Activated carbons derived from organic sewage sludge for the removal of mercury from aqueous solution

F.-S. Zhang[1], H. Itoh[1] & J. O. Nriagu[2]
[1]*Division of Environmental Research, EcoTopia Science Institute, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan*
[2]*Department of Environmental Health Sciences, School of Public Health, The University of Michigan, Ann Arbor, MI 48109, USA*

Abstract

Various types of activated carbons were developed from organic sewage sludge (SS) using H_2SO_4, H_3PO_4 and $ZnCl_2$ as chemical activation reagents. The surface morphology of the SS carbons was examined, and the activation mechanisms of the chemical reagents were extensively discussed. The surface areas of the activated carbons were within 289-555 m^2/g. $ZnCl_2$ activated carbon had the highest adsorption capability for Hg(II), followed by H_3PO_4 and H_2SO_4 activated carbons, and the adsorption followed the Freundlich isotherm model. The leaching amount of As, Cr(VI), Cd, Hg and Pb from the SS carbons was below the wastewater disposal limits issued by the Ministry of Environment of Japan. Accordingly, it is believed that the activated carbons developed in this study are safe and practical for utilization in mercury removal from industrial wastewater.

1 Introduction

In Japan, the major disposal methods for sewage sludge (SS) are incineration, landfill, composting, etc. nowadays. SS is rich in carbonaceous organic material, thus has the potential to be converted into activated carbon. In recent years, some companies are attempting to produce carbonaceous material using SS so as to recycle the waste material and save the landfill sites. Nevertheless, the resulting material is usually consumed within the companies which produce it and is



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difficult to market commercially, because the quality is rather poor compared to commercial activated carbon. Therefore, it is necessary and urgent to improve the quality of the carbonaceous material.

Many studies have been carried out on sludge-based activated carbons, and the products have been investigated for the adsorption of gaseous pollutants such as toluene, hydrogen sulfide, nitrogen dioxide, sulfur dioxide, and liquid pollutants such as phenol, dye, etc. [1-4]. However, little information is available concerning their adsorption properties on the removal of mercury from aqueous solution.

The emphasis of this study was to prepare low-cost and high-quality activated carbons from organic SS, and to examine their possible application for mercury removal from wastewater. Three kinds of chemical reagents, i.e. H_2SO_4, H_3PO_4 and $ZnCl_2$ were employed as activation reagents. Among them, H_2SO_4 and $ZnCl_2$ have been studied by previous researchers and were found to be the most effective chemical reagents in the preparation of activated carbon from sewage sludge [1, 2]. On the other hand, H_3PO_4 has been shown to be the most environmentally sound chemical for activation process [5], and has also been reported to have the effect of in-situ stabilization of toxic heavy metals contained in waste materials [6], therefore it was also employed in this study. The surface morphology of the carbons and heavy metal leaching from the carbons was examined. Furthermore, the adsorption isotherms of mercury from aqueous solution by the carbons were examined.

2 Experimental

2.1 Activated carbon preparation

Sewage sludge (SS) was obtained from the Yamazaki Sewage Sludge Disposal Plant in Nagoya of Japan. The carbon content of the sludge is about 40% at a dry weight basis, and the loss on ignition (LOI) value of the sludge is 77.1%. We therefore call it organic SS. Sludge sample was firstly dried at 105℃ for 24 h in an oven, air-cooled and crashed to uniform size. A portion of 20 g of the sample was added to 50 ml of 3M H_2SO_4, 3M H_3PO_4 or 5M $ZnCl_2$ solutions, then stirred thoroughly until well mixed, and left to stand for 24 h. After the supernatant liquid was removed, the samples were subject to vacuum drying at 105 ℃ for 24 h. The resulting chemical loaded samples were then pyrolyzed in a quartz tube (42mm i.d.) in N_2 atmosphere. The heating rate was 10 ℃ /min, and the N_2 gas flow rate was 300 ml/min. The samples were held at 650 ℃ for 60 min. After cooling the carbonized products that have been activated with H_2SO_4 and H_3PO_4 were washed with 1 M NaOH solution, followed by filtration. The samples were then washed by distilled water for several times until the pH value of the leachate were <7. For the sample treated with $ZnCl_2$, a 1M HCl solution was used instead of NaOH solution in the washing procedure and the sample was then washed by distilled water to reach a pH value above 6. The activated carbons were then vacuum dried at 105 ℃ for 24 h, ground and sieved to <2 mm for use.

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2.2 Characterization of the activated carbons

Surface area of the activated carbons was analyzed by a Monosorb (Quantachrome, MS-21) surface analyzer using nitrogen adsorption-desorption isotherms at 77 K. Samples were out-gassed for 24 h at 120 ℃ in a vacuum oven before analysis.

The surface morphology of the SS and the activated carbons were examined using a scanning electron microscope (SEM, JSM-6330F) coupled with an energy-dispersive X-ray spectrometer (EDS, JED-2140).

Metallic elements were analyzed with inductively coupled plasma atomic emission spectroscopy (ICP-AES, Perkin-Elmer).

The pH value of the adsorption solution was adjusted with diluted HCl or NaOH solutions and determined by a HORIBA D-21 pH meter.

2.3 Adsorption experiment

A series of 250ml capped polyethylene bottles were employed and each bottle was filled with 100 ml of 120 mg/L mercury solution. A known carbon dose varied from 0.01 to 1.0 g was added to each bottle, and the pH was adjusted to 5.0 using diluted HCl or NaOH solutions. The temperature was 25 ℃ and the contact time was 12 h to assure the equilibration of the adsorption according to the preliminary experiments. The amount of mercury removal was calculated from the differences between the concentrations of mercury before and after adsorption. Mercury concentration in the solutions was determined using a Tekran CVAFS mercury detector (Model 2500) connected with a Hewlett-Packard printer (HP 3396A integrator). Method detection limit (MDL) for this instrument is 0.2 ng/L. Carbon-free controls were run concurrently in all experiments.

2.4 Heavy metal leaching experiment

The standard leaching test method known as Bulletin No. 13 of the Ministry of Environment (Japan) was used to examine the metal leaching amount from the SS carbons. Briefly, a solid / liquid ratio of 1:10 was used, and the pH value of the extracting solvent was adjusted to 5.8-6.3 with 0.01M HCl and 0.01M NaOH solutions, then vibrated for 6 h at 20 ℃ and filtrated. Metal concentrations in the filtrate were determined by ICP-AES. The details of the method were presented elsewhere [7].

3 Results and discussion

3.1 Surface physical morphology of the SS activated carbons

Many studies have been conducted on SS carbonization by using different chemical activating reagents and under various conditions. The resulting solids were reported to have a surface area of 100-400 m^2/g [1-3]. Our results are illustrated in Fig. 1. For inactivated SS carbon, the area is 137 m^2/g, but the area

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could be enhanced to 289-555 m^2/g by different chemical activation treatments. Among the chemical reagents, $ZnCl_2$ has the highest activation effect. The carbon contents of SS-C, SS-S, SS-P and SS-Z are 42.2%, 58.7%, 31.9% and 53.6%, respectively. They are generally consistent with the surface area values.

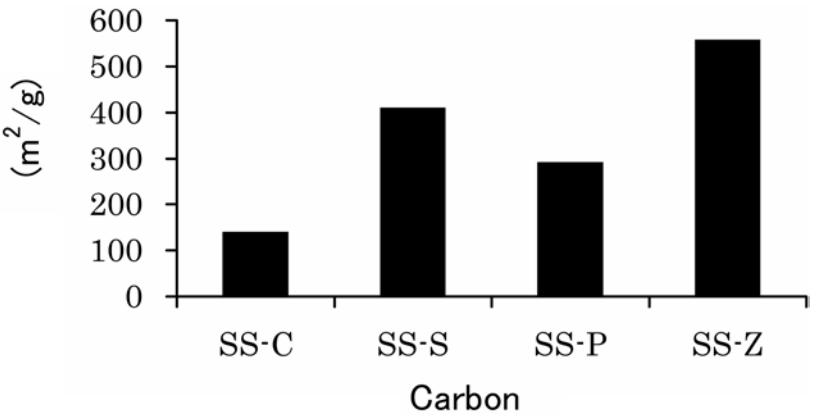


Figure 1: Surface area of various sewage sludge carbons. SS-C: sewage sludge carbon; SS-S: H_2SO_4 activated SS carbon; SS-O: H_3PO_4 activated SS carbon; SS-Z: $ZnCl_2$ activated SS carbon.

Selected SEM photographs of the SS carbons are shown in Fig. 2. As can be seen, the surface morphology of the carbons is quite different according to activation reagents. Relatively larger pores on the surface of SS-C and SS-S could be seen, these pores are supposed mainly to be meso- and macropores. Unlike other carbons, the surface of SS-P is leaf-shape like petals. Although H_2SO_4, H_3PO_4 and $ZnCl_2$ have been found to be effective activating reagents in activated carbon manufacture process, their activation mechanisms are less understood thus far. The pores on the surface of the SS carbons could partly attribute to the evaporation of these chemical reagents during carbonization, leaving the space previously occupied by the reagents. Additionally, H_2SO_4 has the potential of chemically reacting with the mineral components contained in SS sample. For example, it can react with carbonates and generate CO_2 and water; hence pore structure could be formed. H_3PO_4 could function both as an acid catalyst to promote bond cleavage reactions and the formation of crosslinks via processes such as cyclization, and condensation. It could also combine with organic species to form phosphate and polyphosphate bridges that connect and crosslink biopolymer fragments. The addition or insertion of phosphate groups drives a process of dilation that, after removal of the acid, leaves the matrix in an expended state with an accessible pore structure [8]. The external surface appearance of SS-Z is quite different from the other carbons. In the pyrolysis process, $ZnCl_2$ acts as a dehydrating agent that promotes the decomposition of carbonaceous material and restricts the formation of char. The degradation of cellulose material and the aromatization of the carbon skeleton upon $ZnCl_2$

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treatment result in the creation of the porous structure [9]. At high $ZnCl_2$ concentration, such as 3M solution in this study, some $ZnCl_2$ remains in the external part of the carbon particles and widens the porosity by a localized decomposition of the organic matter. This process results in the enhancement of the meso- and macropore formation.

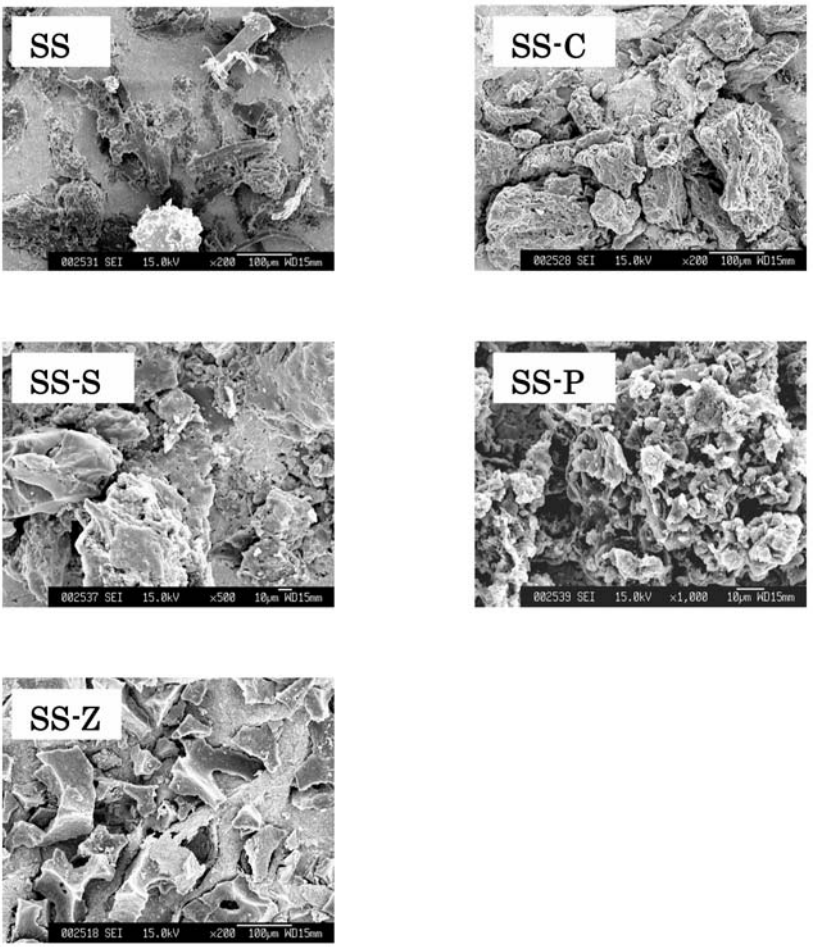


Figure 2: SEM photographs of various sewage sludge carbons. SS: sewage sludge sample; SS-C: sewage sludge carbon; SS-S: H_2SO_4 activated SS carbon; SS-P: H_3PO_4 activated SS carbon; SS-Z: $ZnCl_2$ activated SS carbon.

3.2 Adsorption isotherms

The adsorption isotherms of Hg(II) onto various SS carbons were studied at 25°C with initial Hg(II) concentration of 120 mg/L, and the results were

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illustrated in Fig. 3. The data were fitted to Freundlich isotherm. The Freundlich expression is an empirical equation based on a heterogeneous surface, which is given as follows:

$$\text{Log } q_e = \log K_F + (1/n) \log C_e \quad (1)$$

where q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), and K_F and n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

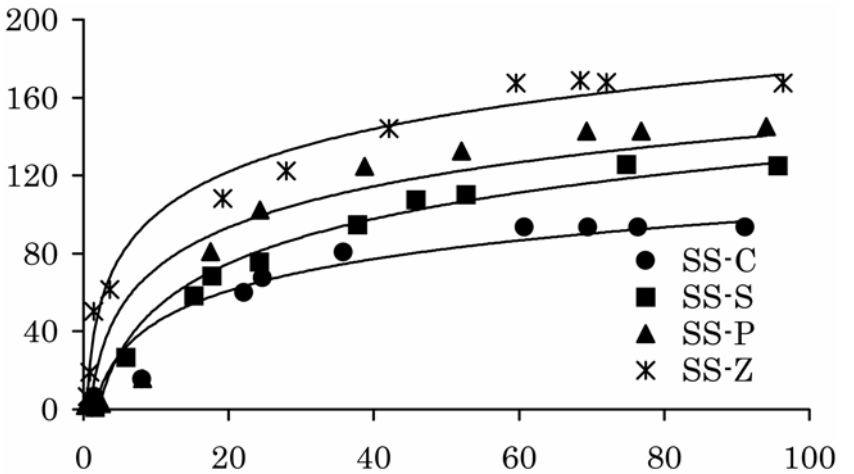


Figure 3: Adsorption isotherm of Hg (II) on various SS carbons.

Table 1: Freundlich constants for Hg (II) uptake by various SS carbons.

	1/n	K_F (mg/g)	R^2
SS-C	0.96	10.1	0.9972
SS-S	0.91	13.6	0.9901
SS-P	0.86	16.0	0.9869
SS-Z	0.32	42.6	0.9926

A plot of log q_e versus log C_e gives linear plots showing that the adsorption follows Freundlich isotherm model (Fig. 4). The Freundlich constants 1/n and K_F were calculated using the slopes and intercepts of the lines and were listed in Table 1. High values of R^2 indicate that the adsorption follows Freundlich isotherm model perfectly. The values of 1/n, between 0 and 1, indicate the

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heterogeneity of the SS carbons [10]. Furthermore, the smaller 1/n and larger K_F values for SS-Z indicate that SS-Z carbon has higher adsorption capacity, intensity and affinity for mercury than the other types of SS carbons [11].

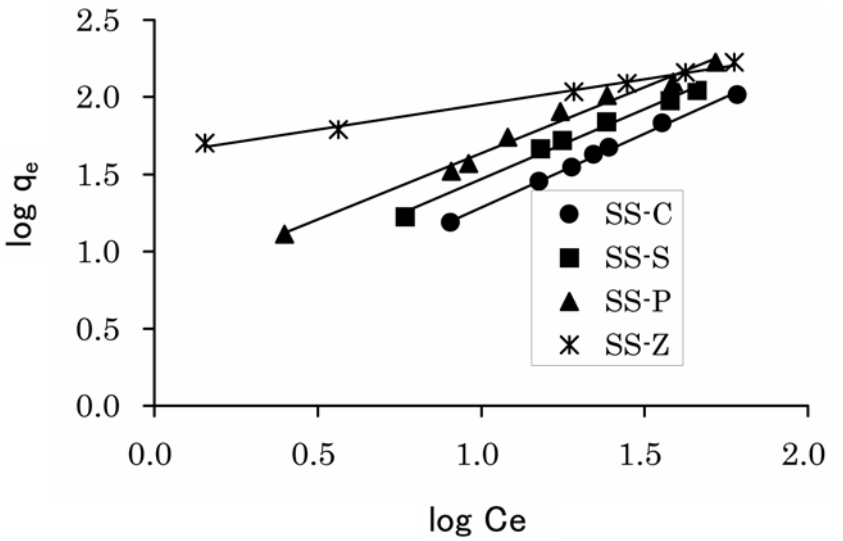


Figure 4: Freundlich isotherm of Hg (II) adsorption onto various SS carbons. Initial Hg (II) concentration = 120 mg/L, pH = 5.0, contact time = 7 h, temperature = 25 ^{o}C.

3.3 Leaching of heavy metals from the SS activated carbons

Heavy metal leaching from the activated carbons was examined so as to assess their possibility of direct utilization in wastewater treatment without causing reverse contamination to aqueous system. Table 2 shows that elements leached out from the carbons were mainly major metals such as Na, Mg, Al, K, Ca and Fe, which are around 1 to 26 mg/L, while the other heavy metals were generally less than 1 mg/L. Among the foregoing, As, Cr(VI), Cd, Hg and Pb have been listed by the Ministry of Environment of Japan as industrial wastewater disposal standards, i.e., the standard limits for these elements are 0.1 mg/L, 0.5 mg/L, 0.1 mg/L, 0.005 mg/L and 0.1 mg/L, respectively [12]. As can be seen from Table 2, the leaching amount of the three elements were all below the restrict limits. Accordingly, it is believed that the activated carbons developed in this study are safe for utilization in industrial wastewater treatment.

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Table 2: Leaching of selected elements from various sewage sludge carbons (mg/L).

	SS-C[a]	SS-S	SS-P	SS-Z
Na	2.11	1.86	3.12	1.24
Mg	6.04	2.91	1.95	1.29
Al	4.72	4.28	2.27	7.04
K	8.67	2.60	1.87	1.64
Ca	18.2	14.4	5.87	3.90
Ti	<0.1	0.32	<0.1	<0.1
V	<0.1	<0.1	<0.1	<0.1
Cr	0.16	0.12	<0.1	<0.1
Mn	0.37	0.16	<0.1	<0.1
Fe	26.3	26.6	1.55	5.69
Co	<0.1	<0.1	<0.1	<0.1
Ni	<0.1	<0.1	<0.1	<0.1
Cu	1.13	<0.1	0.13	<0.1
Zn	1.09	0.23	0.22	60.3
As	<0.1	<0.1	<0.1	<0.1
Sr	0.14	<0.1	<0.1	<0.1
Ba	<0.1	<0.1	<0.1	0.34
Cd	<0.1	<0.1	<0.1	<0.1
Hg	ND[b]	ND	ND	ND
Pb	<0.1	<0.1	<0.1	<0.1

[a]SS-C: sewage sludge carbon; SS-S:H_2SO_4 activated SS carbon; SS-P: H_3PO_4 activated SS carbon; SS-Z: $ZnCl_2$ activated SS carbon. [b]ND: not detectable.

4 Conclusions

Carbonation of waste materials resulted from municipal wastewater treatment plant has been conducted by previous researchers. However, less information is available regarding mercury removal from aqueous solution by the carbonaceous solids. In this study various types of activated carbons were developed from organic SS, and the removal of Hg(II) from aqueous solution by these carbons was effectively demonstrated.

Of the different types of SS carbons, SS-Z has the highest adsorption capability, followed by SS-P, SS-S, and SS-C. Heavy metal leaching from the SS carbons was below the wastewater disposal limits issued by the Ministry of

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Environment of Japan. We believe that the SS activated carbons developed using our methods were sufficient and safe to be applied in industrial wastewater treatment for mercury removal.

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