

# Comparison of Removal Efficiencies for Ammonia and Amine Gases between Woody Charcoal and Activated Carbon

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The removal efficiency of  $\text{NH}_3$ ,  $(\text{CH}_3)\text{NH}_2$ ,  $(\text{CH}_3)_2\text{NH}$  and  $(\text{CH}_3)_3\text{N}$  into woody charcoal carbonized at 500°C and activated carbon was determined by the attenuation of their concentrations in the 5 l bags at cool (5°C) and room temperature (20°C). A discussion follows on the deodorization performance against four gases with attention to the physical and chemical characteristics of adsorbent surfaces. It was found that the high acidity of woody charcoal surface was more suitable for the adsorption of  $\text{NH}_3$  and  $(\text{CH}_3)\text{NH}_2$  gases than the activated carbon under both temperatures, and the activated carbon having larger micro, meso pore volumes following an increase in specific surface area showed higher capacity for  $(\text{CH}_3)_3\text{N}$  gas adsorption than the woody charcoal. Also the activated carbon is more suitable for  $(\text{CH}_3)_2\text{NH}$  gas adsorption than the woody charcoal at 5°C, but its removal efficiency using the activated carbon is lower than the woody charcoal at 20°C. Much acidic functional groups on the adsorbent has high adsorption potential just like chemical adsorption is necessary to enhancement of  $(\text{CH}_3)_2\text{NH}$  gas at 20°C.

**Key words** — removal efficiency, ammonia, amine gases, woody charcoal, activated carbon

## INTRODUCTION

Air pollutants such as malodorous and volatile organic compounds cause various health disorders. Ammonia ( $\text{NH}_3$ ) and trimethylamine [ $(\text{CH}_3)_3\text{N}$ ] are emitted from industrial facilities such as carcass-processing plants, and sewage-treatment plants.<sup>1)</sup> They are major chemicals of malodorous components like  $\text{H}_2\text{S}$ ,  $\text{CH}_3\text{SH}$  and  $(\text{CH}_3)_2\text{S}$ . They have pungent, urinous odor, followed by the irritation of the eyes and respiratory tract and nausea. With increasing concern for public health and environmental quality, more stringent regulations have come into effect on the acceptable levels of these compounds.

A number of studies related to the removal of  $\text{NH}_3$  and  $(\text{CH}_3)_3\text{N}$  by adsorbents have been conducted using zeolite and silicate,<sup>2,3)</sup> activated carbon,<sup>1,4)</sup> activated carbon fiber,<sup>5)</sup> and charcoal.<sup>6,7)</sup> Re-

moval efficiencies over various temperature ranges would be important for practical use, however, most experiments have been designed to at room temperature (*ca.* 20°C).

Activated carbon is known to have a heterogeneous physical and chemical structure. It is characterized by the existence of micro, meso, macro pores of different sizes, while its surface indicates non-polar and hydrophobic characteristics. The activated carbon has a high adsorption performance for volatile organic carbon (VOC), while it is poor for polar chemicals (*e.g.*,  $\text{NH}_3$  and  $\text{H}_2\text{S}$ ) with a high adsorption potential.<sup>7,8)</sup> Woody charcoal is used partly as an adsorbent, and its specific surface area is smaller than that of activated carbon.<sup>9)</sup> Many investigators have found that charcoal changes structurally and chemically as a result of manufacturing temperatures.<sup>7,10)</sup> Asada *et al.*<sup>7)</sup> have clarified that the bamboo charcoal carbonized at 500°C possess as a higher absorbability for  $\text{NH}_3$  gas than those at 700°C and 1000°C. These implies that the acidic functional groups on the woody charcoal surface are forming with increasing carbonized temperature, and in consequence the ammonia adsorption effect of the bamboo charcoal at 500°C is higher than that of 700°C

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(or 1000°C).

Similarly to  $\text{NH}_3$ , methylamine  $[(\text{CH}_3)\text{NH}_2]$ , dimethylamine  $[(\text{CH}_3)_2\text{NH}]$ , and trimethylamine  $(\text{CH}_3)_3\text{N}$  are also major alkaline and malodorous gases. Abe *et al.*<sup>6)</sup> pointed out that  $(\text{CH}_3)_3\text{N}$  gas adsorption is suitable for the adsorbent with well developed pore structure, a larger specific area and pore volume, rather than an acidic or a basic group on the adsorbent surface. We assume that activated carbon is a suitable adsorbent for  $(\text{CH}_3)_3\text{N}$  gas adsorption because of including a large specific area and pore volume. However, the adsorption process of amine gases has not yet been fully investigated, especially for  $(\text{CH}_3)\text{NH}_2$  and  $(\text{CH}_3)_2\text{NH}$ .

In general, an equalization amount of molecular adsorption becomes large at low temperature because of occurring adsorption exothermic of the molecule on the adsorbent surface. On the other hand, physical adsorption of the adsorbate is kept by weak potential due to 'van der Waals attraction' that gives high heat energy to the molecule may break off the weak adsorption potential. Therefore, the removal efficiency of the amine gases on the adsorbent might be different between low and high temperature, respectively.

In this paper, we attempted to clarify the removal efficiencies for major alkaline gases, like  $\text{NH}_3$ ,  $(\text{CH}_3)\text{NH}_2$ ,  $(\text{CH}_3)_2\text{NH}$  and  $(\text{CH}_3)_3\text{N}$ , on the activated carbon and woody charcoal carbonized at 500°C at two temperatures (5°C and 20°C). The dominant mechanism between each adsorbates and adsorbent was discussed.

## MATERIALS AND METHODS

We prepared two adsorbents; *i.e.*, the woody charcoal and granulated activated carbon. Woody charcoal was made from *Cryptomeria Japonica* in the kiln. For carbonizing the wood, the temperature of the kiln was increased automatically at the rate of 1°C/min up to 500°C and maintained for 3 hr without exposure to air. Thereafter woody charcoal was cooled naturally in the kiln and removed to a desiccator. The granulated activated carbon was made from woody material using a chemical activation process with  $\text{ZnCl}_2$  solution, as chemical activation agents, at 700°C (Wako Pure Chemical Industries Ltd., Japan). These two adsorbents in their manufacturing process, however, both the activated carbon depends on physical adsorption and the woody charcoal depends on chemical adsorption is the most

suitable adsorbents on the comparison with the dominant adsorption mechanism. These two adsorbents for adsorption experiments were grounded by a wooden hammer and sieved to make particle diameters in the 25–125 mm range. The adsorbents were degassed at 115°C in an oven prior to analysis.

To evaluate the surface properties of the two adsorbents, specific surface area, the total pore volume, and the micro, meso pore volume were determined by the adsorption isotherms of nitrogen. An automated adsorption apparatus (Autosorb-1MP, Quantachrome, U.S.A.) was employed for these measurements. Adsorption of  $\text{N}_2$  was performed at 77.4 K at the relative pressure from  $10^{-3}$  to 1 after degassing for 3 hr at 200°C. The specific surface areas and total pore volume were determined from application of the BET method and the adsorption volume of 0.95 relative pressure. The micro pore volume was determined by Dubinin-Radushkevich (D-R) equations, and the meso pore volume by the BJH method.

Titration followed using the method proposed by Boehm *et al.*<sup>11)</sup> to determine the total surface acidity of the charcoal is as follows: a charcoal sample of 1.0 g was added to 100 ml of 0.1 mol/l NaOH solution, and residual NaOH was determined by titration with 0.1 M HCl after 67 hr.

Ammonia,  $(\text{CH}_3)\text{NH}_2$ ,  $(\text{CH}_3)_2\text{NH}$  and  $(\text{CH}_3)_3\text{N}$  were employed as the adsorbates in the gas phase adsorption experiments. The concentrations of the commercial adsorbates, supplied by Wako Pure Chemical Industries Ltd., were as follows: 40% methylamine solution, abt. 50% dimethylamine solution, 30% trimethylamine solution, 28% ammonia solution. Therefore, the gases used in the adsorption experiments were prepared by mixing each of the vaporized adsorbates into the pure  $\text{N}_2$  gas (> 99.99%) of a 5 l TEDLAR bag (GL Science Ltd, Japan) up to the required concentrations.

The initial gas concentration in the bag was made in advance, and was defined as the initial concentration. To mix the adsorbate and adsorbent in the bag, 0.05 g of the adsorbent was enclosed. Blank test (without adsorbents) was also conducted for the control experiment. The adsorption temperatures in the incubators were kept at 5°C and 20°C without any lights.

The concentration of  $\text{NH}_3$  gas was measured using a Kitagawa's detector tube (Komyo Rikagaku Kogyo Ltd., Japan; 105SC for  $\text{NH}_3$ ). The concentrations of  $(\text{CH}_3)\text{NH}_2$ ,  $(\text{CH}_3)_2\text{NH}$  and  $(\text{CH}_3)_3\text{N}$  gases in the bag were measured by a portable-type odor

**Table 1.** Specific Surface Area, Micro-, Meso-Pore Volumes of Woody Charcoal Carbonized at 500°C and Activated Carbon, and the Consumption amount of NaOH Absorbed on them

Carbon type	Specific surface area (m <sup>2</sup> /g)	Micro pore Volume (ml/g)	Meso pore Volume (ml/g)	Consumption amount of NaOH (mmol/g)
Woody charcoal carbonized at 500°C	330.2	0.11	0.07	1.27
Activated carbon	1255.9	0.51	0.17	0.52

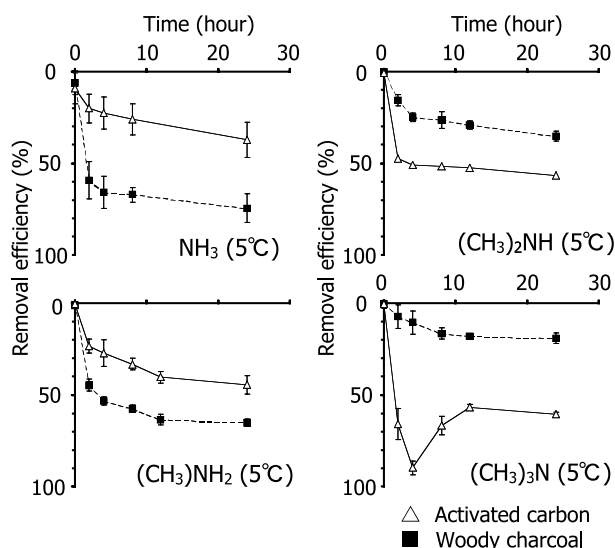
sensor XP-329 (COSMOS Ltd., Japan), which consisted of the semiconductor made by metal oxide. This apparatus expressed the value as the intensity of the smell when a certain amount of gas from the bag was injected into the odor sensor using a gastight syringe. To clarify the differences of adsorption efficiencies among 0.05 g of adsorbents, the initial NH<sub>3</sub> concentrations in the bags were fixed at 150 ppm (5°C) and 100 ppm (20°C). The difference in the initial NH<sub>3</sub> concentrations in the bags at 5 and 20°C was accounted by that the NH<sub>3</sub> concentration in the bag reached at 0 ppm after 8 hr if the initial NH<sub>3</sub> concentrations in the bags at 5°C was fixed at 100 ppm, same concentration at 20°C. As a result of preliminary experiments, it is necessary that the initial gas concentration in the bags should be fix at high because both two adsorbents adsorbed these gases completely at the low concentrations. Therefore, to clarify the difference in the adsorption efficiencies of the gases between two adsorbents, the initial indicated values of (CH<sub>3</sub>)NH<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>NH and (CH<sub>3</sub>)<sub>3</sub>N gases in the bag were fixed at 500, corresponding to 4580, 650, 730 ppm, respectively.

Comparing with blank test, removal efficiencies of experimental gases, *i.e.*, RE (%) was calculated as follows:

$$RE(\%) = \frac{iv_{\text{blk}} - iv_{\text{smp}}}{iv_{\text{blk}}} \times 100 \quad (1)$$

where  $iv_{\text{blk}}$  is the indicated value of the blank test, and  $iv_{\text{smp}}$  is the indicated value of the adsorption experiments.

The results of preliminary experiments showed that the adsorption had attained equilibrium during 24 hr for all adsorbents. Following the measurement of gaseous concentrations in the bag at the 0 hr, the adsorbent and gas were mixed by opening the sealing clip. The concentration of the gas in the bag was measured at 2, 4, 8 and 24 hr. Adsorption experiments were conducted in eight replications, and data were represented as the averaged values of the replications.



**Fig. 1.** Time Course Changes of Removal Efficiencies of NH<sub>3</sub>, (CH<sub>3</sub>)NH<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>NH, (CH<sub>3</sub>)<sub>3</sub>N Gases in the Bags at 5°C  
Data in the graph show mean values, and the vertical bars show the S.D. among eight replications.

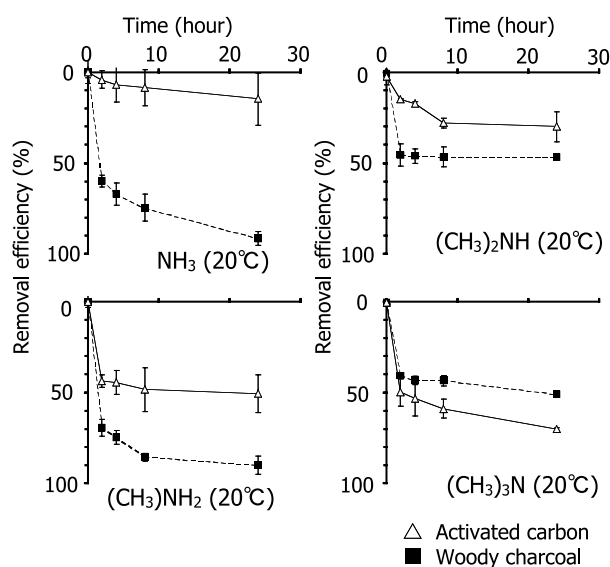
## RESULTS

### Surface Properties of Two Adsorbent

Surface properties of pore structures and chemistries are summarized in Table 1. The specific surface area of the pore volume in the activated carbon is *ca.* four times larger than that in woody charcoal carbonized at 500°C. This tendency coincided with the relationship of the micro and meso pore volume between the activated carbon and woody charcoal. The activated carbon has a larger pore volume: *ca.* five times in micro pore, and *ca.* two times in meso pores, than those of woody charcoal. The consumption amount of NaOH of the woody charcoal, acidic is two times greater than that of the activated carbon.

### Time Course Changes of Removal Efficiencies

Figure 1 shows the time course changes of removal efficiencies of (CH<sub>3</sub>)NH<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>NH, (CH<sub>3</sub>)<sub>3</sub>N and NH<sub>3</sub> gases in the 5 l bags at 5°C. The (CH<sub>3</sub>)NH<sub>2</sub> and NH<sub>3</sub> adsorption on the woody charcoal were



**Fig. 2.** Time Course Changes of Removal Efficiencies of  $\text{NH}_3$ ,  $(\text{CH}_3)\text{NH}_2$ ,  $(\text{CH}_3)_2\text{NH}$ ,  $(\text{CH}_3)_3\text{N}$  Concentrations in the Bags at  $20^\circ\text{C}$

Data in the graph show mean values, and the vertical bars show the S.D. among eight replications.

more effective than those of the activated carbon. In contrast to these gases, the  $(\text{CH}_3)_2\text{NH}$  and  $(\text{CH}_3)_3\text{N}$  adsorption of the activated carbon were more effective than those of the woody charcoal.

Figure 2 shows the time course changes of  $(\text{CH}_3)\text{NH}_2$ ,  $(\text{CH}_3)_2\text{NH}$ ,  $(\text{CH}_3)_3\text{N}$  and  $\text{NH}_3$  concentrations in the bags at  $20^\circ\text{C}$ , respectively. The  $(\text{CH}_3)\text{NH}_2$ ,  $(\text{CH}_3)_2\text{NH}$  and  $\text{NH}_3$  adsorption on the woody charcoal were more effective than those of activated carbon. The adsorption efficiencies of  $(\text{CH}_3)_3\text{N}$  gas on the activated carbon was constantly higher than that of woody charcoal. Although it indicated exceptionally low value at the 8 hr, its small S.D. guaranteed the value that is not an error.

## DISCUSSION

### Difference in the Surface Properties between Woody Charcoal and Activated Carbon

The carbonization temperature for preparing the charcoal is well known as a factor that determines the pore structure.<sup>10)</sup> As shown in Table 1, woody charcoal carbonized at  $500^\circ\text{C}$  and activated carbon were different in the specific surface area and pore volumes. Activated carbon showed that the specific surface area ( $\text{m}^2/\text{g}$ ) and micro pore volume ( $\text{ml}/\text{g}$ , pore diameter;  $< 2 \text{ nm}$ ) were 3.8, and 4.8 times larger than those of woody charcoal, while the difference

in meso pore volume (pore diameter;  $> 2 \text{ nm}$ ) was small. These results showed that a carbonization temperature is higher than  $500^\circ\text{C}$  resulting in the development of the pore structure in the micro pore class, following the specific surface area.

The acidity of the woody charcoal surface was *ca.* two times higher than that of activated carbon, although the woody charcoal did not develop sufficiently for surface pore structures (Table 1). In general, thermolysis of cellulose or lignin, which are the main components of wood, occurred actively when the carbonization temperature reached up to  $400\text{--}500^\circ\text{C}$ . A consequence of thermolysis, acidic functional groups, such as carboxyl and phenolic hydroxyl groups, were formed on the charcoal surface.<sup>12–14)</sup> The relationship between the carbonization temperature of *Cryptomeria Japonica* and the amounts of acidic functional groups on the charcoal, the charcoal prepared at  $400^\circ\text{C}$  possesses a maximum absorbability for base as like ammonia gas while the specific surface area is not well developed. Moreover, the amounts of acidic functional groups on the charcoal at  $500^\circ\text{C}$  and after  $600^\circ\text{C}$  decreased up to one third, and one tenth of  $400^\circ\text{C}$ , respectively.<sup>10)</sup> The difference in the amounts of acidic groups between two adsorbents could be caused by the difference of carbonization temperature between two adsorbents.

### Adsorption Efficiencies at $5^\circ\text{C}$ and $20^\circ\text{C}$

From the results of the time course changes (Figs. 1 and 2), adsorption efficiencies of  $\text{NH}_3$ ,  $(\text{CH}_3)\text{NH}_2$ ,  $(\text{CH}_3)_2\text{NH}$ , and  $(\text{CH}_3)_3\text{N}$  at  $5^\circ\text{C}$  and  $20^\circ\text{C}$  are summarized as follows: ammonia and  $(\text{CH}_3)\text{NH}_2$  are removed more effectively by woody charcoal than activated carbon at  $5^\circ\text{C}$  and  $20^\circ\text{C}$ , dimethylamine is removed more effectively by activated carbon than woody charcoal at  $5^\circ\text{C}$ , by woody charcoal at  $20^\circ\text{C}$ , trimethylamine is removed more effectively by activated carbon than woody charcoal at  $5^\circ\text{C}$  and  $20^\circ\text{C}$ .

Our results showed that the acidity of woody charcoal surface was higher than that of activated carbon surface, which suggests the existence of acidic functional groups on the surface. These results are in agreement with Asada *et al.*<sup>7)</sup> who confirmed that many acidic functional groups remained on the surface of bamboo charcoal carbonized at  $500^\circ\text{C}$  by using ESR spectra measurements. Many authors have reported there is a correspondence between the compatibility of ammonia gas and the amounts of acidic groups on the surface.<sup>10)</sup> As a con-

sequence of the reaction between an acid and a base, therefore, the woody charcoal at 500°C has greater number of acidic functional groups, which lead to the higher removal efficiencies of  $\text{NH}_3$  and  $(\text{CH}_3)_2\text{NH}$  gases than those of activated carbon.

Compared with  $\text{NH}_3$  and  $(\text{CH}_3)_2\text{NH}$  gases, the removal efficiency of  $(\text{CH}_3)_3\text{N}$  gas using two adsorbents is inverted (Figs. 1 and 2). A larger amount of the  $(\text{CH}_3)_3\text{N}$  molecule impregnates into the porous on the activated carbon than those on the woody charcoal carbonized at 500°C, resulting the development of larger specific surface area and pore volume as shown in Table 1. The adsorption capacity of adsorbents depends on the integrated pore volume which the adsorbate can enter.<sup>1,15)</sup> Moreover, the adsorption potential increases with decreasing the distance between adsorbate and pore walls.<sup>6)</sup> The molecule size of  $(\text{CH}_3)_3\text{N}$  is larger than that of  $\text{NH}_3$ , which explain the adsorption potential of  $(\text{CH}_3)_3\text{N}$  gas is higher than that of the  $\text{NH}_3$  gas on the activated carbon surface. This is due to the fact that the removal efficiency of  $(\text{CH}_3)_3\text{N}$  gas against the activated carbon was higher than this the woody charcoal. This can be concluded by physical adsorption, where was slight acidic functional groups was present on the activated carbon surface.

Concerning  $(\text{CH}_3)_2\text{NH}$  gas adsorption, its removal efficiency using the activated carbon is higher than the woody charcoal at 5°C, and lower at 20°C (Figs. 1 and 2). An equalization amount of molecular adsorption becomes large at low temperature because the presence of adsorption exothermic of the molecule on the adsorbent surface. The  $(\text{CH}_3)_2\text{NH}$  gas adsorption at 5°C could be based on physical adsorption which activated carbon has the large specific surface area and pore volume. At higher temperature, however, high heat energy to the molecule enables to break off the weak adsorption potential. Much acidic functional groups on the adsorbent has high adsorption potential just like chemical adsorption is necessary to enhancement of  $(\text{CH}_3)_2\text{NH}$  gas adsorption at 20°C.

The four gases tested in our study,  $(\text{CH}_3)_2\text{NH}$ ,  $(\text{CH}_3)_2\text{NH}$ ,  $(\text{CH}_3)_3\text{N}$  and  $\text{NH}_3$ , are similar chemicals in terms of alkalinity. The main conclusions that the four gases were effectively adsorbed against the activated carbon and woody charcoal carbonized at 500°C are presented using the physical or chemical characteristics of the adsorbent surface. Moreover, the most suitable adsorbents against a chemical depended on temperature, just like  $(\text{CH}_3)_2\text{NH}$ . The

present work suggests that the temperature range during practical use can be changed accordingly on good or poor performances of the adsorbents.

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