

## CARBONIZED MATERIAL ADSORBENTS FOR THE REMOVAL OF MERCURY FROM AQUEOUS SOLUTIONS

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### Introduction

Although wood has essentially been excluded as a starting material for the production of granular activated carbon because of the poor strength and friability of the products <sup>1)</sup>, powdered wood based activated carbons are still being used in water treatment and other liquid phase applications. However, the capability of powdered wood-based charcoal which in itself porous has not been fully known. Few studies have been conducted in harnessing its potential for adsorption purposes especially in water treatment.

This study was conducted to investigate the possibility of using wood based carbonized materials from Sugi (*Cryptomeria japonica* D. Don) as adsorption materials in aqueous solutions of heavy metals like mercury, zinc, lead, cadmium and arsenic. However, of all the heavy metals investigated, mercury is considered to be the most toxic so this paper describes only the adsorption ability of the carbonized materials in adsorbing this metal from aqueous solutions of different concentrations.

### Materials and Methods

#### A. Materials

The raw materials used in this study were Sugi, activated carbon from coconut shell and Mercuric chloride ( $\text{HgCl}_2$ ) as heavy metal.

#### B. Methods

1. Preparation of Materials: Small diameter logs of Sugi were cut into flakes and made into powder. Wood powder was passed through a 20-mesh size sieve. The wood powder was oven-dried at  $105 \pm 2$  °C prior to carbonization.

2. Carbonization Process: Wood powder was carbonized in a furnace with the desired temperatures of 200, 400, 600, and 1000 °C. Nitrogen ( $\text{N}_2$ ) gas of 1500 ml/min. was flowed in a heating rate of 4 °C/min. After getting the desired temperature, it was kept for one hour and then turned it off. The charcoal was cooled naturally before it was taken out of the furnace.

3. Adsorption Experiment: Aqueous solutions of 5, 50 & 100 ppm  $\text{HgCl}_2$  were prepared. Each of the carbonized materials with a weight of 0.5 g was mixed with 50-ml  $\text{HgCl}_2$  solution and continuously stirred in a hotting bath at  $30 \pm 2$  °C for 1, 4, 8 and 24 hours of soaking time. The mixtures were filtered with ADVANTEC Toyo glass fiber filter paper. The concentration of the filtered solution was determined using an Inductively Coupled Plasma machine.

4. Determination of Acidity and Dissolved Oxygen of the Solute: The acidity of the solution was measured using a pH meter while that of the dissolved oxygen was measured using a COD meter.

### Results and Discussion

#### 1. Adsorption ability of carbonized wood materials

Figures 1-3 show the relationship between total soaking time and adsorption of carbonized materials. Based from Fig. 1, similar adsorption behavior was observed in all the carbonized materials. The adsorption was highest in 1000 °C in all the total soaking times, and then followed by 600 °C and 200 °C. It can be observed that the adsorption in activated carbon is not comparable with the high temperature carbonized materials. Further, adsorption in 1000 °C was almost the same in all the total soaking times.

In Fig.2, adsorption was still highest in 1000 °C in all the soaking times and then followed by 600 °C and activated carbon. However, it can be observed that 105 °C and 200 °C had a remarkable adsorption compared when soaked at 5 ppm solution and even comparable with the high carbonized materials (8 & 24 hours).

Different results were observed in 100 ppm solution (Fig.3). Although the adsorption trend of all the carbonized materials in all the total soaking hours was the same with that of 5 and 50 ppm, it can be observed that at higher concentrations of HgCl<sub>2</sub> solution, higher adsorption is observed not only at 1000 °C but also in activated carbon. Moreover, it can be noticed that activated carbon adsorbed almost the same as the high carbonized materials unlike in the low concentrations.

Generally, the extent of adsorption depends mainly on the surface area and the chemical nature of the adsorbents.<sup>2)</sup> Based from the preliminary measurement of the specific surface area of the adsorbents, high carbonized materials have higher specific surface areas. However, in this study, it is clear that surface area was independent of the adsorption. The higher temperature carbonized materials with a high specific surface area performed almost the same with the low temperature materials. The chemical properties which can be a source of explanation on certain extent seem not to have any effect especially on lower concentrations of HgCl<sub>2</sub> solutions. The elemental analysis results of the carbonized materials<sup>3)</sup> revealed that the carbon contents increases with the increase of temperatures. Consequently, carbonized materials with high carbon content adsorb more than those with low carbon content materials. However, in higher concentrations of HgCl<sub>2</sub>, higher carbonized materials adsorb more than those of low carbonized materials.

According to Lee, et al.<sup>4)</sup>, in general, adsorption capacity can be influenced both by the microspore structure and also by the surface chemistry interactions. Carbon surfaces are covered with chemisorbed oxygen species which have a profound influence on surface properties.<sup>5)</sup> In a study conducted on the removal of chromium (metal) from aqueous solutions by activated carbon adsorbents, it has been observed that not only the microporous structures and the surface area but the chemical structure of the carbon surface plays an important role in the adsorption. In particular, the nature of the surface-oxygen chemical structure present in the carbon surface, not the total amount of oxygen determines the adsorption of chromium.<sup>6)</sup> The addition of oxygen-containing functional groups to the carbon surface caused by the exposure in the atmospheric thus altering its adsorptive properties<sup>7)</sup> is a probable source of change in the surface oxygen chemical structure which in turn affects its adsorption capability.

In another study conducted on the lightest metal, Lithium(Li), diffusion is the main parameter in controlling the adsorption of this metal. Interaction of Li with surface groups may also play an important role in the adsorption process.<sup>8)</sup>

## 2. Water purification ability of carbonized materials

In connection with the pollution of water, the content of dissolved oxygen in water is of prime concern. The overuse of water systems for disposal purposes in many instances had almost fully depleted the dissolved oxygen available for life support.

In this study, the amount of COD was monitored with soaking time. Table 1 shows the decrease in the amount of COD of the HgCl<sub>2</sub> solution

after 24 hours of soaking the carbonized materials. Rate of decrease is somewhat higher for the high carbonized materials and activated carbon. The decrease in the COD values through time can be observed through a sample graph as shown in Fig.7.

The pH values after treating the carbonized materials in 24 hours is shown in Table 2. The original  $\text{HgCl}_2$  solutions which was acidic was made close to neutral or neutral for 600 °C and 1000 °C, and activated carbon after it was treated with carbonized materials. However, at 105 °C and 200 °C, the pH values also increased but at low concentrations only. Fig. 9 shows the behavior of pH value with total soaking time.

#### Conclusion

Wood based carbonized materials can be used as adsorption materials in treating aqueous solutions of heavy metals like mercury. However, the behaviour of the adsorption of carbonized materials in  $\text{HgCl}_2$  solutions cannot still fully explained because of lack of basic information on the nature of the adsorbent materials. Microporous structure and surface-oxygen chemical structure present in the carbon surface will be investigated in future studies to further explain the adsorption ability of this heavy metal.

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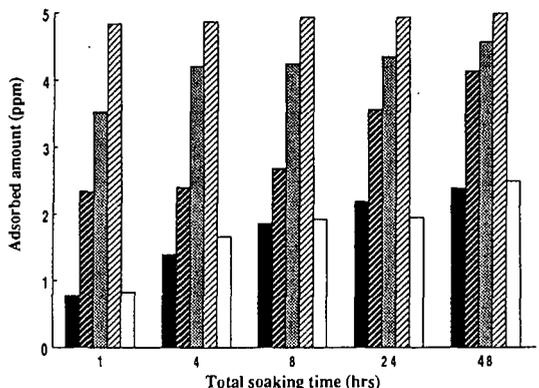


Fig. 1. Relationship between total soaking time and adsorbed amount of HgCl in 5 ppm aqueous solution.

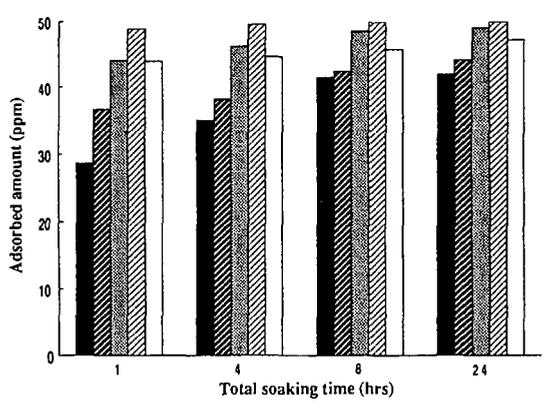


Fig. 2. Relationship between total soaking time and adsorbed amount of HgCl in 50 ppm aqueous solution.

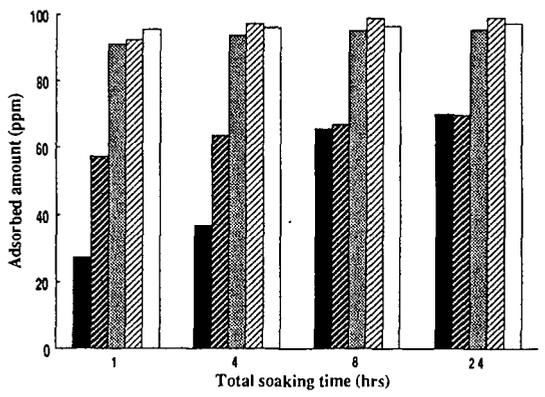


Fig. 3. Relationship between total soaking time and adsorbed amount of HgCl in 100 ppm aqueous solution.

Legend: ■ Control  
 ▨ 200°C  
 ▩ 600°C  
 ▤ 1000°C  
 □ Activated charcoal

Note: Control - wood powder oven-dried at 105°C

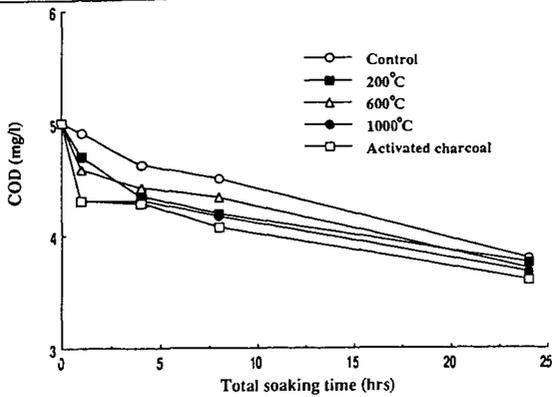


Fig. 4. Relationship between total soaking time and COD in 100 ppm aqueous solution.

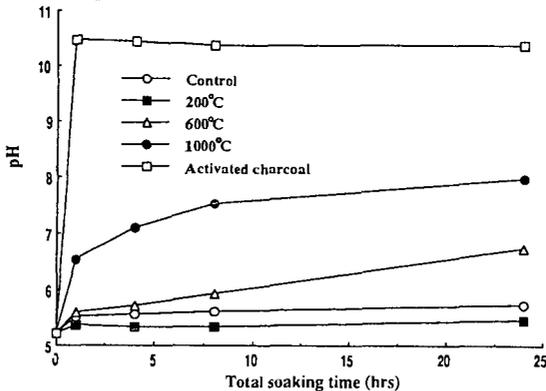


Fig. 5. Relationship between total soaking time and pH in 5 ppm aqueous solution.

Table 1. Effects of carbonized materials on the COD of HgCl<sub>2</sub> aqueous solutions after 24 hours.

	COD (mg/l)			Rate of decrease (%)		
	1	2	3	1	2	3
Original HgCl <sub>2</sub> solution	5.600	5.050	5.000	-	-	-
Carbonized materials						
Control	3.570	3.650	3.790	36	28	24
200 °C	3.520	3.620	3.750	38	28	25
600 °C	3.460	3.600	3.100	38	29	38
1000 °C	3.460	3.500	3.070	38	31	39
Activated charcoal	3.390	3.450	3.000	39	32	40

Legend: 1 - 5 ppm; 2 - 50 ppm; 3 - 100 ppm

Table 2. pH values of HgCl<sub>2</sub> aqueous solutions treated with carbonized materials after 24 hours.

	pH		
	1	2	3
Original HgCl <sub>2</sub> solution	5.21	4.92	5.23
Carbonized materials			
Control	5.72	5.12	4.45
200 °C	5.45	4.88	4.69
600 °C	6.73	5.98	5.79
1000 °C	7.96	7.56	7.34
Activated charcoal	10.35	9.60	9.11

Legend: same as in Table 1.