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Adsorption of mercury by sugi wood carbonized at 1000°C

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Abstract The ability of sugi wood carbonized at 1000°C to adsorb mercury was examined using aqueous solutions of mercuric chloride. Parameters studied include contact time, pH, adsorption temperature, and initial concentration of mercury in solution. Results showed that sugi wood carbonized at 1000°C could effectively remove mercury from aqueous solutions. The carbonized wood showed high adsorption ability for mercury at a wide pH range (pH 3–9), but its ability drastically decreased at pH 11. Adsorption decreased with increases in adsorption temperatures, indicating that the processes were exothermic in nature. Adsorption was found to follow the Freundlich isotherm model. The adsorption capacity of carbonized sugi wood was comparable to that of commercial activated carbon.

Key words Carbonized sugi wood · Mercury adsorption

Introduction

Mercury is one of the most toxic heavy metals in the environment. Because of its high toxicity, it is necessary to reduce its spread in the environment. Considerable research has been conducted on the reduction of this metal, but there is still an urgent need for immediate removal of mercury in wastewater systems.

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Activated carbons have been widely used to remove mercury,[1–3] but the high capital costs have demanded that we look for alternative materials. Fertilizer waste,[4] bituminous coal,[3,5–7] and waste tire rubber[8] have shown high potential capacities to adsorb mercury from industrial wastewater. Effective, economical adsorbents such as fly ash, iron oxide dispersed activated carbon fibers, waste rubber, polymerized onion skin, peat moss, polymerized sawdust, cellulose, and "waste" Fe(III)/Cr(III) hydroxides were also used to remove mercury from waste waters.[9] Recently, carbonized waste newsprint,[10] activated carbons from peat, lignin, and pitch[11] and coirpith carbon[9] were found to have high adsorption potential for mercuric ions.

In our previous studies,[12–14] we found that carbonized sugi (*Cryptomeria japonica* D. Don) woods at high temperatures could completely remove mercury from aqueous solutions. These adsorbent materials could also selectively removed mercury from aqueous solutions containing $HgCl_2$, $Zn(NO_3)_2$, $Pb(NO_3)_2$, and $AsCl_2$. Within the limited range of concentration studied, maximum loading of mercury on the adsorbent materials made comparison of adsorption performances impossible. Additional laboratory studies using either low adsorbent doses or high contaminant concentrations are needed to examine the type of adsorption.

This study was conducted to determine the adsorption capacity of carbonized sugi (*Cryptomeria japonica* D. Don) wood for mercury. Among the carbonized woods tested, sugi wood carbonized at 1000°C showed high adsorption capacity to mercury. The effects of contact time, pH, adsorption temperature, and initial concentration of mercury were examined in this study.

Materials and methods

Materials

Wood powder from sugi (*Cryptomeria japonica* D. Don) passing a 20 mesh (840 μm) sieve was used. Commercial activated carbon (reagent grade powdered, Nacalai tesque product) was used as a reference material.

Carbonization process

Wood powder was oven-dried at 105°C for 24h before carbonization. Wood powder was carbonized in a nitrogen flow at 600°C followed by further carbonization at 1000°C in a nitrogen atmosphere, an airflow rate of 2000ml/min for 1h, or both.

Adsorption experiment

The carbonized material was soaked in dilute HNO_3 overnight and then washed thoroughly with deionized water until the pH became neutral. This step eliminated the effect of the original pH of this material when soaked in $HgCl_2$ solution adjusted to a desired pH. The material was then dried at 105°C in an electric oven after the pretreatment. The commercial activated carbon was treated in the same manner described for preparation of the carbonized sugi wood.

The ability of carbonized sugi wood to remove mercury from $HgCl_2$ solutions containing 10–1000mgHg/l was determined in batch mode conditions. The test solution (50ml) was added to the adsorbent (about 100mg), and the suspension was shaken from 10°C to 60°C. The initial pH of the solution was adjusted from pH 3 to pH 11 with dilute HCl or 0.01M NaOH. At the end of the designed contact time, the suspension was filtered off. The filtrate was oxidized using sulfuric acid, and then the Hg^{2+} formed was reduced by adding tin(II) chloride. The amount of mercury vapor generated was measured at a wavelength of 253.7nm using an NIC mercury analyzer RA-2A (Nippon Instruments, Tokyo, Japan). Experiments were duplicated, and the results were averaged.

Results and discussion

In previous studies we reported that carbonized sugi woods showed high affinity for mercury in the concentration range 1–10ppm.[12–14] Of the carbonized sugi woods tested, the adsorbent carbonized at 1000°C could completely remove mercury from aqueous solutions. Likewise, this adsorbent showed the highest iodine adsorption capacity,[15] indicating its high potential for removing heavy metals from wastewater.

The effect of contact time on the adsorption of mercury using sugi wood carbonized at 1000°C and activated carbon is shown in Fig. 1. The activated carbon was employed as a reference to compare the performance of the carbonized wood. The amounts of mercury adsorbed onto these adsorbents increased rapidly during the first hour (46.7mg/g, 92% removal) and then reached equilibrium within 16–24h. Carbonized sugi wood and activated carbon are comparable in terms of their initial rates of adsorption and equilibrium mercury adsorption capacities. For the subsequent studies a contact time of 24h was employed.

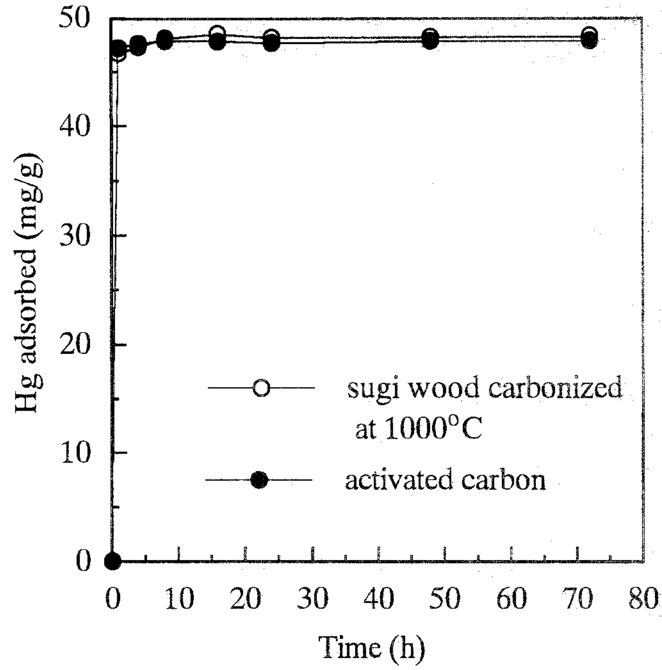

Fig. 1. Effect of soaking time on mercury adsorption onto sugi wood carbonized at 1000°C and activated carbon from $HgCl_2$ solution of pH 6. Adsorbent material (0.1g) was shaken with 50ml of $HgCl_2$ solutions containing 100mgHg/l at 30°C

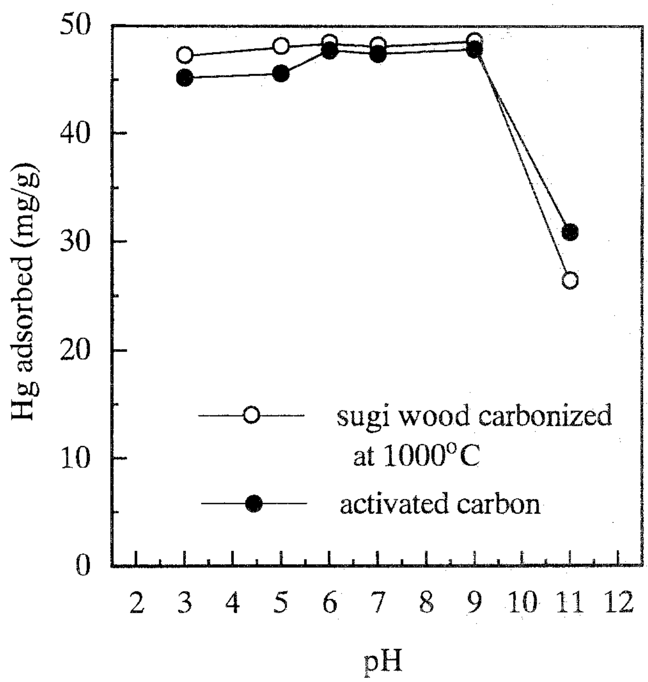

Fig. 2. Effect of pH of $HgCl_2$ solution on mercury adsorption onto sugi wood carbonized at 1000°C and activated carbon. Adsorbent material (0.1g) was shaken with 50ml of $HgCl_2$ solutions containing 100mgHg/l at 30°C for 24h

As shown in Fig. 2, carbonized sugi wood was efficient in adsorbing mercury at a wide pH range (pH 3–9). The predominant mercuric ion species in acidic medium are $HgCl_2$,

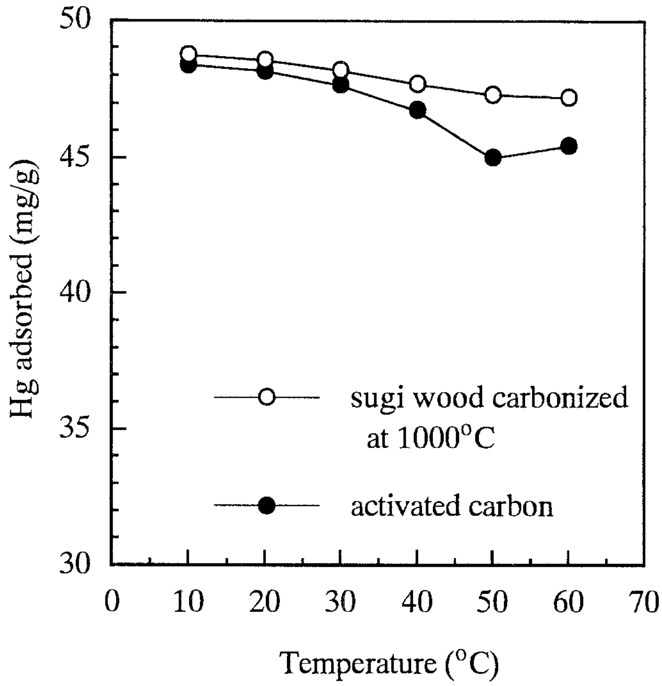

Fig. 3. Effect of temperature on mercury adsorption onto sugi wood carbonized at 1000°C and activated carbon. Adsorbent material (0.1 g) was shaken with 50 ml of $HgCl_2$ solutions containing 100 mg Hg/l at pH 6 for 24 h

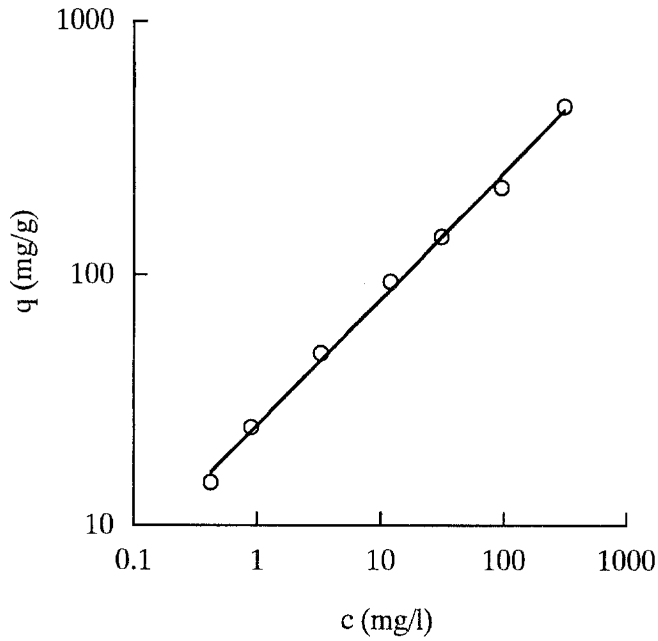

Fig. 4. Freundlich plots of the isotherm data for mercury adsorbed onto sugi wood carbonized at 1000°C. Adsorbent material (0.1 g) was shaken with 50 ml of $HgCl_2$ solutions containing 10–1000 mg Hg/l at a fixed initial pH of 6 and a constant temperature of 30°C. *q*, amount adsorbed; *c*, equilibrium concentration

$HgCl^+$, and Hg^{2+}.[3,8,9] When mercuric chloride is dissolved in dilute HCl, their corresponding chloro complexes, such as $HgCl_4^{2-}$ and $HgCl_3^-$, may be formed.[7] However, it has been reported that mercury adsorption markedly decreased with increasing concentration of mercury-chloro complexes.[3,16] Because the dominant mercury (II) species is $HgCl_2$ (more than 80%) in 0.01 N HCl,[16] the carbonized wood have high affinity for $HgCl_2$ in acidic medium. On the other hand, the dominant mercury species in neutral and basic solutions are $Hg(OH)_2$ and some other anionic hydroxo complex species.[3] Therefore, mercury adsorption mechanism for H-type carbon in basic and neutral media may differ from that in acidic medium.

Mercury adsorption onto carbonized sugi wood was temperature-dependent, as shown in Fig. 3. The adsorption capacity for mercury decreased from 48.5 to 47.7 mg/g when the solution temperature rose from 20° to 40°C. The decrease in adsorption capacity with an increase in adsorption temperature can be explained by the thermodynamic parameters computed using the following equations.

An equilibrium is established between the liquid and solid phases for adsorption of an adsorbate from solution to solid phase. The equilibrium constant K_c is calculated[17] as:

$$K_c = C_{Be}/C_{Ae} \quad (1)$$

where C_{Be} and C_{Ae} are the equilibrium concentrations for mercury on the adsorbent and in solution, respectively. The thermodynamic parameters, that is, the standard free energy (ΔG^o) and enthalpy (ΔH^o) changes, are calculated using the following equations.[18]

$$\Delta G^o = -RT \ln K_c \quad (2)$$

$$\Delta H^o = R(T_2T_1/KT_2 - T_1) \ln(T_{c2}/K_{cl}) \quad (3)$$

where Kc_1 and Kc_2 are the equilibrium constants at T_1 *and* T_2 °K, and R is the universal gas constant (8.314 J/mol/°K). The values of ΔG^o at 20° and 40°C were found to be −22.1 and −22.3 kJ/mol, respectively. The negative values of free energy change indicate the feasibility of the adsorption process. The standard enthalpy change between 20° and 40°C was found to be −19.4 kJ/mol, indicating that the adsorption was exothermic.

At a fixed initial pH 6 and a constant temperature of 30°C, the initial concentration of mercury was varied from 10 to 1000 mg/l. Mercury adsorption increased with increases in the initial concentration. The Freundlich isotherm model,[19] represented by the following equation, was used to explain the adsorption behavior.

$$\log q = \log k + 1/n \log c \quad (4)$$

where c is the equilibrium concentration (mg/l), q is the amount adsorbed (mg/g), and k and $1/n$ are Freundlich constants. The intercept of the straight line ($\log k$), roughly indicates the adsorption capacity, and the slope ($1/n$) indicates the adsorption intensity. The data are fitted to the logarithmic form of the Freundlich equation (Fig. 4). The constants k and $1/n$ were found to be 25.004 and 0.504, respectively, as shown in Table 1. From the k values, the adsorption of carbonized sugi wood was found to be comparable to that of activated carbon.

The Langmuir isotherm model was also used to explain the adsorption behavior.[19] The equilibrium data were fitted to the Langmuir isotherm, but the correlation coefficient

Table 1. Freundlich isotherm constants

Adsorbent material	Freundlich isotherm		
	k	$1/n$	r^2
Sugi wood carbonized at 1000°C	25.004	0.504	0.996
Activated carbon	24.605	0.509	0.996

Adsorbent material (0.1 g) was shaken with 50 ml of $HgCl_2$ solutions containing 10–1000 mg Hg/l at 30°C. r^2, coefficient of correlation

(r^2) was 0.897. That is, the equilibrium data cannot be analyzed using the Langmuir isotherm model.

In conclusion, carbonized sugi wood can effectively adsorb mercury from an aqueous solution of mercuric chloride. It can be used as an alternative material for the treatment of wastewater containing mercury.

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