Gas and Mercury Adsorption Properties of Woodceramics Made from Chicken Waste

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Gas-adsorption properties of woodceramics prepared from chicken waste, which was found to be amorphous carbon reinforced by glassy carbon generated from phenolic resin, was studied. The specific surface area as determined by the multipoint BET method was 33.41 $m^2\ g^{-1}$ (N_2, 77 K) and 63.40 $m^2\ g^{-1}$ (CO_2, 195 K), and the adsorption isotherm was of Type IIb (IUPAC classification). These results suggested the presence of narrow micropores and the formation of aggregates with nonrigid slit-shaped pores. Furthermore, from gas-adsorption studies and by preliminary field testing for mercury adsorption using flue gas from a coal-firing power plant, chicken-waste woodceramics was found to function as active carbon. The chicken-waste woodceramics was found to have higher mercury adsorption properties as compared with other woodceramics or a commercially available active carbon. It was presumed that calcium, potassium, sulfur, and other chemical species which were contained as impurities increased the sorption capacity for mercury.

Introduction

Woodceramics are porous carbon/carbon composites or hybrid materials consisting of cellulose-originated amorphous carbon reinforced by glassy carbon generated from resin. They are produced by impregnating carbonaceous materials with thermosetting resin, such as phenol resin, and by then carbonizing the resin-impregnated material in a vacuum furnace.[1] Woodceramics obtained from wood are generally porous and have macropores with diameters ranging from 1 to 50 μm. Their specific surface area (BET) is generally greater than about 500 $m^2\ g^{-1}$.

Woodceramics are also attracting attention as environmentally benign materials in that they can be produced from lignocellulosic industrial wastes, such as waste paper, olive pomace and olive stones, and apple pomace.[2] Woodceramics are advantageous in that they not only make use of wastes, but also they are stronger and resistant to higher temperatures than the original carbonaceous material, and other functions can be imparted thereto. For instance, woodceramics prepared from apple pomace showed potential for gas adsorbents.[3] Although woodceramics produced from apple pomace typically has a small BET specific surface area lower than 0.5 $m^2\ g^{-1}$ (nitrogen), it shows oxygen and nitrogen gas-adsorption capacities very comparable to molecular sieve carbon (MSC). Other attempts have been made to produce woodceramics from carbonaceous materials.[4] Similarly, since broiler litter generally contains about 40 mass % (dry basis) carbon,[5,6]an attempt to produce woodceramics from biomass based on chicken wastes has been made.[7] As compared with carbonized chicken wastes, the product (woodceramics) is advantageous in that it is free of unfavorable odor, the reason for which is reported elsewhere.[8]

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(1) Okabe, T.; Saito, K. Production of Woodceramics. Jpn. Patent Publication A, No. H04-164806, 1992.
(2) Ozao, R.; Pan, W.-P.; Whitely, N.; Okabe, T. Coal-like Thermal Behavior of a Carbon-Based Environmentally Benign New Material: Woodceramics. *Energy Fuels* **2004**, *2*, 638−643.
(3) Ozao, R.; Arii, T.; Okabe, T. Thermoanalytical Characterization of Apple-based Woodceramics Using TG-DTA/MS. *Trans. Mater. Res. Soc. Jpn.* **2003**, *28*, 1075−1078.
(4) Shibata, K.; Okabe, T.; Saito, K.; Okayama, J.; Shimada, M.; Yamamura, A.; Yamamoto, R. Electromagnetic Shielding Properties of Woodceramics Made from Wastepaper. *J. Porous Mater.* **1997**, *4*, 269−276.
(5) Falcone Miller, S.; Miller, B. G. The Occurrence of Inorganic Elements in Various Biofuels and Its Effect on the Formation of Melt Phases During Combustion. *2002 International Joint Power Generation Conference*, Phoenix, Arizona, June 24−26, 2002.
(6) Falcone Miller, S.; Miller, B. G.; Tillman, D. The Propensity of Liquid Phases Forming During Coal-Opportunity Fuel (Biomass) Cofiring as a Function of Ash Chemistry and Temperature. *27th International Technical Conference on Coal Utilization & Fuel Systems*, Clearwater, Florida, March 4−7, 2002.
(7) Okabe, T.; Ozao, R.; Nishimoto, Y.; Yamamoto, R.; Zhang, D. Woodceramics − novel type of ecoceramics − its production, characterization, and application. *Abstract 2 of IUMRS−ICAM* **2003**, 34.
(8) Ozao, R.; Okabe, T.; Arii, T.; Nishimoto, Y.; Cao, Y.; Whitely, N.; Pan, W.-P. TG-DTA/MS Study of Odorless Woodceramics from Chicken Wastes. *13th International Congress on Thermal Analysis and Calorimetry*, Chia Laguna, Italy, September 12−19, 2004; p 279.

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Table 1. Composition of Samples (SQX results in mass %)

element	CH800 (mass %)
O	24.8
Na	0.6
Mg	1.4
Al	0
Si	0.3
P	3
S	0.4
Cl	0.7
K	6.1
Ca	11.5
Cu	0
Zn	0

An object of the present study is to characterize the gas-adsorption properties of chicken-waste woodceramics (referenced hereinafter as "CH800"). Furthermore, because woodceramics exhibit adsorption properties similar to active carbon, preliminary field testing for mercury adsorption from flue gas using CH800 was carried out in a coal-combusting power plant. The results are also reported.

Experimental Section

Sample. Woodceramics using chicken wastes (CH800) was prepared in a similar manner as before.[1] More specifically, 600 g of chicken wastes (originally containing about 40 wt % water) was bone-dried at 378−383 K, and it was mixed with 400 g of BellPearl S890 to be molten at 573 K for 3 h. CH800 was finally obtained by carbonizing the resulting product at 1073 K. The content of elements other than carbon was determined by a Rigaku ZSX system (SQX; XRF semiquantitative analysis), and is given in Table 1.

X-ray Diffraction (XRD). XRD patterns of the samples were obtained by using a Brucker MF18XH222 diffractometer (Cu $K\alpha_1$, 35 kV/200 mA), at a scanning rate of 5 deg min^{-1} over an angle range of 10−60 deg (2θ), with $K\alpha_2$ diffractions removed.

Adsorption Isotherm and Specific Surface Area (SSA). Specific surface area (SSA) of the sample was determined by mercury porosimetry (Poremaster, Quantachrome Instruments). Adsorption isotherms and SSA (Multipoint Brunauer−Emmett−Teller (BET) method) were obtained using nitrogen gas as adsorbate at 77 K (Autosorb 1, Quantachrome Instruments) and gaseous CO_2 as adsorbate at 195 K (BELSORP-mini, BEL Japan).

Oxygen and Nitrogen Gas-Adsorption Capacity. Figure 1shows the system for measuring basic gas-adsorption capacity of the sample. The gas-adsorption capacity of the sample is calculated in the following manner. Under applied pressure, the limited system 1 to 3 is so controlled to satisfy the following eq 1:

$$P_c V_{c1} = n_0 RT \quad (1)$$

where P_c (2.7 kgf cm^{-2} in the present case) and V_{c1} are the controlled constant pressure and controlled constant volume, and n_0 is the total amount (mol) of gas introduced into the system. By opening valve 3 and introducing gas into the sample chamber 4, the closed system 1 to 4 obeys the following eq 2:

$$P_{obs}(V_{c2} - V_x)n_1 RT \quad (2)$$

where P_{obs} is the observed pressure, V_{c2} is the total volume of the system, and V_x is the sample volume; n_1 is the amount (mol) of free gas.

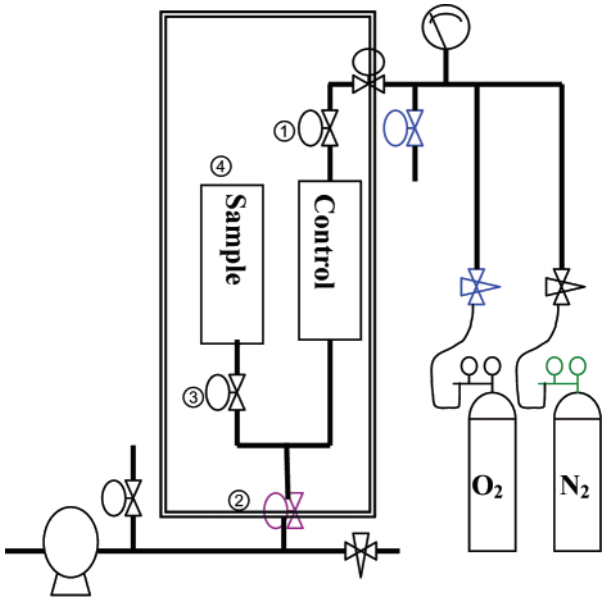

Figure 1. System setup for measuring basic gas-adsorption capacity.

Thus, the gas-adsorption capacity qO_2 (mg g^{-1}) (for oxygen) can be obtained by

$$qO_2\ (\text{mg g}^{-1}) = (n_0 - n_1) \times \text{mw}_{O_2}/\text{sw} \times 1000$$

$$= (P_c V_{c1}/RT - P_{obs} \times (V_{c2} - V_x)/RT) \times \text{mw}_{O_2}/\text{sw} \times 1000 \quad (3)$$

where mw_{O_2} is the molecular weight of oxygen (32 g), and sw is the sample mass (g). The nitrogen gas-adsorption capacity qN_2 (mg g^{-1})(for nitrogen) can be obtained by analogy to the case of oxygen gas adsorption eq 3, except for substituting mw_{N_2} (28 g) for mw_{O_2}.

Gas-adsorption properties were obtained for CH800 and a control, BellPearl (product of Kanebo, Ltd.), a commercially available molecular sieve carbon (MSC).

Field Testing of Mercury Adsorption. The testing facility setup[9] in a coal-firing power plant is shown in Figure 2. About 0.5−1.0 g each of CH800 was placed between two 80-mm diameter porous glass plates tightly held together and connected to a 3/8-in. (0.94-cm) diameter tube, and was placed in the sorbent trap. The adsorption temperature was set at the same as the flue gas, which was changed in three levels, that is, 120, 150, and 180 °C. All tests were performed during the period August 25−27, 2003, in which flue gas containing total mercury Hg(T) of 5 μg L^{-1} was allowed to flow at 0.98−1.0 Nm^3 for 1 h. The results are given in Table 3, together with comparative examples (AP: apple woodceramics,[2] SSA 2.6 m^2 g^{-1}; BF: BellFine BGF15-1, commercially available granulated active carbon from Kanebo Ltd., SSA 1687 m^2 g^{-1}; and Fluka: Fluka 05120, commercially available active charcoal from Sigma-Aldrich, SSA913 m^2 g^{-1}). The mercury content was analyzed using a Leco Advanced Mercury Analyzer 254 (AMA 254; detection limit 0.01 ng, and detection range 0.05−600 ng).

Results and Discussions

Identification of Samples. Figure 3 shows the field-emission scanning electron microscope (FESEM) photograph of CH800. The sample consists of fine powder

(9) Kellie, S.; Duan, Y.; Cao, Y.; Chu, P.; Mehta, A.; Carty, R.; Liu, K.; Pan, W.-P.; Riley, J. T. Mercury emissions from a 100-MW wall-fired boiler as measured by semicontinuous mercury monitor and Ontario Hydro Methodol. *Fuel Process. Technol.* **2004**, *85*, 487−499.

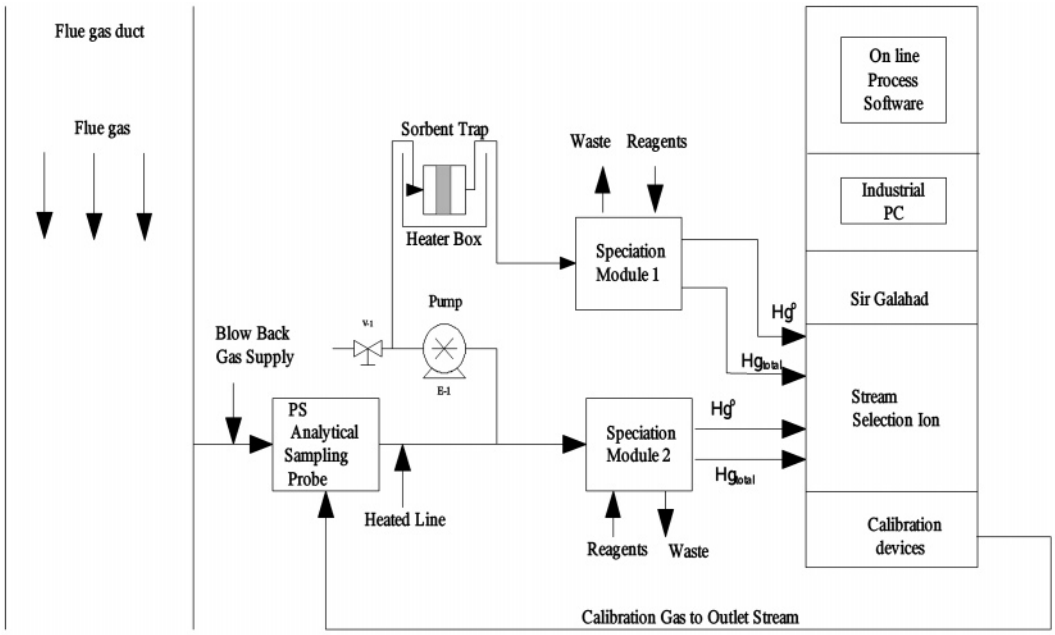

Figure 2. Mercury capture testing facility setup at a power plant.

Table 2. Specific Surface Area Obtained by Three Different Methods

method	SSA ($m^2\ g^{-1}$)	note
mercury porosimetry	0.7148	mode, at a diameter of 3.937×10^{-3} μm
N_2 adsorption (77 K), multipoint BET	33.41	C value = 154.8
CO_2 adsorption (195 K), multipoint BET	63.40	C value = 38.932

Table 3. Mercury Adsorption Field Test Results

test code	sample name	test conditions: sample weight (g)	test conditions: temp. (°C)	mercury content in sample (ppm)
Test 1	AP	0.5519	120	0.056
Test 2	CH800	0.5367	120	1.130
Test 3	BF	0.5752	120	0.768
Test 4	BF	0.5986	120	0.822
Test 5	AP	0.5678	120	0.006
Test 6	CH800	0.5432	120	0.567
Test 7	Fluka	0.5483	120	0.483
Test 8	Fluka	0.555	120	0.480
Test 11	CH800	0.5842	150	0.345
Test 12	CH800	0.5642	180	0.558
Test 21	AP	0.5939	150	0.019
Test 22	AP	0.5934	180	0.004
Test 31	CH800	1.9821	120	0.284
Test 32	AP	2.0232	120	0.157

aggregates. Table 1 shows the results of elemental analysis for a representative sample. It shows that chicken wastes contain Ca, K, P, Mg, and other metals; in general, CH800 generally contains, by mass, about 30% C, 10% Ca, 7% K, 3% P, and 1% Mg. It is also known that chicken wastes also contain about 3−4% nitrogen.

Figure 3 shows the XRD patterns for (1) CH800, (2) CH800 heated to 1273 K in air, and (3) Fluka05120 (comparative sample, commercially available activated charcoal from Sigma-Aldrich). From the XRD pattern, the original sample shows a broad peak at 0.544 nm ($2\theta = 15.90°$). This is the so-called γ-band, which is believed to be derived from aliphatic chains.[10] As seen in Figure 3, this peak is not found in commercially available active carbon such as Fluka05120. However, when heated to 1273 K in air, a sharp peak appears at ca. 0.344 nm, which is near to the d(002) spacing of glassy carbon (nongraphitizing carbon) or turbostratic structure.[11] Thus, this suggests that the original CH800 contains micro-graphitelike structures having short-range ordering similar to active carbon fibers, which develop into graphenelike layers on heating.[12]

Adsorption Isotherm and Specific Surface Area (SSA). SSA obtained by mercury porosimetry and by adsorption methods using N_2 and CO_2 are summarized in Table 2. The population of macropores (>50-nm pore width) is very low. As shown in Figure 3, the fine particles less than one micrometer in size accounts for

(10) Watanabe, K.; Sakanishi, K.; Mochida, I. Changes in Coal Aggregate Structure by Heat Treatment and Their Coal Rank Dependency. *Energy Fuels* **2002**, *16*, 18−22.

(11) Hirsh, P. B. X-ray Scattering from Coals. *Proc. R. Soc. London* **1954**, *A226*, 143−169.

(12) Suzuki, T.; Kaneko, K. The micrographite growth of activated carbon fibers with high-temperature treatment studied by computer-aided X-ray diffraction. *Carbon* **1993**, *31*, 1360−1361.

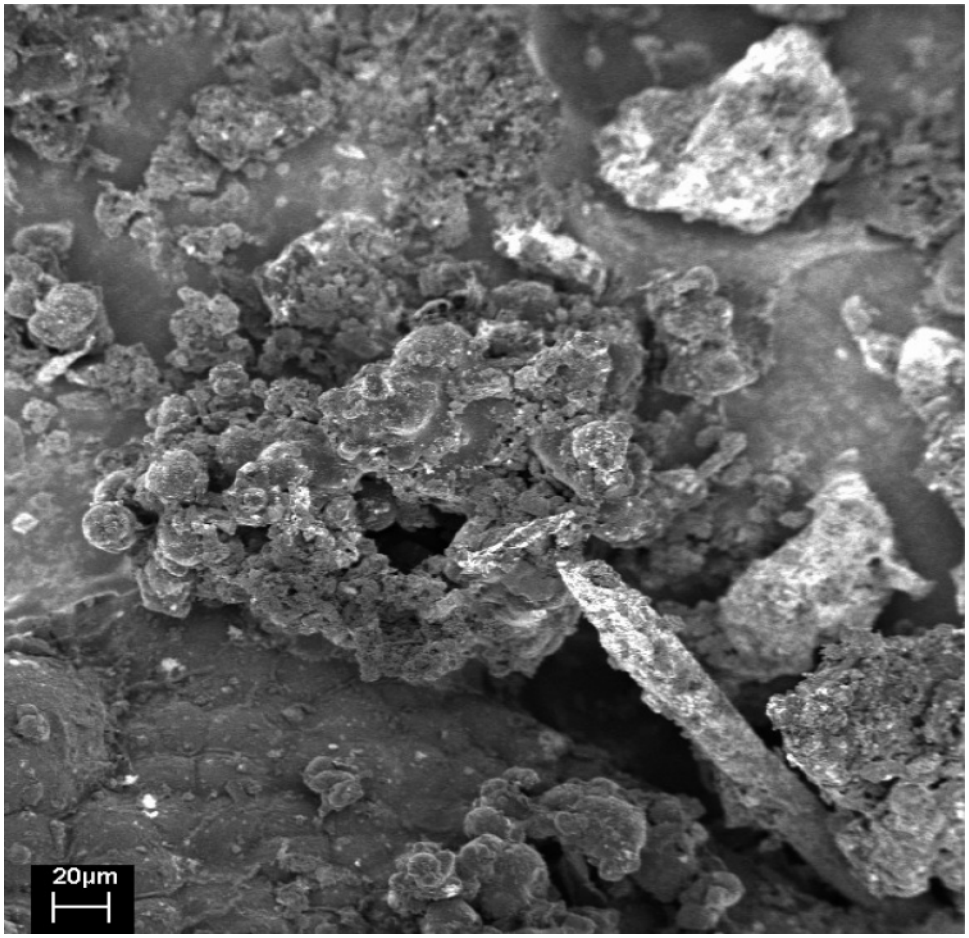

Figure 3. FESEM photograph of CH800 (magnification 200×).

the extremely low SSA obtained by mercury porosimetry. Although CO_2 is larger in molecular size than N_2, the resulting SSA using CO_2 as the "yardstick" is about twice as large as that obtained by using N_2. This suggests the presence of narrow micropores not accessible by N_2.[13−16]Figure 5 shows the adsorption isotherm of Type IIb (IUPAC 1985 classification) obtained by gas-adsorption methods. It can be seen that monolayer adsorption takes place up to a relative pressure of about 0.1, and then multilayer adsorption partly overlaps. The hysteresis may be due to the formation of aggregates consisting of platelike particles, which have nonrigid slit-shaped pores.

Oxygen and Nitrogen Gas-Adsorption Capacity. The gas-adsorption properties were observed at a gas pressure of 2.7 kgf cm^{-2} on 1.5-g samples at room temperature. The results for CH800 in comparison with those for BellPearl are given in Figure 6. From Figure 6, CH800 has a gas-adsorption capacity of 28 mg g^{-1} for N_2 and 35 mg g^{-1} for O_2, whereas BellPearl shows gas-adsorption capacity of 38 mg g^{-1} for N_2 and 45 mg g^{-1} for O_2. Assuming that the gases condense in a liquidlike cross-packing manner and that the cross section area is 0.162 nm^2 for N_2 and 0.141 nm^2 for O_2, the total pore volume can be calculated to be about 0.030 cm^3 g^{-1} for CH800, whereas that for BellPearl is calculated to be about 0.039 cm^3 g^{-1}. This also shows the presence of microporosity in CH800, as is the case of BellPearl. BellPearl has high selectivity for oxygen, as observed by a quick rise with time, but CH800 is lower in the selectivity and in response time.

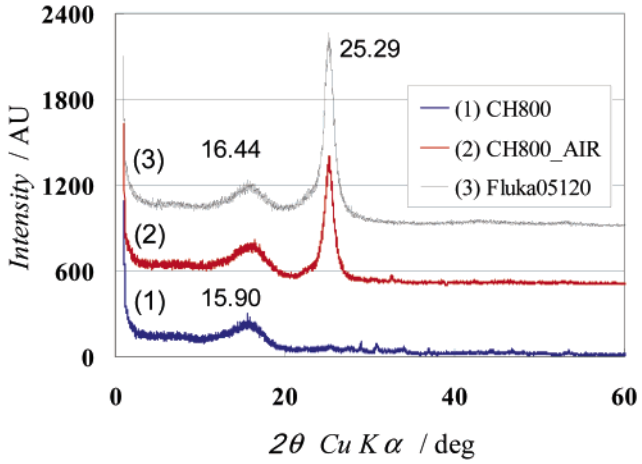

Figure 4. XRD patterns for (1) CH800, (2) CH800 heated to 1273 K in air, and (3) comparative active carbon (Fluka05120).

(13) Jagiello, J. Stable Numerical Solution of the Adsorption Integral Equation Using Splines. *Langmuir* **1994**, *10*, 2778−2785.

(14) Rodriguez-Reinoso, F.; Garrido, J.; Martin-Martinez, J. M.; Molina-Sabio, M.; Torregrosa, R. The combined use of different approaches in the characterization of microporous carbons. *Carbon* **1989**, *27*, 23−32.

(15) Molina-Sabio, M.; Munecase, M. A.; Rodriguez-Reinoso, F.; McEnaney, B. Adsorption of CO_2 and SO_2 on activated carbons with a wide range of micropore size distribution. *Carbon* **1995**, *33*, 1777−1782.

(16) Linares-Solano in Questions and Comments for Jagiello, H.; Thommes, M. Comparison of DFT characterization methods based on N_2, Ar, CO_2, and H_2 adsorption applied to carbons with various pore size distributions. *Carbon* **2004**, *42*, 1227−1242.

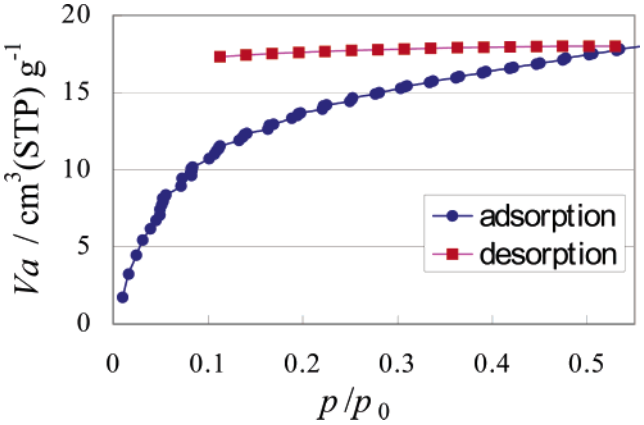

Figure 5. Adsorption−desorption isotherm for CH800 obtained at 195 K using CO_2.

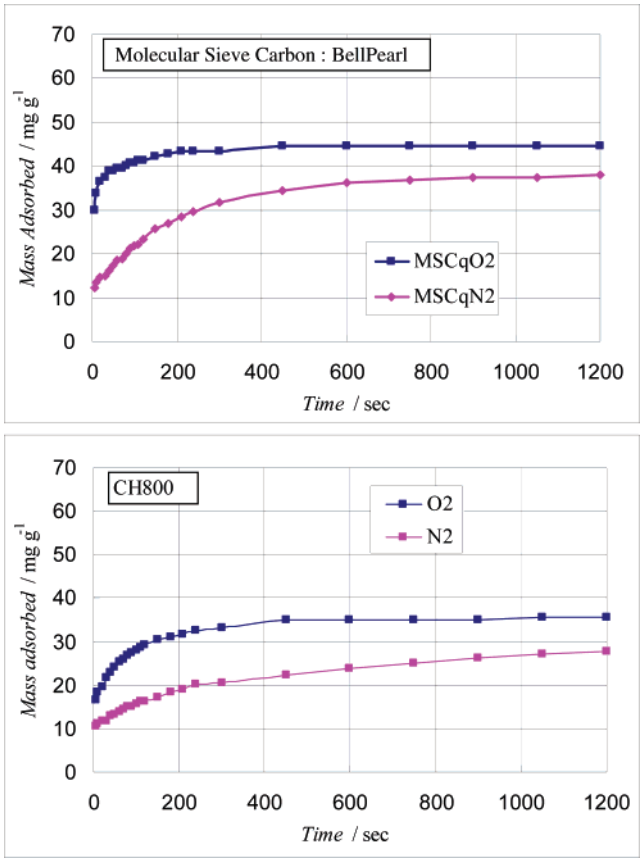

Figure 6. Oxygen and nitrogen gas-adsorption properties for commercially available molecular sieve carbon (MSC, BellPearl)(upper) and CH800 (lower).

Field Test of Mercury Adsorption. Table 3 shows the amount of total mercury (Hg(T)) adsorbed by the sorbents, because in flue gas, mercury exists in three primary forms, that is, elemental mercury (Hg^0), which is the most abundant and persistent form that is dispersed globally with a life cycle in the atmosphere of about 1−2 years;[17−20]oxidized mercury (II)(Hg^{2+}); and particulate mercury (Hg_p). As described above, comparative samples AP, BF, and Fluka stand for apple woodceramics, a commercially available granulated active carbon BellFine (Kanebo, Ltd.), and a commercially available active carbon Fluka 05120 (Sigma-Aldrich), respectively.

Tests 1−8 were performed at 120 °C. From the results, it can be seen that Test 2 using CH800 yielded a maximum capture of mercury (1.130 ppm), and Test 6 using CH800 also yielded high mercury capture (0.567 ppm), but it is about half the amount of Test 2. On the other hand, commercial samples yield results with high reproducibility (BF: 0.768−0.822 ppm and Fluka: 0.483−0.480 ppm). AP showed very poor results. AP is very low in SSA and contains almost no metals such as calcium. Tests 11−12 and 21−22 were carried out at higher temperatures. In general, the mercury-capturing ability decreases with increasing temperature. However, CH800 seems unaffected by the temperature. In Tests 31−32, the amount of the sorbents was increased to about 3 times the amount used in the other tests. An increase in amount was not effective, presumably due to clogging which occurred inside the sorbent trap.

Since mercury undergoes heterogeneous reactions in coal combustion gas, it is necessary to consider how the solid surfaces of active carbon and the composition affect the oxidation and capture of mercury. It is reported that Hg content increases with increasing BET surface area of active carbon[21,22] and with sulfur content in active carbon sorbents.[23] The high mercury capture results for BF and Fluka can be partly explained by their high SSA (about 1700 $m^2\ g^{-1}$ for BF and 910 $m^2\ g^{-1}$ for Fluka); however, CH800 adsorbed a larger amount of mercury in spite of its low SSA. It is also reported that the treatment of activated carbon with calcium chloride significantly increased the mercury-capturing capacity.[24,25] Although CH800 has low SSA, it has been shown above in section 3.3 that gas adsorption is greatly influenced by chemical adsorption. Thus, it is likely that calcium, potassium, sulfur, and so forth, that are contained in CH800 have favorable effects on capturing mercury, although further systematic studies are required for a clear understanding.

Conclusions

Gas-adsorption properties of woodceramics prepared from chicken waste, which was found to be amorphous carbon reinforced by glassy carbon generated from phenolic resin, was studied. The specific surface area

(17) Lindqvist, O.; Rodhe, H. Atmospheric Mercury − a Review. *Tellus, Series B, Chem. Phys. Meteorology* **1985**, *37B*, 136−159.
(18) Slemr, F.; Seiler, W.; Schuster, G. Distribution, speciation, and budget of atmospheric mercury. *J. Atmos. Chem.* **1985**, *3*, 407−434.
(19) Lindqvist, O.; Johansson, K.; Aastrup, M.; Anderson, A.; Bringmark, L.; Hovenius, G.; Håkanson, L.; Iverfeldt, Å.; Meili, M.; Timm, B. Mercury in the Swedish environment-Recent research on causes, consequences, and corrective methods. *Water Air Soil Pollut.* **1991**, *55*, 1−261.
(20) Hall, B. The gas-phase oxidation of mercury by ozone. *Water Air Soil Pollut.* **1995**, *80*, 301−315.
(21) Hower, J. C.; Maroto-Valer, M. M.; Taulbee, D. N.; Sakulpitakphon, T. Mercury capture by distinct fly ash carbon forms. *Energy Fuels* **2000**, *14*, 224−226.
(22) Vidic, R. D.; Kwon, S.; Siler, D. P. Impregnated activated carbons for elemental mercury adsorption. *Proceedings of the 17th Annual Pittsburgh Coal Conference*, Pittsburgh, PA, September 11−14, **2000**; p19a-3.
(23) Krishnan, S. V.; Gullett, B. K.; Josewicz, W. Sorption of elemental mercury by activated carbon. *Environ. Sci. Technol.* **1994**, *28*, 1506−1512.
(24) Livengood, C. D.; Mendelsohn, M. H.; Huang, H. S.; Wu, J. M. Development of mercury control techniques for utility boilers. *Proceedings of the Air and Waste Management Association 88th Annual Meeting*, San Antonio, TX, 1995; MP21.07.
(25) Gale, T. K. Mercury control with calcium-based sorbents and oxidizing agents. Quarterly Report−DE-PS26-02NT41182 for period Oct. 1 through Dec. 31, 2002.

as determined by multipoint BET method was 33.41 m^2 g^{-1} (N_2, 77 K) and 63.40 m^2 g^{-1} (CO_2, 195 K), and the adsorption isotherm was of Type IIb (IUPAC classification). These results suggested the presence of narrow micropores and the formation of aggregates with nonrigid slit-shaped pores. Furthermore, from gas-adsorption studies and field testing of mercury adsorption, chicken-waste woodceramics was found to function as active carbon. The chicken-waste woodceramics was found to have higher mercury adsorption properties as compared with other woodceramics or a commercially available active carbon. It was presumed that calcium, potassium, sulfur, and other chemical species contained as impurities increased the sorption capacity for mercury. Further studies are necessary for a clear understanding of the mercury adsorption mechanism.

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