

## NOTE

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## Removal of mercury and other metals by carbonized wood powder from aqueous solutions of their salts\*

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**Abstract** Sugi (*Cryptomeria japonica* D. Don) wood powder was carbonized at varying temperatures and used as a material to remove heavy metals from their aqueous solutions. Single solutions of mercuric chloride and mixed aqueous solutions containing lead nitrate, arsenic chloride, and cadmium chloride as well as mercuric chloride (1, 5, and 10 ppm) were prepared to determine the efficiency of removing heavy metals by these materials. Wood powder and carbonized wood at 200°, 600°, and 1000°C removed mercury within the concentration range 1–10 ppm; mercury was preferentially removed even when mixed with other heavy metals. Wood powder carbonized at 1000°C achieved the best removal of heavy metals among the wood-based materials and even commercial activated carbon in both single and mixed solutions.

**Key words** Carbonized wood powder · Removal · Mercury · Specific surface area · Environmental pollution

### Introduction

Toxic substances in wastewater have been causing environmental pollution, and their removal is an important problem in the field of water purification. Municipal wastes, urban and agricultural runoff, and industrial wastes are principal pollutants in water systems. The pollutants of special importance are the residues of toxic and hazardous

materials, mostly metallic compounds that seep into the surface and ground water systems. In particular, mercury (Hg), which is toxic, quite mobile, and active in biochemical metabolism, is still spreading in the environment.<sup>1,2</sup> Considerable research has been conducted on the reduction of this metal; and research on the immediate removal of this metal, especially Hg(II) in wastewater, is significant for environmental protection purposes.<sup>3</sup>

The use of charcoal for fuel has been declining for decades, and chemical uses such as filtration and adsorption in the chemical industry are again on the rise.<sup>4</sup> Activated carbon is one of the materials being used to remove impurities from liquid solutions; and it has been widely used to treat industrial and household water<sup>5,6</sup> because of its excellent absorption properties, characterized by a high specific surface area.<sup>7,8</sup> It is also used to remove metallic ions from solutions.<sup>9</sup> The increasing varieties and amounts of potentially hazardous impurities in water have led to the increasing use of activated carbon. The problem associated with its use as a water purifier is largely economic; that is, activated carbon is expensive. As this problem limits its use on a large industrial scale, more economical materials are needed. Although much work has been done on the use of activated carbon for water purification, the problem of heavy metal pollution is still present.

Wood has essentially been excluded as a starting material for the production of activated carbon because of the poor strength and friability of the products in some cases. A few studies have been conducted on harnessing the potential of wood-based charcoal, which is as porous as activated carbons, for water treatment purposes,<sup>10</sup> but, its capability is not yet known. The residues and wastes from wood industries, forestry wastes, and unused wood species, which have increased considerably in recent years, are a good source of material for charcoal production.

This paper discusses the performance of the carbonized wood material from a softwood species, *Cryptomeria japonica*, when used to remove heavy metals from aqueous solutions, dissolving their salts. The surface area, which is considered to be a dominant factor in the purification of water, is also described. Raw wood powder and activated

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carbon made from coconut shell were also tested for comparison. The purpose of this experiment was to find the best carbonization temperature for removal of mercury and to characterize the performance of this carbonized wood material in single and mixed solutions of mercuric chloride with other metallic salts.

## Materials and methods

### Materials

The materials used were (1) wood powder (WP) from sugi (*Cryptomeria japonica* D. Don), passed through a no. 20 mesh sieve; (2) WP carbonized at various levels of carbonization temperatures; and (3) commercial Japan; activated carbon (AC) made from coconut shell powder provided from Nacalai tesque, Japan; code 079-31.

For single solutions, mercuric chloride ( $\text{HgCl}_2$ ), zinc nitrate [ $\text{Zn}(\text{NO}_3)_2$ ], lead nitrate [ $\text{Pb}(\text{NO}_3)_2$ ], and arsenic chloride ( $\text{AsCl}_3$ ) salts were dissolved separately in distilled water at various levels of concentrations. Mercuric chloride ( $\text{HgCl}_2$ ), cadmium chloride ( $\text{CdCl}_2$ ), lead nitrate [ $\text{Pb}(\text{NO}_3)_2$ ], and arsenic chloride ( $\text{AsCl}_3$ ) salts were prepared in mixed solutions. Zinc nitrate was not used in the mixtures because the performance of the materials in a single solution of zinc nitrate was similar when soaked in lead nitrate, as seen before the main experiment. Cadmium chloride was used as a new metal compound in the mixed solutions.

### Carbonization process

Separate samples of wood powder from sugi were carbonized in a nitrogen atmosphere at varying furnace temperatures of 200°, 600°, and 1000°C (hereafter called C200, C600, and C1000, respectively). Nitrogen gas was passed through the materials at a rate of 100ml/min and heated at 4°C/min. The temperature was kept at the target level for 1h, after which the heater and gas flow were turned off. The carbonized materials were cooled naturally inside the furnace to room temperature before they were removed for analysis.

### Characterization of physical properties

The surface area of the wood powder, carbonized wood powder, and activated carbon were measured using BELSORP 36. The BET (Brunauer-Emmet-Teller) multi-point method was used to determine the surface area. Nitrogen ( $\text{N}_2$ ) gas at 77°K was used to determine the adsorption isotherms.

### Removal experiment

Separate solutions of  $\text{HgCl}_2$ ,  $\text{Zn}(\text{NO}_3)_2$ ,  $\text{Pb}(\text{NO}_3)_2$  and  $\text{AsCl}_3$  in distilled water were prepared at 1, 5, and 10ppm concen-

trations on the basis of weight by weight (w/w) of each metal molecule. On the other hand, mixed solutions of  $\text{HgCl}_2$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{CdCl}_2$ , and  $\text{AsCl}_3$  in distilled water at a ratio of 1:1:1:1 were prepared using the same concentrations. The solutions were stirred thoroughly at room temperature using an automatic stirrer until the compounds were completely dissolved.

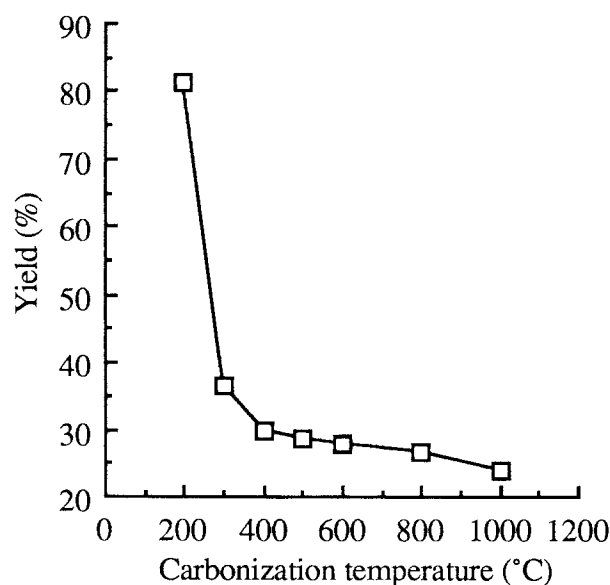
The WP, C200, C600, C1000, and AC (1g each) were mixed separately in 200ml of each of the heavy metal solutions. The mixtures were stirred continuously in a constant temperature-controlled bath at 30°C and were left to settle before samples were taken after 1, 4, 8, 24, and 48h. The concentrations of heavy metals in the samples were measured using a Z-8000 Hitachi atomic absorption spectrometer.

## Results and discussion

### Characterization of materials

#### *Yield of carbonized materials*

The composition of charcoal depends mainly on the final carbonization temperature. When the final carbonization temperature is increased, the amount of carbon increases and hydrogen and oxygen decrease; hence the yield of charcoal decreases.<sup>11</sup> When wood is heated, volatile substances are evolved. The emission of these substances begins at a temperature lower than that in the distillation process, and under these conditions the yield of charcoal is not as low. As shown in Fig. 1, the decreased yield of charcoal with the



**Fig. 1.** Yield of sugi wood charcoal at various carbonization temperatures

increased carbonization temperature can be attributed to the amount of tar derived from the carbonization.

#### *pH Values of carbonized materials*

The pH values of carbonized materials is shown in Fig. 2. C200 had a low pH value, which is almost the same as that of WP, which was 6.54. This result is not different from the pH value of wood.<sup>12</sup> No distinct difference was observed between WP and C200, indicating incomplete carbonization in the latter sample. The acidic pH of wood, due to the presence of acid extractives, might have contributed to the acidic nature of C200. Because slight changes in the physical properties of wood could be observed in this temperature, the acidic pH of the parent material contributed to the acidic character of this material. As the carbonization temperature increased, the pH value increased because the tarry deposits of the wood, which decompose into gases and distillates, have been removed. The change in pH can be attributed to the surface chemical characteristics of the wood carbonized at a certain temperature.<sup>13</sup> In contrast, the pH of activated carbon from coconut shell powder was 10.25.

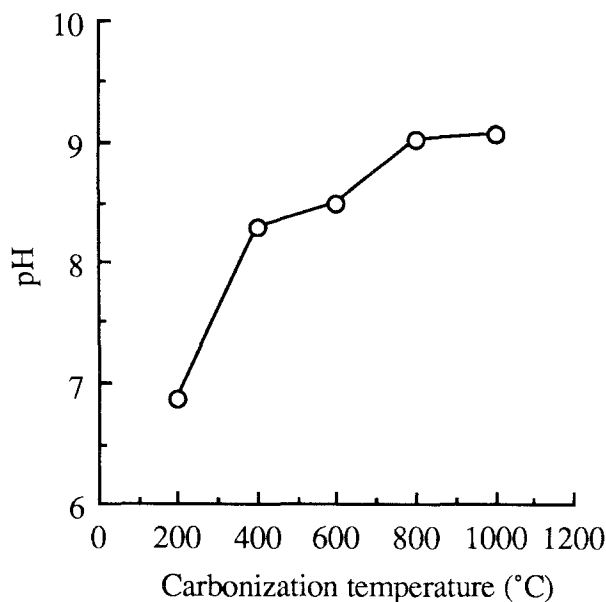
#### Removal of heavy metal

##### *Effect of carbonization temperature on the removal of mercury*

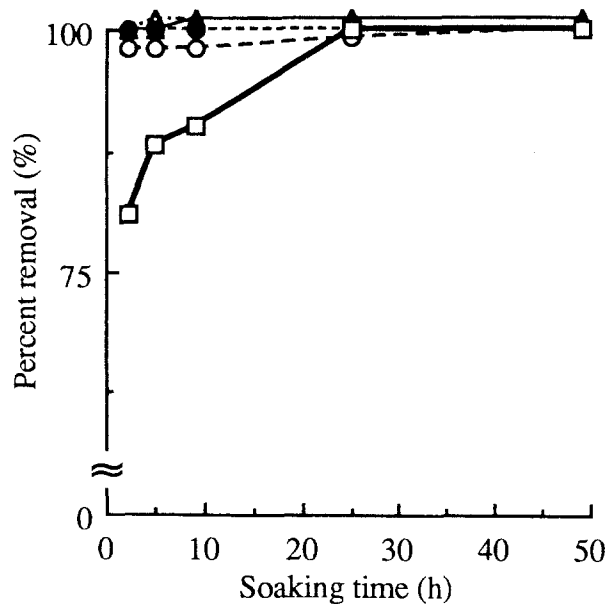
Figure 3 shows the result of the removal of mercury from 1 ppm mercuric chloride solution using sugi wood powder, carbonized wood powder, and activated carbon. When the wood materials with or without carbonization were soaked in the solutions, mercury was removed at a much faster rate than when activated carbon from coconut shell was used. Carbonized wood powder removed almost all the mercury after 1 h of soaking, whereas it took about 24 h for AC to reach the same level of removal.

The raw wood powder also removed a considerable amount of mercury, but, carbonization improved the capacity of the wood powder to remove mercury, especially in 5 and 10 ppm solutions. Mercury was removed to a greater degree by C1000 and C600 than by C200 or WP. The ability of noncarbonized wood to remove the metals could be attributed to the original nature of the raw wood and an increased specific surface area due to swelling in water.

When the mixed solutions containing the heavy metals of mercuric chloride, zinc nitrate, lead nitrate, and arsenic chloride were tested, the distinction between the removal performance of noncarbonized wood powder and carbonized wood powder was prominent, as shown in Fig. 4. C1000 removed mercury faster, followed by AC and C600; removal of mercury by C1000 was especially higher during the early stage of the soaking time compared to that by C600 or AC. Equilibrium was attained in a short time (within 4 h) by C1000 and C600 compared to that by AC which was within 8 h. WP and C200 also removed a considerable amount of mercury, but it was remarkably lower than that removed by C1000 and C600.



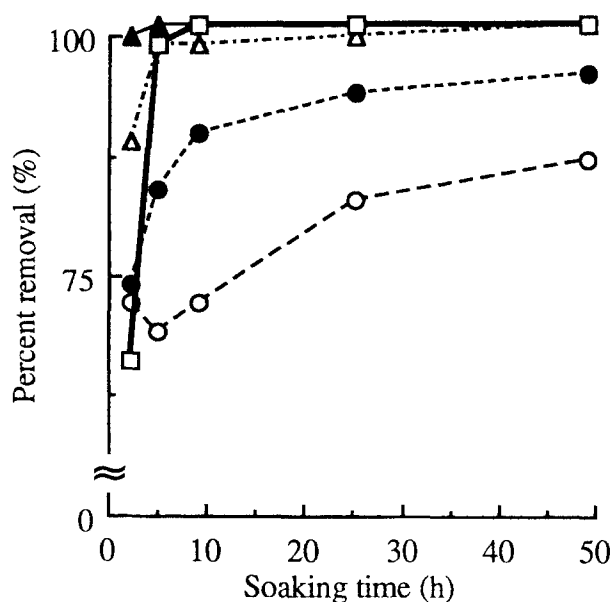
**Fig. 2.** pH values of sugi wood powder carbonized at various temperatures. The pH values for sugi wood powder oven-dried at 105°C and activated carbon from coconut shell powder were 6.54 and 10.25, respectively



**Fig. 3.** Percent removal of mercury using raw wood powder, carbonized wood powder, and activated carbon in 1 ppm mercuric chloride solution. *Open circles*, oven-dried at 105°C; *filled circles*, carbonized at 200°C; *open triangles*, carbonized at 600°C; *filled triangles*, carbonized at 1000°C; *squares*, activated carbon

##### *Specific surface area of materials and its effect on removal of mercury*

The specific surface areas of wood powder and carbonized wood powder from sugi, and activated carbon from coconut shell powder are shown in Table 1. No distinct difference was observed between WP and C200, indicating incomplete



**Fig. 4.** Percent removal of mercury using raw wood powder, carbonized wood powder, and activated carbon in 1 ppm mixture solutions containing mercuric chloride, cadmium chloride, lead nitrate, and arsenic chloride. For explanation of symbols see Fig. 3

**Table 1.** Specific surface area of wood powder, carbonized wood powder, and activated carbon

Material	Specific surface area (m <sup>2</sup> /g)
Raw wood powder	0.541
Carbonized wood powder	
200°C	1.939
600°C	1.127
1000°C	616.600
Activated carbon	1209.000

Wood powder was obtained from sugi (*Cryptomeria japonica*). Raw wood powder was oven-dried before analysis. Activated carbon was prepared from coconut shell powder.

carbonization in the latter. However, in the wet condition, such as dipping in aqueous solutions, the specific surface area of raw wood powder should be increased by about 400 times that of the dry condition.

Carbonization at 1000°C was assumed to have resulted in the larger specific surface area. The large amount of energy supplied during carbonization should promote an increase in specific surface area. On the other hand, the specific surface area of AC was 1209 m<sup>2</sup>/g, which was higher than that of the wood materials after carbonization.

For HgCl<sub>2</sub> solutions, the specific surface area of the materials was considered to have a secondary effect on the capacity to remove mercury. All materials could be used to remove mercury, although the removal rate varied such that AC exhibited the slower removal rates despite its highest surface area. C1000, which had a greater specific surface area than C600, showed almost the same percent removal of mercury from the low-concentration solutions. It was observed that the attraction of the material was enhanced by

the increase in specific surface area, but some other factors, such as the surface characteristics, would promote removal ability as well.

#### Comparison of the removal of mercury and other heavy metals

It was observed that for all concentrations mercury was easily removed by C1000 compared to lead, zinc, or arsenic. In lead nitrate solutions, the removal was similar to that with mercuric chloride solutions, but the difference between the carbonization temperatures was pronounced. C1000 took only 1 h for 1 ppm solutions, whereas it required about 4 h for C200 to attain the same equilibrium condition. Removal of lead by C200 was much lower than that by C1000 for the 5 ppm solutions. Carbonized wood powder of C200 and C600 had limited capacity to remove lead, especially in the 10 ppm solutions. Among the wood-based materials, C1000 removed the largest amount of lead but it was much less than for mercury.

The same trend was observed for the zinc nitrate solutions (Fig. 5). Removal was relatively higher than that of lead nitrate in almost all the materials; and among them C1000 removed the largest amount of zinc.

In the mixed solutions containing the various heavy metals, all materials except raw wood powder and C200 could remove 100% of the mercury present in the 1 ppm solutions. The only difference between the single and mixed solutions was the time required to reach a state of equilibrium. C1000 removed 100% of the mercury fastest, followed by AC and C600. The removal capacity of C200 and WP was also high, although it did not reach 100% removal.

Figure 6 shows that the amount of mercury removed by C1000 attained at 100% in 1 ppm mixture solution. The mercury was removed within a short period. Lead reached equilibrium removal after 4 h, and cadmium and arsenic continued to be removed with the increased soaking time.

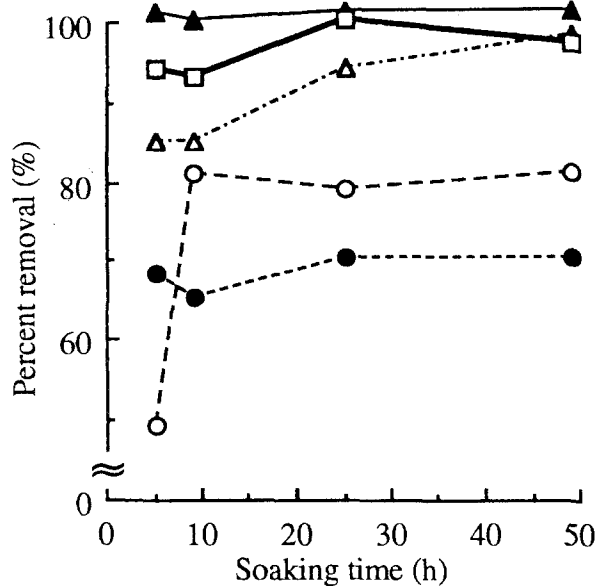
The removal of arsenic was negatively observed as plotted by the minus values, a characteristic described in our previous paper in which arsenic was not removed by wood charcoal except by activated carbon.<sup>10</sup> The behavior of arsenic, which was dissolved in water and coexisted with the carbonized wood, should be studied more.

The same results were observed for 10 ppm solutions; that is, mercury was still the dominant metal removed from the solutions. Moreover, despite the higher concentration of mercury presented in the 5 and 10 ppm solutions, C1000 removed mercury at a rapid rate within 8 and 24 h, respectively, which was faster than the rest of the materials.

#### Effect of initial concentration on the removal of mercury

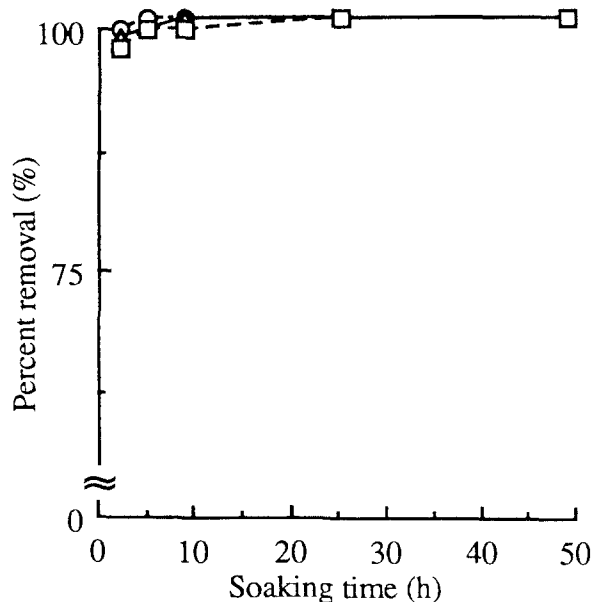
The effect of the initial concentration on the percent removal of mercury is shown in Fig. 7. In the single solution, the removal rate varied somewhat, although little difference was observed at all concentrations. The same characteristic was seen when the same material, C1000, was soaked in the

mixed solutions. After the longer soaking time, the amount of mercury was removed to the same level at all concentrations, suggesting a high affinity of mercury for C1000 within this concentration range. The performance of C600 was similar, in both single and mixed solutions, but the equilibrium time was different.

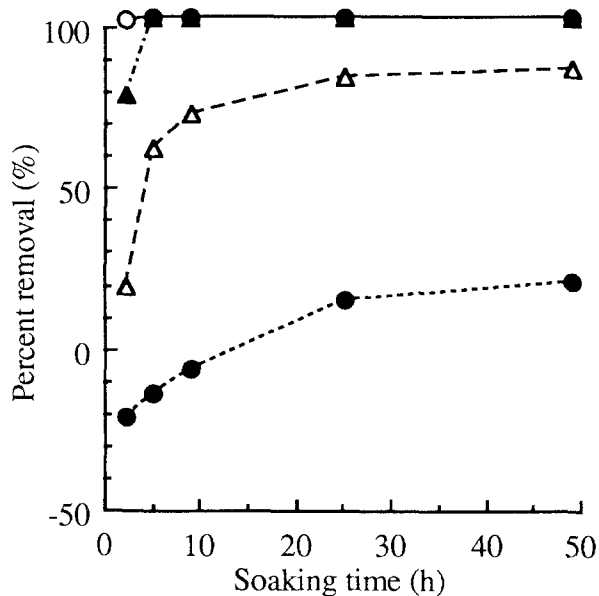


**Fig. 5.** Percent removal of zinc using raw wood powder, carbonized wood powder, and activated carbon in 1 ppm zinc nitrate solution. For explanation of symbols see Fig. 3

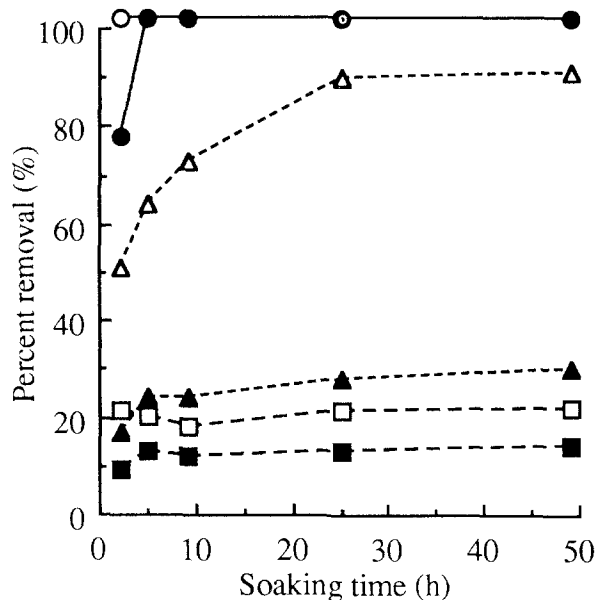
The effect of the initial concentrations on the removal of lead was different from that of mercury, as shown in Fig. 8. One-hundred percent of lead removal was attained within the short period in 1 ppm solution, although, the effectiveness of removal was remarkably reduced in 5 and 10 ppm solutions for both of the single and mixed solutions.



**Fig. 7.** Percent removal of mercury using wood powder carbonized at 1000°C in solutions with different initial concentrations. The solution contained mercuric chloride, lead nitrate, arsenic chloride, and cadmium chloride. Circles, 1 ppm; triangles, 5 ppm; squares, 10 ppm



**Fig. 6.** Percent removal of metal ion using wood powder carbonized at 1000°C in 1 ppm mixture solution of mercuric chloride, lead nitrate, arsenic chloride, and cadmium chloride. Open circles, mercury; filled circles, arsenic; filled triangles, lead; open triangles, cadmium



**Fig. 8.** Percent removal of lead using wood powder carbonized at 1000°C in single and mixed solutions with different initial concentrations. Open symbols are for the single solution; filled symbols are for the mixed solutions. See Fig. 7. for explanation of the concentrations

### Soaking performance of materials in single and mixed solutions

As shown in Table 2, wood-based materials removed mercury at a much faster rate than did activated carbon. In 1 ppm solutions carbonized wood powder removed most of the mercury after 1 h of soaking, whereas it took more than 24 h for AC to reach the same level of removal. For 5 and 10 ppm solutions, among the wood-based materials only C1000 and C600 removed mercury rapidly (within 1 h), although removal in C200 and WP was still fast (within 8 and 4 hours, respectively).

In lead solution at 1 ppm, total removal could be attained by C1000 in a short time (within 1 h). At the higher concentration of 10 ppm, soaking for 48 h seemed not to be enough to reach the equilibrium condition.

Equilibrium was also attained in the short time of 1 h for C1000 in zinc nitrate solution. However, it took about 24 h for C1000 to remove almost the same amount of zinc in the 5 ppm solution. Furthermore, for the 10 ppm solution, although less zinc was removed even after 48 h, more zinc was believed to be removed as the soaking time was prolonged.

In the mixed solutions C1000 removed almost all the mercury after 4, 8, and 24 h, as observed in 1, 5 and 10 ppm concentrations (Table 3). C600 performed almost the same removal as C1000 in 1 ppm solution, and mercury removal

was low even after a longer soaking time for WP and C200. For instance, in 5 ppm solution, only about 60% and 65% of mercury have been removed by these materials, respectively, after 48 h of soaking. This finding could serve as primary data in future experiments on water purification by wood charcoal, and further studies should be conducted.

### Conclusion

Sugi (*Cryptomeria japonica* D. Don) wood and its carbonized wood powder removed mercury in mercuric chloride solutions within the concentration range of 1–10 ppm. Wood powder carbonized at 1000°C performed best among the wood charcoals and even better than activated carbon in both single and mixed solutions. Equilibrium was attained rapidly, within only 1 h. Using C1000, mercury removal was more efficient than removal of zinc, lead, or arsenic at all concentrations, suggesting that mercury was preferentially removed even when mixed with other heavy metals. The removal efficiency of AC was not higher than that of the carbonized wood-based materials that contained lower specific surface areas. The surface chemistry of the materials and the specific surface area were assumed to have contributed to their capacity to remove mercury.

**Table 2.** Removal performance of heavy metals by wood powder, carbonized wood powder, and activated carbon in single aqueous solutions of heavy metallic compounds

Material	1 ppm			5 ppm			10 ppm		
	Hg	Pb	Zn	Hg	Pb	Zn	Hg	Pb	Zn
Wood powder	48 <sup>a</sup>	8 <sup>b</sup>	8 <sup>b</sup>	8 <sup>b</sup>	1 <sup>b</sup>	48 <sup>a</sup>	4 <sup>b</sup>	1 <sup>b</sup>	8 <sup>b</sup>
Carbonized wood powder									
200°C	1 <sup>b</sup>	4 <sup>b</sup>	24 <sup>b</sup>	8 <sup>b</sup>	4 <sup>b</sup>	4 <sup>b</sup>	4 <sup>b</sup>	1 <sup>b</sup>	24 <sup>b</sup>
600°C	1 <sup>b</sup>	24 <sup>b</sup>	48 <sup>a</sup>	1 <sup>b</sup>	1 <sup>b</sup>	48 <sup>a</sup>	1 <sup>b</sup>	1 <sup>b</sup>	24 <sup>b</sup>
1000°C	1 <sup>b</sup>	1 <sup>b</sup>	1 <sup>b</sup>	1 <sup>b</sup>	48 <sup>a</sup>	24 <sup>b</sup>	1 <sup>b</sup>	48 <sup>a</sup>	48 <sup>a</sup>
Activated carbon	24 <sup>b</sup>	4 <sup>b</sup>	24 <sup>b</sup>	48 <sup>b</sup>	48 <sup>a</sup>	24 <sup>b</sup>	1 <sup>b</sup>	48 <sup>a</sup>	8 <sup>b</sup>

Removal was negligible for arsenic.

<sup>a</sup>Removal is still increasing over the denoted time.

<sup>b</sup>Time to attain the equilibrium condition for metal removal.

**Table 3.** Removal of heavy metals by wood powder, carbonized wood powder, and activated carbon in mixed aqueous solutions

Material	1 ppm				5 ppm				10 ppm			
	Hg	As	Pb	Cd	Hg	As	Pb	Cd	Hg	As	Pb	Cd
Wood powder	48 <sup>a</sup>	c	48 <sup>a</sup>	c	48 <sup>a</sup>	c	1 <sup>b</sup>	c	48 <sup>a</sup>	c	c	c
Carbonized wood powder												
200°C	48 <sup>a</sup>	c	48 <sup>a</sup>	c	48 <sup>a</sup>	c	4 <sup>b</sup>	c	c	c	48 <sup>a</sup>	8 <sup>b</sup>
600°C	4 <sup>b</sup>	c	48 <sup>a</sup>	48 <sup>a</sup>	24 <sup>b</sup>	c	48 <sup>a</sup>	c	48 <sup>a</sup>	c	c	c
1000°C	4 <sup>b</sup>	c	4 <sup>b</sup>	48 <sup>a</sup>	8 <sup>b</sup>	c	48 <sup>a</sup>	c	24 <sup>b</sup>	c	48 <sup>a</sup>	c
Activated carbon	8 <sup>b</sup>	24 <sup>b</sup>	48 <sup>b</sup>	48 <sup>a</sup>	24 <sup>b</sup>	c	48 <sup>a</sup>	c	48 <sup>a</sup>	c	48 <sup>a</sup>	c

<sup>a,b</sup>Same as in Table 2.

<sup>c</sup>Removal was negligible.

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