FUNDAMENTAL CHARACTERISTICS OF ACTIVATED CARBONS AND COKES FOR 1,2,3,4-TETRACHLOROBENZENE ADSORPTION IN FLUE GAS

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Introduction

Activated carbons and cokes have been employed as a sure technical means of reducing the emission of dioxins from incineration plants. However, with this method, the quantities of materials to be used are judged empirically, which may lead to overuse. Hence, various activated carbons and coke have been tested to clarify their fundamental adsorption characteristics[1]. This study was conducted to further clarify the adsorption characteristics of several kinds of activated carbons and coke that are sprayed in powder form into flue gas ducts. The study focused on determining the adsorption amount in equilibrium and identifying the relationship between physical properties and adsorbability. 1,2,3,4-Tetrachlorobenzene was used as an alternative compound to dioxins.

Methods and Materials

Adsorbents

Four activated carbons (A, B, C, D) and one activated coke (E) were employed in the experiment. All of the adsorbents were in fine powder form, and so an inert carrier medium (granular calcium carbonate, mean particle diameter: 2.4 mm) was used as a carrier by coating it with the fine powder. The apparent packed volume was 9.8 ml. In order to clarify the fundamental physical properties of the samples, mean particle diameter, specific surface area and total pore volume were measured. The mean particle diameter was measured by the laser diffraction method. The specific surface area and total pore volume for pore diameter of 60 nm or less were measured by the N_2 adsorption BET method. The total pore volume for pore diameter of 60 nm – 200 μm was measured by the mercury press-in method.

Test equipment

A schematic diagram of the adsorption test system is illustrated in Fig. 1. Purified air was dosed to the diffusion tube, and then 1,2,3,4-tetrachlorobenzene in the tube diffused and was mixed with air. Carbon dioxide and water were added to produce a model gas for incinerator flue gas. 1,2,3,4-Tetrachlorobenzene in the model gas was adsorbed on the adsorbent in the oven. Next, the model gas was dosed to the impingers filled with n-hexane for collecting 1,2,3,4-tetrachlorobenzene after the drain. An intermittent automatic sampling device was developed and used in order to obtain 1,2,3,4-tetrachlorobenzene data. Trapped 1,2,3,4-tetrachlorobenzene in n-hexane was determined quantitatively by gas chromatograph mass spectrometry (Saturn 2200, Varian Technologies Japan Ltd.).

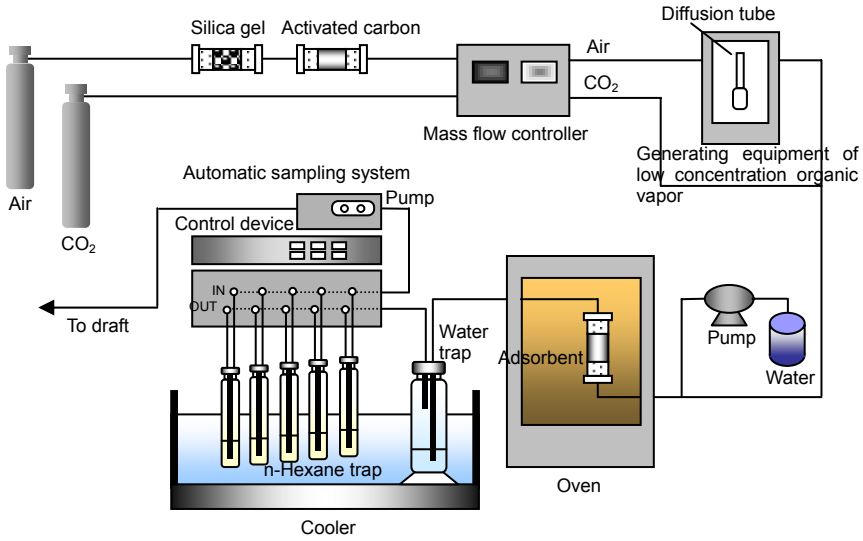

Fig. 1 Schematic diagram of adsorption test system

Experimental conditions

The space velocity was set at 5000 h^{-1} and temperature of the adsorbent in the oven was kept at 170°C. 1,2,3,4-Tetrachlorobenzene concentration was varied from 8 to 27 ppb (v/v). Moisture content in the gas was set at 40% (v/v).

Results and Discussion

Physical properties

The detailed physical properties of the activated carbons and coke employed in this experiment are shown in Table 1. All of the adsorbents were in fine powder form and their mean particle diameter ranged from 9 to 30 μm. The BET specific surface area of activated carbons ranged from 590 to 1200 m^2/g, and that of activated coke was 285 m^2/g. The total pore volume was divided into micro pore (pore diameter: 2 nm or less), meso pore (2 – 60 nm) and macro pore (60 nm – 200 μm), and was evaluated in comparison with the adsorption ability.

Table 1 Fundamental properties of adsorbents employed

	A	B	C	D	E
Raw material	Activated carbon palm shell	Activated carbon palm shell	Activated carbon coal	Activated carbon peat	Activated coke lignite
Mean particle diameter (μm)	9.24	18.7	29.6	21.0	23.5
BET specific surface area (m^2/g)	1213	1097	833	590	285
Total pore volume (ml/g)					
Pore diameter < 2 nm	0.46	0.40	0.31	0.19	0.09
2 ~ 60 nm	0.10	0.09	0.19	0.25	0.14
60 nm ~ 200 μm	1.20	0.76	0.83	1.07	0.79

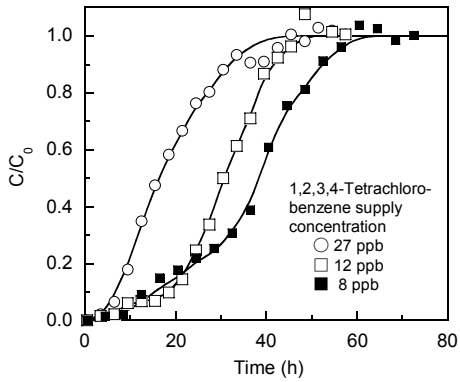

Fig. 2 Breakthrough curves of adsorbent C (activated carbon) for 1,2,3,4-tetrachlorobenzene
Space velocity: 5000 h^{-1}
Temperature: 170°C Moisture: 40% (v/v)

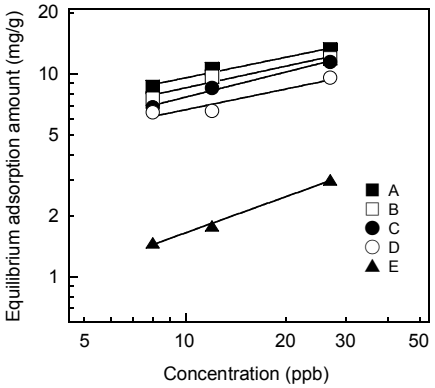

Fig. 3 Adsorption isotherms of various adsorbents for 1,2,3,4-tetrachlorobenzene
Space velocity: 5000 h^{-1}
Temperature: 170°C Moisture: 40% (v/v)

Breakthrough curves

The breakthrough curves at three concentrations of material C (activated carbon) for 1,2,3,4-tetrachlorobenzene are shown in Fig. 2. It is confirmed that the time to reach breakthrough decreased as the supply concentration was increased. It was shown that the curve at the supply concentration of 8 ppb reached saturation in around 60 hours, while those at the supply concentration of 27 ppb reached saturation in around 40 hours. It was also found that the adsorbed amounts at supply concentrations of 8, 12 and 27 ppb were 6.9, 8.6 and 11.5 mg-1,2,3,4-tetrachlorobenzene/g respectively when obtained by the integral of the breakthrough curves. Experiments were performed similarly for the other four kinds of adsorption sample, then the adsorption isotherms were obtained.

Adsorption isotherm

As illustrated in Fig. 3, the influence of 1,2,3,4-tetrachlorobenzene supply concentration was examined at 170°C and the adsorption isotherms were obtained. The breakthrough time of all adsorbents decreased as 1,2,3,4-tetrachlorobenzene concentration increased. Adsorption isotherms were nearly straight lines for all of the adsorbents and were well expressed as the adsorption isotherm of Freundlich's formula:

$$q = k C^{\frac{1}{n}} \qquad (1)$$

Table 2 Adsorption properties of various adsorbents

	k	n
A	4.4	2.9
B	3.7	2.8
C	3.0	2.4
D	3.0	2.9
E	0.4	1.7

where q is equilibrium adsorption amount and C is equilibrium concentration of 1,2,3,4-tetrachlorobenzene. The values of coefficients k and n in the equation were arranged in Table 2, revealing that there was a difference of around 11 times at the k value in materials A and E. Activated coke had a smaller value than the activated carbons.

Relationship between physical properties and adsorption potential

From the adsorption isotherms shown in Fig. 3, the equilibrium adsorption amount at the supply concentration of 10 ppb was calculated. As shown in Fig. 4, it was confirmed that the adsorbed amount increased as the BET specific surface area of the adsorbents was higher. The dependence of this adsorbed amount on the pore volume for each pore diameter is shown in Figs. 5(a)-(c). The results showed that there was a close positive correlation between adsorption ability and pore volume for pore diameter of 2 nm or less. Fig. 5(a) suggests that the micro pore volume of 2 nm or less diameter was the most important factor governing the adsorption ability for all adsorbents.

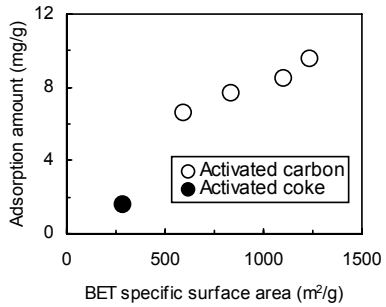

Fig. 4 Relationship between the BET specific surface area and adsorbed amount

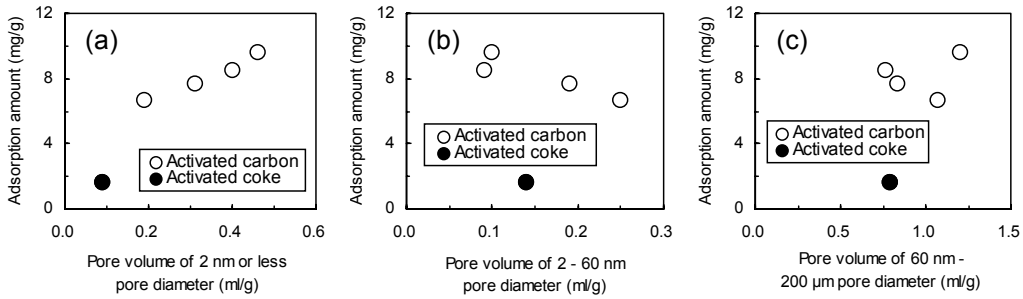

Fig. 5 Relationships between pore volume of up to 2 nm (a), 2 – 60 nm (b), 60 nm – 200 µm (c) pore diameter and adsorption amount. The value required to make the supply concentration 10 ppb was calculated as the absorbed amount.

Conclusion

The basic adsorption characteristics of activated carbon and coke adsorbents were examined considering the fundamental physical properties of the adsorbents. The results indicated that the equilibrium adsorption amount of materials depended closely on BET specific surface area and micro pore volume. This knowledge may be useful for choosing the most appropriate material in flue gas treatment.

Reference

1 Komatsu T., Moriya K., Kawamoto K., Nagase K. (2001) Basic adsorbability of dioxin surrogate compounds on various adsorbents, Organohalogen Compounds, 54, 203