to 5 h, the removal rate of lead from the charcoal was 10.6 ± 3.2%. The ratio of residual lead in the electrolyte was as small as 0.2 ± 0.1%, with approximately 90% remaining in the charcoal. Compared with copper, the efficiency of removing lead by energization was found to be much lower. Many challenges remain to be overcome including prevention of polarization on the electrodes and promotion of elution into electrolyte. Further research is required to improve the recovery rate.

The experiments conducted this time clarified the behavior of heavy metals during the carbonization and energization processes. Cadmium was found to volatilize if wood was carbonized at 600°C or higher, which confirmed the feasibility of removing cadmium from cadmium-contaminated wood. On the other hand, lead did not volatilize but remained in charcoal even if the wood was carbonized at the temperature of 1,000°C or higher. By examining the behavior of the residual lead in the charcoal due to energization, it was found that approximately 10% was recoverable. However, since approximately 45% of copper could be removed by using the same method, further study is required to establish conditions for increasing the removal rate, including increasing the surface area contacting the electrolyte, adopting pressurized energization, and studying the types of electrodes.

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