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LETTER

Carbonaceous adsorbents produced from coffee lees

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Carbons derived through thermal decomposition of natural products usually showed a texture reflecting the original structure of the starting material such as the cellular structure. The present authors have been studying structure and properties of carbons derived from various natural products [1–3]. It has been found that the charcoal derived from ground coffee lees showed a peculiar texture with pock mark and showed an excellent gas-phase adsorption of toluene, and that the activated carbon (AC) derived from the coffee lees-based charcoal showed an excellent liquid-phase adsorption of 2-methylisoborneol (2-MIB).

Benzene, toluene, xylene are the harmful volatile organic compounds (VOCs) and the removal of such VOCs from emission stream is recently of considerable interest. Adachi et al. [4] have investigated the adsorption behavior of coffee lees waste and have reported that the spherosome fraction contained can adsorb benzene efficiently. In the present paper, however, we use the charcoal derived from coffee lees waste as adsorbents. Thus the adsorption mechanisms will become different.

On the one hand, the development of effective and low cost elimination method of 2-MIB from drinking water is a problem of urgent necessity. In the case of Japan, for example, a new law dealing with the quality of drinking water has been passed in 2003 in which the concentrations for two chemicals, 2-MIB and geosmin, causing musty smells are regulated below 10 ng/L.

Leaving the mechanisms of adsorption for further study, the experimental results are described below.

The ground coffee lees were supplied from Ueshima Coffee Co. Ltd. (UCC, Kobe, Japan). The coffee lees-based charcoal was produced by heating the ground coffee lees at a rate of 2 °C/min, kept at a desired temperature in a range from 350 to 650 °C for 5 min, and cooled to room temperature. This heat treatment was carried out using 18 kg of coffee lees in an electric furnace with the net volume of 93 L. During the heat treatment, N_2 gas flowed through the furnace at a rate of 1 L/min at atmospheric pressure.

The yield of coffee lees based-charcoals derived at various heat-treatment temperatures (HTTs) and the contents of C, H, N in these charcoals are shown in Table 1. In this table, the yield of the charcoal was defined as the relative mass of charcoal against the mass of starting coffee lees. The elemental compositions of C, H, N were measured using a MT-6 elemental analyzer (Yanaco, Kyoto, Japan).

The scanning electron micrograph of the surface of the charcoal obtained at the HTT of 450 °C is shown in Fig. 1. A rather homogeneous cellar texture with a character of pock marks can be observed. This texture is a peculiar one since such a texture cannot be observed with the charcoals

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Table 1 Yield and C, H, N contents of coffee lees-based charcoal

HTT (°C)	Yield (%)	Contents (%)		
		H	C	N
350	31.4	6.1	74.8	3.6
450	21.5	4.1	75.1	3.9
550	18.6	2.8	77.6	3.9
650	17.1	2.0	79.9	3.4

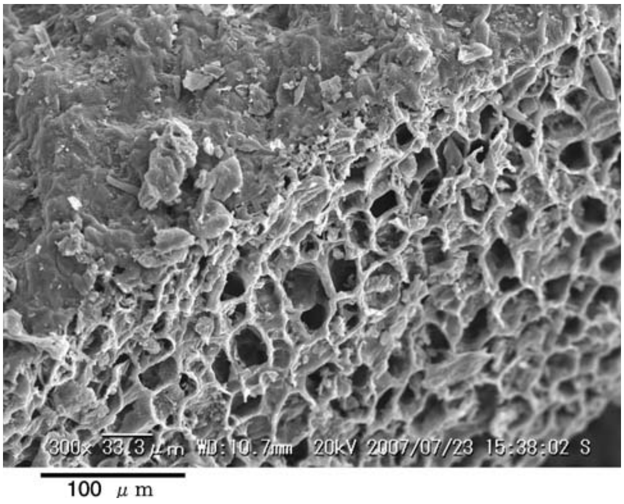

Fig. 1 Scanning electron micrograph of the surface of coffee lees-based charcoal produced at a HTT of 450 °C

produced from cellulosic biomass. The coffee lees contain protein fractions which cause the partial liquefaction at a temperature beyond 400 °C.

The adsorption tests for toluene were carried out as follows. First, the charcoal of ca. 2 g was put into a Tedlar gas sampling bag of 1 L and the air in the bag was evacuated using a vacuum pump. Then N_2 gas of 0.63 L containing toluene by 90 ppm was introduced into the bag. The concentration of toluene in the bag was monitored by GC/FID (GC-14A, Shimadzu, Kyoto, Japan).

Figure 2 shows the toluene adsorption behavior of coffee lees-based charcoals. It is seen that the charcoal obtained at HTT of 450 °C adsorbs toluene rapidly as compared with the charcoals obtained at different HTTs. The removal of toluene with the charcoal obtained at HTT of 450 °C reached to 98%. The iodine adsorption capacity of this charcoal, determined with the titration method using 0.1 M sodium thiosulfate [5], was no more than 10 mg/g. It seems, therefore, that the adsorption of toluene on this charcoal relies not only on the pore structure but also on the chemical composition and functional groups on the surface of charcoal. In Table 1, the charcoals obtained at the HTTs of 450 and 550 °C have a larger N content than the charcoals obtained at different HTTs.

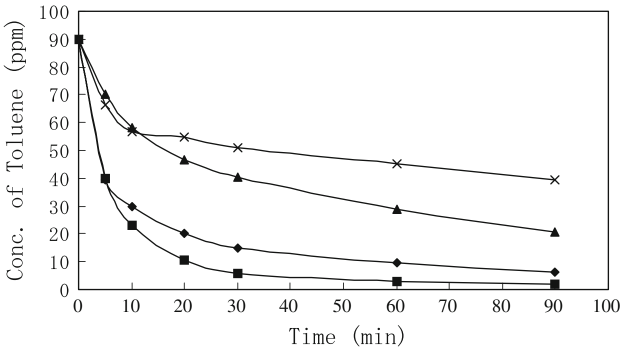

Fig. 2 Concentration of toluene in the gas contacted with coffee lees-based charcoals versus contact time. The charcoals were produced at the HTTs of (◆) 350, (■) 450, (▲) 550, and (X) 650 °C

The adsorption tests for toluene were also made for coffee lees-based AC in Table 2. In this case, the concentration of toluene in the bag decreased to almost zero after 30 min of gas-phase contact.

The charcoal was activated using a rotary kiln as follows. First, the charcoal obtained at the HTT of 450 °C was heated up to 900 °C at a heating rate of 30 °C/min under N_2 gas flow at a rate of 1 L/min. Then the gas was changed to CO_2 and the activation was made for 450 min. The yield of AC, which is defined as the relative mass of AC against the mass of charcoal before activation, was 35.0%.

Surface characteristics of coffee lees-based AC, coconut shell-based AC of laboratory grade (Lot. 07930-65, Nacalai Tesque Co., Kyoto, Japan), and AC of water treatment grade (PW-20, Asahirokazai Co., Mitake, Gifu, Japan) were determined from nitrogen adsorption isotherms measured using a surface area and pore size analyzer (Autosorb-1-C/VP, Yuasa Ionics Inc., Osaka, Japan) and the results are shown in Table 2. In this table, specific surface area (S) was determined from BET plots in the relative pressure range from 0.01 to 0.1. The pore volume (V) was determined from adsorbed amount of N_2 at the relative pressure of 0.99. Mean pore diameter (D) was calculated as $D = 4V/S$ by assuming that the pores are uniform cylindrical nonintersecting capillaries [6]. The micro-pore volume (V_{micro}) was estimated using Horvath-Kawazoe method [7] and the meso-pore volume (V_{meso}) was determined as $V_{\mathrm{meso}} = V - V_{\mathrm{micro}}$. It is seen that in all these parameters, the coffee lees-based AC showed larger values than other ACs, especially with respect to the meso-pore volume.

Small-angle X-ray scattering was also measured for estimating pore size, and according to the method shown previously [8], the size parameter (l_2) representing the average pore size, which is defined as the weighted average of the length of the line between two points on the contour of pores, was determined. The value of l_2 for the coffee lees-based AC was 2.53 nm, which is close to the pore diameter determined with N_2 adsorption tests, 2.02 nm.

Table 2 Surface characteristics for ACs

Source	BET area (m^2/g)	Iodine-adsorption capacity (mg/g)	Mean pore diameter (nm)	V (mL/g)	V_{micro} (mL/g)	V_{meso} (mL/g)
Coffee lees-based AC	1350	1320	2.02	0.68	0.58	0.10
Coconut shell-based AC	1256	1050	1.69	0.51	0.507	0.003
Commercial AC for water treatment	1137	980	1.88	0.53	0.48	0.05

This suggests that the aspect ratio of the pores revealed in an arbitrary cross section of the specimen is small. In other words, the pores are not straight but follow winding paths.

The AC rich in meso-pore will be advantageous for the adsorption of globular shaped molecules with large sizes. Thus the adsorption behavior of coffee lees-based AC was investigated using 2-MIB as an adsorbate.

The liquid-phase adsorption of 2-MIB on ACs was measured as follows. The ACs were ground to powder and passed through a 45 μm sieve. The powders were washed, dried, and preserved in a desiccator containing silica gel. An aqueous solution of 2-MIB with a concentration of 1.0 mg/L was prepared. AC powder of 0.15–0.45 mg was added into the solution of 50 mL. After the solution was shaken for 1 h, AC powder was removed by centrifugation. The supernatant was conducted through the solid phase separation column (Empore SDB-XC, 3M, Tokyo, Japan) at 10 mL/min. The column was dried and the trapped 2-MIB was extracted with dichloromethane. The amount of 2-MIB extracted, which equals the amount of 2-MIB in the bath after the adsorption test, was determined using GC/MS (QP-5050A, Shimadzu, Kyoto, Japan). The amount of 2-MIB adsorbed on AC was calculated as the difference in the amounts of 2-MIB in the bath before and after the adsorption test. Adsorption isotherms of ACs for 2-MIB adsorbate are shown in Fig. 3. At the same concentration, the amount of 2-MIB adsorbed is the largest for the coffee lees-based AC which showed the largest meso-pore volume.

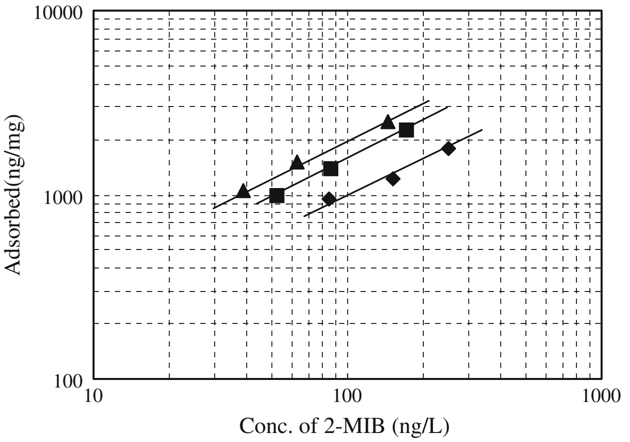

Fig. 3 Adsorption isotherms of (▲) coffee lees-based AC, (◆) coconut shell-based AC, and (■) commercial AC of water treatment grade measured using 2-MIB as an adsorbate

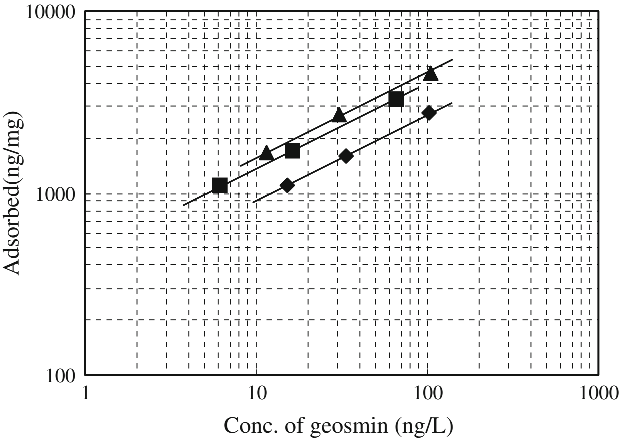

Fig. 4 Adsorption isotherms of (▲) coffee lees-based AC, (◆) coconut shell-based AC, and (■) commercial AC of water treatment grade measured using geosmin as an adsorbate

The liquid-phase adsorption of geosmin on ACs was measured similarly. Adsorption isotherms of ACs for geosmin adsorbate are shown in Fig. 4. As compared to 2-MIB, geosmin can be removed easily through the water treatment using commercial AC. However it is seen that the adsorption property of coffee lees-based AC is a little superior to other ACs.

In summary, the coffee lees-based charcoal obtained at the HTT of 450 °C showed a pock mark texture and effective adsorption of toluene. The AC derived from this charcoal worked comparably well to commercial AC for the liquid-phase extraction of 2-MIB and geosmin.

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