Science of Bamboo Charcoal: Study on Carbonizing Temperature of Bamboo Charcoal and Removal Capability of Harmful Gases

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We examined the relationship between the carbonizing temperature of bamboo carbide made from Moso bamboo (*Phyllostachys pubescens*) and the removal effect of harmful gases and odorants, and the use of a bamboo charcoal as a countermeasure for “Sick Building Syndrome” or “Chemical Sensitivity” and the use as a deodorant. With regard to the carbonizing temperature of the bamboo charcoal, a temperature sensor was installed inside each bamboo material and the carbonizing temperature was controlled at 500, 700 and 1000ºC. The removal effect was tested for formaldehyde, toluene and benzene that are known to cause “Sick Building Syndrome” or “Chemical Sensitivity” and for ammonia, indole, skatole and nonenal as odorants. The formaldehyde removal effect was only slightly different in the charcoal at all the carbonizing temperatures. The benzene, toluene, indole, skatole and nonenal removal effect were the highest for the bamboo charcoal carbonized at 1000ºC and tended to increase as the carbonizing temperature of the bamboo charcoal increased. The removal effect for ammonia was the highest on the bamboo charcoal carbonized at 500ºC. It is concluded that the effective carbonizing temperature is different for each chemical, and a charcoal must be specifically selected for use as an adsorbent or deodorant.

Key words —— bamboo charcoal, carbonizing temperature, Sick Building Syndrome, Chemical Sensitivity

INTRODUCTION

The carbide of trees such as wood charcoal or bamboo charcoal has been used as a fuel for a long time. Recently, they have been studied as a humidity control substance,[1] adsorbent,[2] substance of wastewater purification,[3,4] and catalyst.[5]

Recently, health problems such as “Sick Building Syndrome (Sick House Syndrome)” and “Chemical Sensitivity” are occurring due to an increase in indoor air pollution from chemicals. Although the Ministry of Health, Labour and Welfare of Japan has established a guideline value for the indoor concentrations of formaldehyde, toluene, xylene, *p*-dichlorobenzene, ethyl benzene, styrene, chlorpyrifos, di-*n*-butyl phthalate, tetradecane, diethylhexyl phthalate, diazinon, acetaldehyde and fenobucarb at the examination conference about problems of “Sick House Syndrome” (indoor air pollution) in February 2002, concrete countermeasures to decrease harmful indoor chemicals have not been indicated till now.

We have studied the countermeasures against “Sick Building Syndrome” using the removal capability of charcoal such as wood charcoal or bamboo charcoal to adsorb chemicals. The adsorption of chemicals on the charcoal is classified by physical adsorption due to “van der waals attraction” or chemical adsorption by a chemical reaction, and characteristics of the adsorption are influenced by the chemical structure of the surface and pore structure. Recently, the relation between the carbonizing

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conditions and adsorption effect of chemicals has been reported on the carbides of *Cryptomeria* and *Chamaecyparis*.[6–8] However, there has been a misapprehension that all charcoals have the same adsorption effect when used as a adsorbent or deodorant. We examined the relation between the carbonizing temperature of bamboo carbide and its removal effect for chemicals such as harmful gases and odorants, and the use of bamboo charcoal as a countermeasure against "Sick Building Syndrome" and "Chemical Sensitivity" and the use as a deodorant.

MATERIAL AND METHODS

Production Method of Bamboo Charcoal —— Bamboo charcoal was made from Moso bamboo (*Phyllostachys pubescens*). A charcoal kiln, which was used to make the bamboo charcoal, can make about 50 kg of bamboo charcoal at a time and can mechanically control the temperature by setting the carbonizing temperature. A temperature sensor was installed inside of each bamboo material and the ceiling of the charcoal kiln and temperature of each sensor was monitored. The carbonizing temperature was that of the inside temperature of each bamboo material. Air was hold up and the temperature program rate was 1ºC/min. After reaching the set carbonizing temperature, each bamboo material was carbonized for about 1 hr at that temperature and was then left to cool at the temperature of the charcoal kiln. A yield of the bamboo charcoal was about 45% under the condition.

The bamboo charcoal was then crushed and sieved, and a bamboo charcoal powder with a particle diameter of 25–125 μm was obtained. With regard to the samples for the experiments, the bamboo charcoal powder was heated for 3 hr at 115 ± 5ºC to dry, and then left in a desiccator.

Measurement of Surface Area and Pore Size Distribution —— ASAP 2010 micro pore system (Shimadzu, Kyoto, Japan) was used for measuring specific surface area and pore size distribution of 5–20 Å. The adsorption of carbon dioxide was measured at an adsorption temperature of 194.65 K. Specific surface areas were determined from carbon dioxide isotherms from 0.03 to 0.15 of the relative pressure range using the BET equation. The pore size distributions were determined by HK (Harvath-Kawazoe) method. The pore size distributions of 3.7–140000 nm was measured by the mercury intrusion porosimetry using Auto Pore III (Shimadzu).

Measurement of Electric Resistance —— A digital multimeter 7537 01 (Yokogawa M&C Corporation, Tokyo, Japan), which can measure to 40 MΩ, was used for measuring the electric resistance of the bamboo charcoal.

Removal Test of Harmful Gas —— The removal effect of harmful gases was tested in a 5-liter sampling bag (tedlar bag) (GL Sciences Inc., Tokyo, Japan). A 0.5 g bamboo charcoal piece for formaldehyde, ammonia, indole, and skatole or a 0.05 g piece for formaldehyde, benzene, toluene, and nonenal was placed in the sampling bag and a sealing clip isolated the bamboo charcoal. Nitrogen was pumped into the sampling bag and then each gas (formaldehyde, benzene, toluene, ammonia, indole, skatole, and nonenal) was added at the specific concentration to the sampling bag using a gastight syringe. The prepared sampling bag was incubated at 20ºC. After the gas concentration in the sampling bag stabilized, the bamboo charcoal and gas was mixed by opening the sealing clip. The time mixing for the bamboo charcoal and gas was initially 0. The concentration of the gas in the sampling bag was determined after 0, 1, 3, 5, 8, and 24 hr.

Method for Determination of Gas Concentration —— The concentration of formaldehyde was determined using a Formaldemeter 400 (JMS, Tokyo, Japan). The concentration of ammonia was determined using Kitagawa's detector AP-1 (Komyo Rikagaku Kogyo, Tokyo, Japan) and Kitagawa's detector tube No.105SC (Komyo Rikagaku Kogyo). The concentrations of indole and skatole were determined using a portable type odor sensor XP-329 (COSMOS, Osaka, Japan). The concentrations of benzene, toluene and nonenal were determined using a gas chromatograph GC-8A (Shimadzu), which was equipped with a flame ionization detector (FID). The packed column filled with polyethyleneglycol 20 M as the liquid phase on Chromosorb W (60–80 mesh, AW-DMCS) for benzene and toluene, and Thermon-3000 (5%) as the liquid phase on Chromosorb W (80–100 mesh, AW-DMCS) for nonenal was used. The temperatures of the column and the injector were 100ºC and 150ºC for benzene and toluene, and 150ºC and 200ºC for nonenal, respectively. The concentration was determined by the calibration curve method.

Measurement of Electron Spin Resonance —— Each bamboo charcoal was put in an measurement of electron spin resonance (ESR) sample tube (5 mmϕ) and the ESR spectra (X-band) were measured using an ESR JES-TE200 (JEOL, Tokyo, Ja-

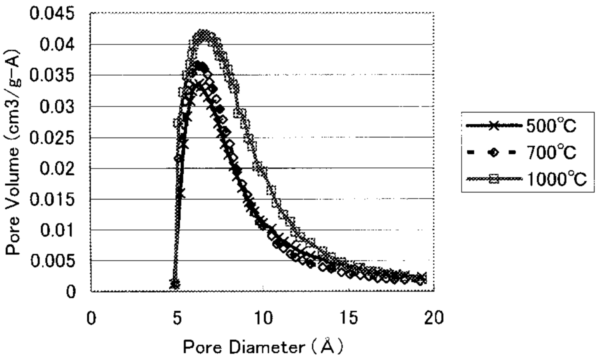

Fig. 1. Pore Size Distribution of 5–20 Å (Horvath-Kawazoe Differential Pore Volume Plot)

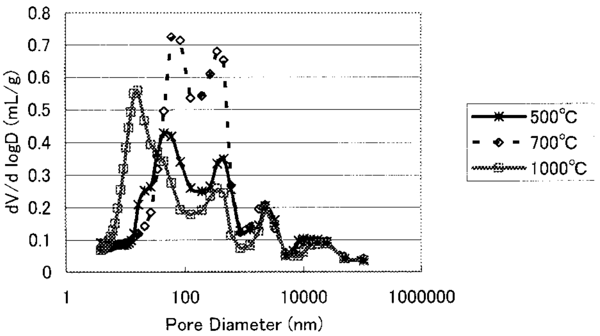

Fig. 2. Pore Size Distribution of 3.7–140000 nm (Log Differential Intrusion)

pan) with conditions as follows: temperature, 23ºC; microwave frequency, 9.18 GHz; microwave power, 8 mW; field, 327.5 mT ± 5 mT; sweep time, 0.5 min; modulation, 2 μT; amplitude, 100; time constant, 0.3 sec.

RESULTS

Measurement of Surface Area and Pore Size Distribution

Each specific surface area of the bamboo charcoal carbonized at 500, 700 and 1000ºC was 360.2, 361.2 and 490.8 m^3/g, respectively. Although the specific surface area of the bamboo charcoal carbonized at 500ºC and that at 700ºC was slightly different, that of 1000ºC was about 1.35 times as large as that of 500ºC or 700ºC. The pore size distribution of 5–20 Å and 3.7–140000 nm was shown in Figs. 1 and 2. On the micro-pore range, a pore size peak of the bamboo charcoal was about 6.5 Å and pore volumes tended to increase as the carbonizing temperature of the bamboo charcoal increase. On the meso-pore and macro-pore range, pore size peaks of the bamboo charcoal carbonized at 500 and 700ºC were about 60, 450 and 2250 nm, and that of 1000ºC was about 15 nm, which was smaller than that of 500 and 700ºC. As the pore volume, that of 1000ºC was the largest, and that of 500ºC was larger than that of 700ºC on the meso-pore range. On the macro-pore range, the pore volume of 700ºC was the largest, and that of 500ºC larger than that of 1000ºC.

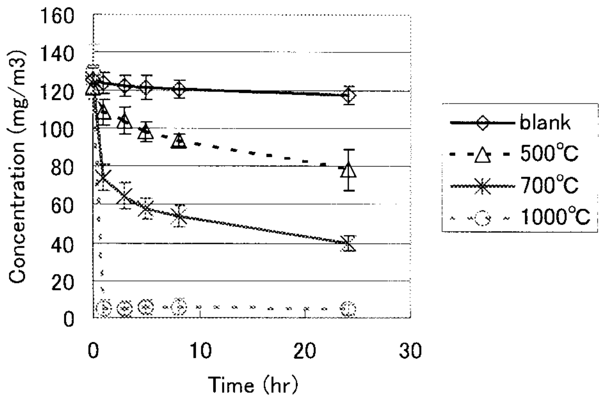

Fig. 3. Time Course of Benzene Concentration in Sampling Bag

Measurement of Electric Resistance

The electric resistance of the bamboo charcoal carbonized at 500, 700, and 1000ºC were above 40 M, 10^4–10^5, and 10–100 Ω, respectively. The electric resistance decreased as the carbonizing temperature of the bamboo charcoal increased, that is, the correlation between the carbonizing temperature and the electric resistance of the bamboo charcoal was negative. Because it is known that the correlation between the carbonizing temperature and the electric resistance exists,[6,9] the smelting degree of charcoal can be estimated by measuring the electric resistance. In this study, the smelting progress can be confirmed as the carbonizing temperature of the bamboo charcoal increases.

Removal Test of Harmful Gas

The results of the removal tests for benzene, toluene and formaldehyde are shown in Figs. 3, 4 and 5, respectively. Bamboo charcoal carbonized at 1000ºC had the best removal effect for benzene and toluene. For the other carbonizing temperatures of 500 and 700ºC, the removal effect was poor compared to that at 1000ºC. The removal effect for benzene and toluene tend to increase as the carbonizing temperature

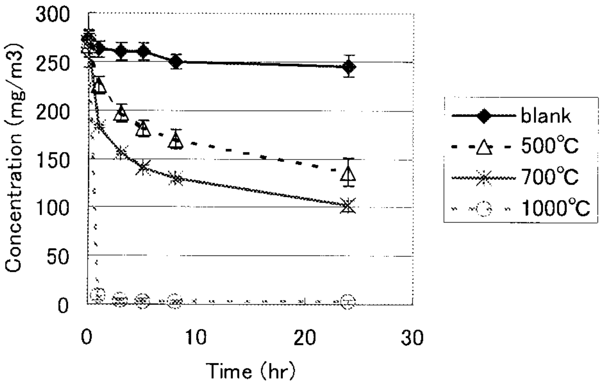

Fig. 4. Time Course of Toluene Concentration in Sampling Bag

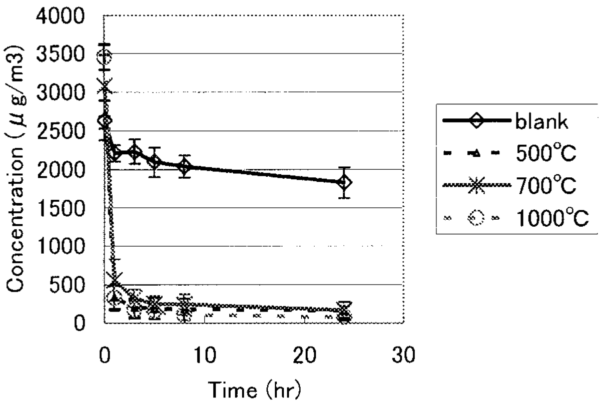

Fig. 5-1. Time Course of Formaldehyde Concentration in Sampling Bag on 0.5 g Bamboo Charcoal

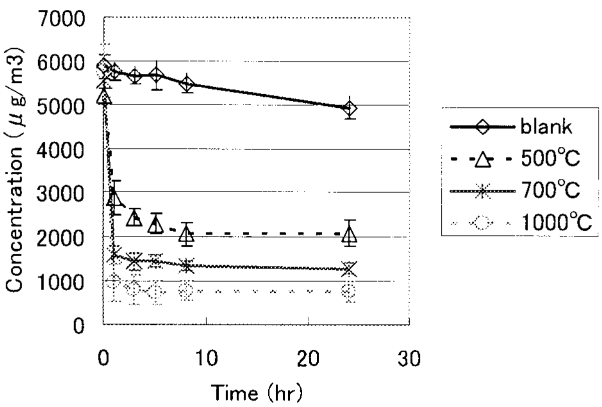

Fig. 5-2. Time Course of Formaldehyde Concentration in Sampling Bag on 0.05 g Bamboo Charcoal

of the bamboo charcoal increases. The bamboo charcoal at all carbonizing temperatures removed formaldehyde well, and the removal effect for formaldehyde was only slightly different for the bamboo charcoal at all carbonizing temperatures. When the

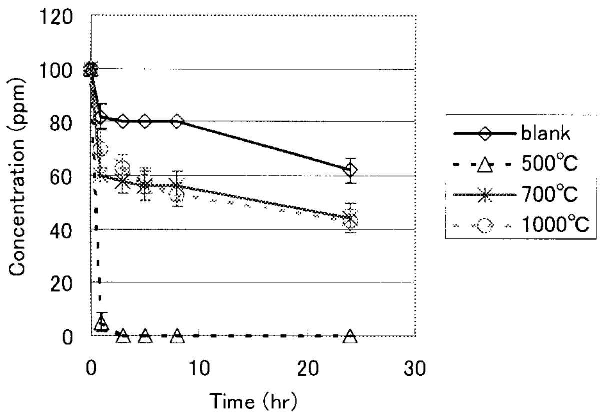

Fig. 6. Time Course of Ammonia Concentration in Sampling Bag

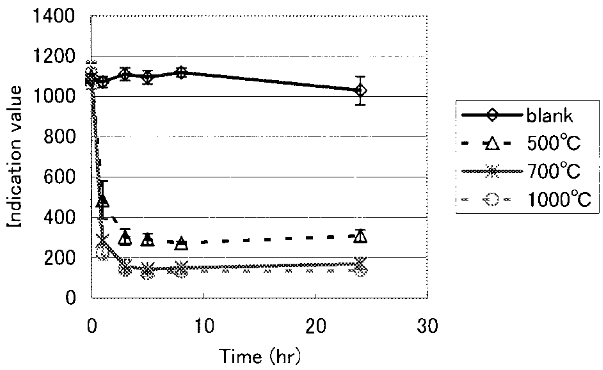

Fig. 7. Time Course of Indole Concentration in Sampling Bag

weight of the bamboo charcoal was reduced and the primary formaldehyde concentration was increased, the removal effect of formaldehyde tended to increase as the carbonizing temperature of the bamboo charcoal increased similar to benzene and toluene. However, for an indoor condition, the difference in the removal effect for formaldehyde was not clear, and all the bamboo charcoals carbonized at 500–1000ºC had equal removal effects.

Removal Test of Odorant

The results of removal test for ammonia, indole, skatole and nonenal are shown in Figs. 6, 7, 8 and 9, respectively. Bamboo charcoal carbonized at 500ºC had the highest removal effect for ammonia. The bamboo charcoal carbonized at the other temperatures of 700 and 1000ºC had a poor removal effect for ammonia compared to that at 500ºC. For indole, skatole and nonenal, the bamboo charcoal carbonized at 1000ºC had the highest removal effect. The bamboo charcoal carbonized at the other tempera-

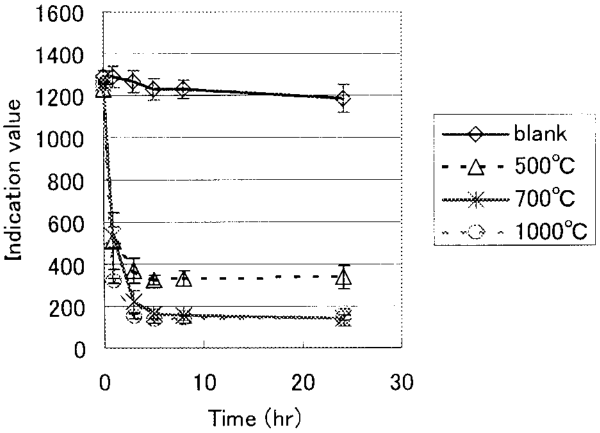

Fig. 8. Time Course of Skatole Concentration in Sampling Bag

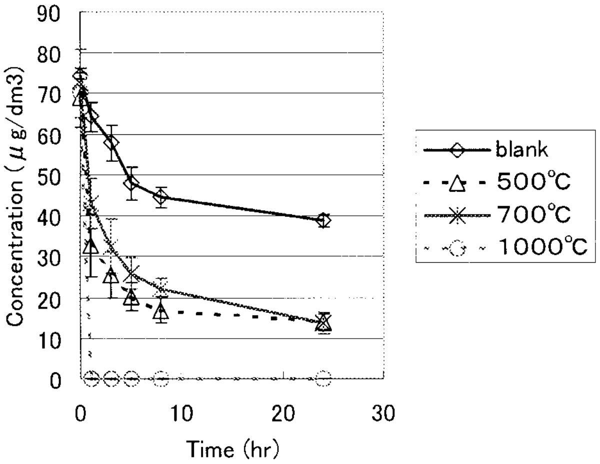

Fig. 9. Time Course of Nonenal Concentration in Sampling Bag

tures of 500 and 700ºC had a poor removal effect for indole, skatole and nonenal compared to that of 1000ºC. The removal effect for these odorants tended to increase as the carbonizing temperature increased.

Measurement of Electron Spin Resonance

The ESR spectra of a bamboo charcoal carbonized at 200, 300, 400, 500, 700 and 1000ºC are shown in Fig. 10. Radical species with ESR activity were detected in the bamboo charcoal carbonized at 300–500ºC. Many radical species were detected in the bamboo charcoals carbonized at 500ºC. The detection of the radical species decreased as the deviation increased from the carbonizing temperature of 500ºC, and the radical species were hardly detected in the bamboo charcoals carbonized at 200, 700 and 1000ºC.

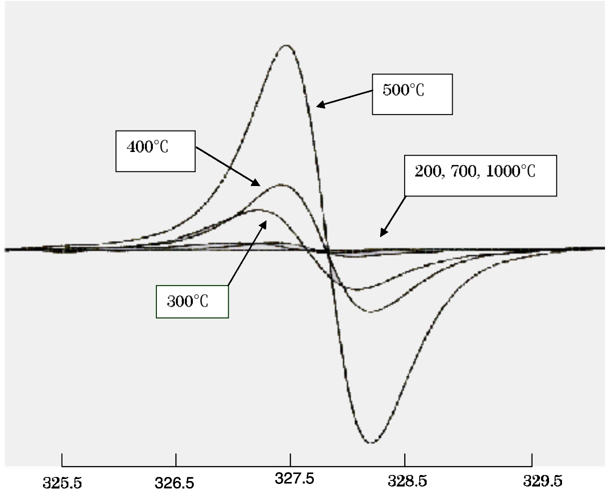

Fig. 10. ESR Spectra of Bamboo Charcoal Carbonized at a Temperatures of 200, 300, 400, 500, 700 and 1000ºC

DISCUSSION

The indoor guideline concentration for volatile organic carbon (VOC) has been prescribed for 13 chemical species by the Ministry of Health, Labor and Welfare of Japan. They include formaldehyde, toluene, xylene, *p*-dichlorobenzene, ethylbenzene, styrene, chlorpyrifos di-*n*-butyl phtalate, tetradecane, di(2-ethylhexyl)phthalate, diazinon, acetoaldehyde and fenoucarb. Of these chemicals, formaldehyde, which is released from the adhesives in plywood, *etc*., is the main chemical causing "Sick Building Syndrome," and the indoor guideline concentration for formaldehyde is 100 $\mu g/m^3$. In this study, although the primary concentration of formaldehyde in a 5 l sampling bag was about 35 times the guideline concentration, a 0.5 g piece of bamboo charcoal carbonized at 1000ºC reduced the concentration of formaldehyde to less than the guideline concentration after 24 hr. For toluene used as a solvent in paint, although the primary concentration of toluene in the 5 l sampling bag was about 1000 times the guideline concentration, a 0.05 g piece of bamboo charcoal carbonized at 1000ºC reduced the concentration of toluene to less than 1/100 the initial concentration after 24 hr. Although the guideline concentration was not established for benzene, it is considered that benzene can become a reference for toluene, xylene, *p*-dichlorobenzene, ethylbenzene and styrene, *etc*., as it has a similar benzene ring structure. Practically, the removal effects for benzene and toluene were almost equal. It is presumed that bamboo charcoal carbonized at a temperature of 1000ºC is effective for removing these chemicals. At temperatures of 900–1000ºC, the carbonization significantly progressed and the specific surface area becomes the highest.[7,8] In this study, the specific surface area was the highest and the electric resistance was the lowest at 900–1000ºC. Although specific surface areas of the bamboo charcoal carbonized at 500 and 700ºC were slightly different, the removal effect of the bamboo charcoal carbonized at 700ºC was higher than that of 500ºC. The results make us conjecture that pores of micro-pore range are especially concerned with the adsorption of benzene and toluene, because the pore volume of micro-pore range on the bamboo charcoal carbonized at 700ºC is larger than that of 500ºC. Therefore, it is considered that the removal of chemicals, which depend on physical adsorption, is effective in bamboo charcoal carbonized at a temperature of 1000ºC, which has the largest specific surface area and pore volume of the micro-pore range.

The bamboo charcoal showed a sufficient removal effect for odorants such as ammonia, indole, and skatole contained in the excreta of man or animals, and nonenal that is a human body odor to increase with aging. Different from the other chemicals, the removal effect for ammonia was the best on the bamboo charcoal carbonized at 500ºC. The concentration of ammonia decreased to under a concentration of 5 ppm, at which the odor is hard to detect, from the primary concentration of 100 ppm after 3 hr using the 0.5 g bamboo charcoal carbonized at 500ºC. At that carbonizing temperature of 400–500ºC, the thermolysis of cellulose or lignin, which are the main components of bamboo, actively occurred and it is reported that acidic functional groups such as carboxyl were formed by the thermolysis.[8–10] In the ESR spectra measurement, many radical species with ESR activity were detected on the bamboo charcoal carbonized at 500ºC, so that the existence of many carboxyl groups was presumed. Therefore, it was concluded that the bamboo charcoal carbonized at 500ºC, which has acidic functional groups to be effective for the chemical adsorption of ammonia, is more effective for the removal of basic substances such as ammonia rather than bamboo charcoal carbonized at 1000ºC, which has a higher physical adsorption capability. It is presumed that the removal of other basic chemicals would show a similar tendency. The removal effects of other odorants such as indole, skatole, and nonenal were the most effective in the bamboo charcoal carbonized at 1000ºC, which has a higher physical adsorption capability, just like benzene and toluene. Furthermore, because the results for toluene, benzene and ammonia in this study showed tendencies similar to that reported on wood charcoal,[6,8] it is considered that there is a relation between the capability of charcoal as an adsorbent and the carbonizing temperature of the charcoal, but not the tree species.

As a result of our study, it is concluded that the effective carbonizing temperature is different for each chemical and a specific charcoal must be selected for each specific use as an adsorbent or deodorant. It is expected that charcoal can be effectively used as a countermeasure against "Sick Building Syndrome" or as a deodorant.

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