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Intraparticle Diffusivity of Methylene Blue into Pores of Activated Carbon and Pyrolysis Ash Derived from Organic Surplus Sludge

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In recent years, the number of sewers in Japan has greatly increased. Consequently, the amount of sludge to be treated by disposal plants has also increased proportionately. The treatment of sludge is aimed at processing the constituents of sludge into materials which may be used to fill up holes or which may be buried beneath the surface of the earth or safely dumped into the sea. Other uses include fertilizers and soil conditioners for foresting land. Approximately 80 % of sludge is for hole filling. Consequently, suitable sites for this purpose are difficult to find within a large city. Thus, it has been necessary to reduce the amount of sludge by incineration. It is necessary to find some profitable use for pyrolysis ash which up to now has been simply dumped as industrial waste. This ash has the property of a small amount of adsorption capacity because of small surface area but in particular, its rate of adsorption should qualify it for some useful function.

In this paper, we report on the efforts being made to find a use for pyrolysis ash such as the removal of certain injurious materials by adsorption. As a part of this research the intraparticle diffusivity of methylene blue into the pores of pyrolysis ash was investigated.

EXPERIMENTAL

Materials: Three kinds of commercial activated carbon (4-7 mesh) and three kinds of pyrolysis ash (4-7 mesh) separated by specific gravity were used as samples. The pyrolysis ash was obtained from a sewage disposal plant in the spring at Osaka, Japan. Methylene blue was of reagent grade quality (Wako Chemicals Co., Ltd., Osaka) and used without further purification.

Procedure for Equilibrium Isotherm: It took 8 days to attain equilibrium adsorption at 25 C with constant shaking. The equilibrium amount of methylene blue adsorbed on activated carbon and pyrolysis ash were measured at 665 nm with a spectrophotometer (Hitachi 100-10).

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Measurement of Adsorption Rate: Four grams were accurately weighted from each sample and added to 800 mL of 100 ppm methylene blue solution which was adsorbed with shaking at 400 r.p.m. and at 25 C. 20 mL of the suspension were taken up from suspension by a 20 mL pipet at regular intervals, and 1 mL of the suspension was accurately diluted to 100 mL with purified water, and the concentration of diluted methylene blue solution was measured. A solution of methylene blue (ca,1000 ppm) and purified water were added to the suspension until its concentration and its volume became 100 ppm and 800 mL, respectively. The amount adsorbed was determined by an isotherm run.

Pore Size Distribution: The pore size distribution of activated carbon and pyrolysis ash was measured by method described previously (BOKI 1977).

RESULTS AND DISCUSSION

1. Physicochemical Properties of Activated Carbon and Pyrolysis Ash and Equilibrium Adsorption of Methylene Blue on Them.

Table 1 shows the physicochemical properties of activated carbon (Nos.1-3) and pyrolysis ash (Nos.4-6). In general, the amount adsorbed on adsorbent is dominated by its surface area, pore volume, and surface polarity such as pH. The surface areas and pore volumes of the pyrolysis ash were 1/20-1/40 and 1/6-1/15 that of the activated carbon, respectively. The pHs of the pyrolysis ash were as same as those of the activated carbon. Figure 1 shows the adsorption isotherm of methylene blue on activated carbon and pyrolysis ash.

TABLE 1. Properties of Activated Carbon and Pyrolysis Ash

Adsorbent No.	a) Surface Area (m^2/g)	b) Pore Volume (mL/g)	c) pH	d) Particle Diameter (mm)	e) Q_∞ at 100ppm (mg/g)
1	1384.5	0.7714	6.68	4.53	360.4
2	906.0	0.5416	6.95	4.65	180.3
3	642.9	0.3328	6.32	4.61	52.1
4	35.4	0.0516	6.01	3.80	9.3
5	42.5	0.0692	6.01	3.78	7.4
6	71.5	0.1182	6.01	3.80	8.3

a) By N_2 BET method
b) Integral pore volume of pore radii up to 100Å
c) By the method of URANO et al. (1976).
d) Geometric particle radius was measured by using a reading microscope.
e) Equilibrium amount of methylene blue adsorbed at equilibrium concentration 100 ppm and at 25 C.

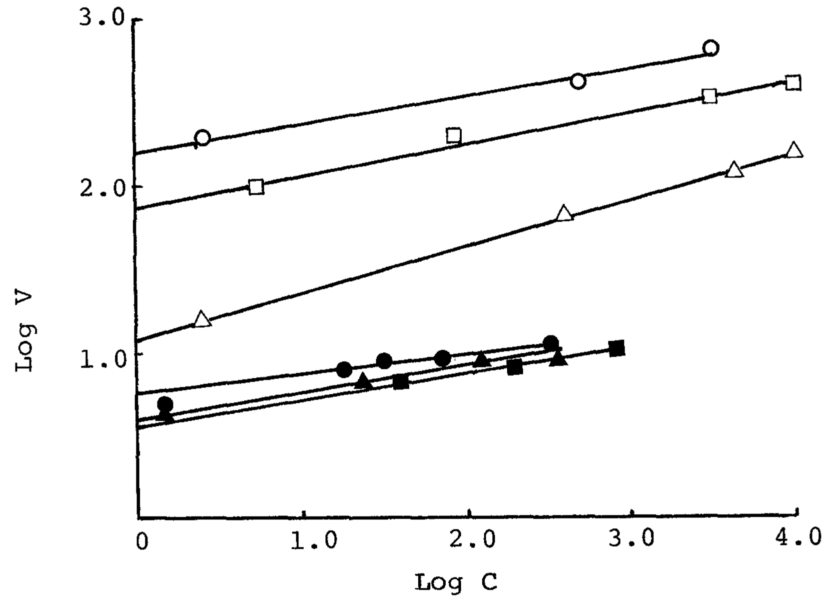

Fig. 1. Adsorption Isotherms of Methylene Blue on Activated Carbon and Pyrolysis Ash at 25 C. V: amount of Methylene Blue adsorbed (mg/g); C: equilibrium concentration of Methylene Blue (ppm); ○:No.1; □:No.2; △:No.3; ●:No.4; ■:No.5; ▲:No.6.

The amounts adsorbed on the pyrolysis ash were smaller than those on the activated carbon over the whole range of less than Log C=4.0 (Fig.1), and the amounts adsorbed on former were 1/5-1/43 as much as those on the latter at an equilibrium concentration 100 ppm (Table 1). The relationship between the amounts adsorbed at 100 ppm and pHs indicates that the amounts adsorbed are not dominated by their pHs. The pore size distributions of activated carbon and pyrolysis ash were obtained in order to elucidate their porous structure and the relationship between their porous structure and the amounts adsorbed. Figure 2 shows the pore size distribution curves of activated carbon and pyrolysis ash in the range of pore radii up to 100 Å. The pore size distribution curves of activated carbon rose sharply at the range of pore radii 7-20 Å and then reached a plateau. Another the pore size distribution curves of pyrolysis ash rose sharply at the ranges of radii 15-30 Å, and then the curves of Vp against r became concave towards r to 100 Å. It was concluded that the pores of activated carbon distribute convergently at micropores (r<15-16Å DUBININ 1966), while those of pyrolysis ash, at the transitional pores (15-16<r< 1000-2000Å DUBININ 1966). The molecule of methylene blue can easily enter into the micropores because of its diameter being 9.3 Å (KITAGAWA 1972). The results between the amount adsorbed and the pore size distribution can

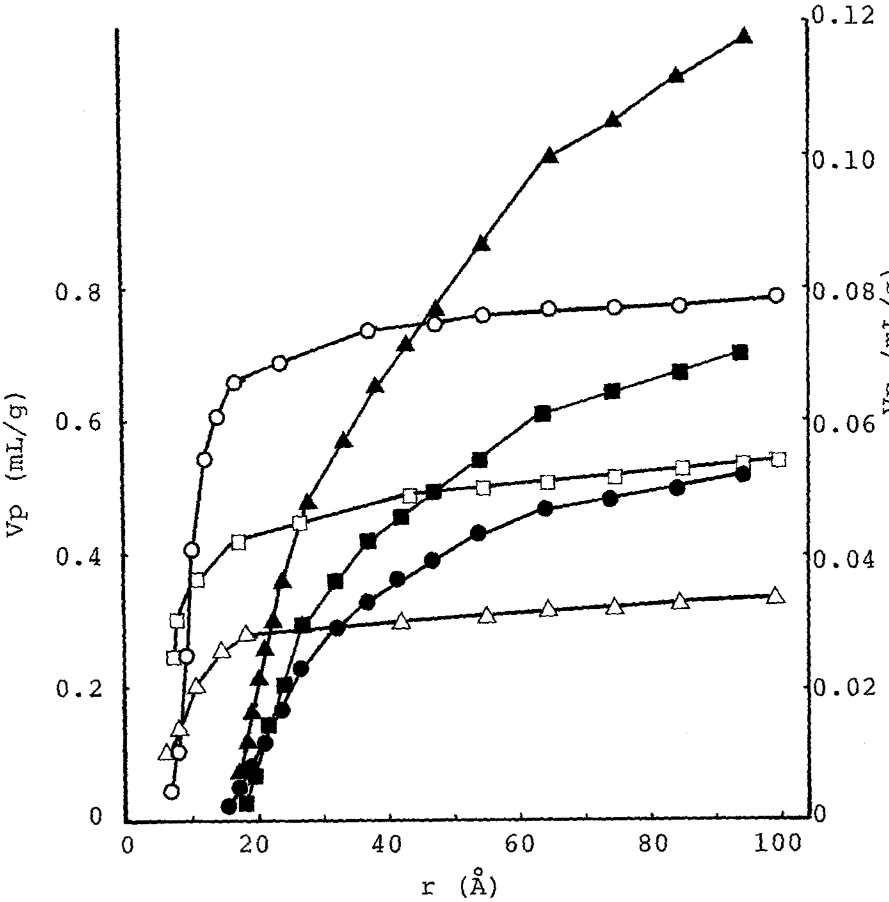

Fig. 2. Pore Size Distribution Curves of Activated Carbon and Pyrolysis Ash. Curves of open symbols and closed symbols are plotted the relationships between 0-0.8 and 0-0.12, respectively, as ordinate and pore radius as abscissa. Vp: integral pore volume(mL/g); r: pore radius; ○:No.1, □:No.2, △:No.3, ●:No.4, ■:No.5, ▲:No.6.

best be explained by assuming that methylene blue was mainly adsorbed in the micropores of activated carbon and in the transitional pores of pyrolysis ash.

2. Rate of Adsorption of Methylene Blue on Activated Carbon and Pyrolysis Ash

In order to clarify the adsorption rate of methylene blue on activated carbon and pyrolysis ash, the relationship between the adsorption ratio and adsorption time was obtained, as shown in Fig.3. Figure 3 denotes that the adsorption time of pyrolysis ash took 15-30 minutes to reach 0.1 of F, while that of activated carbon required from 70-180 minutes. It is concluded that the pyrolysis ash possesses the outstanding characteristics for the apparent rate of adsorption.

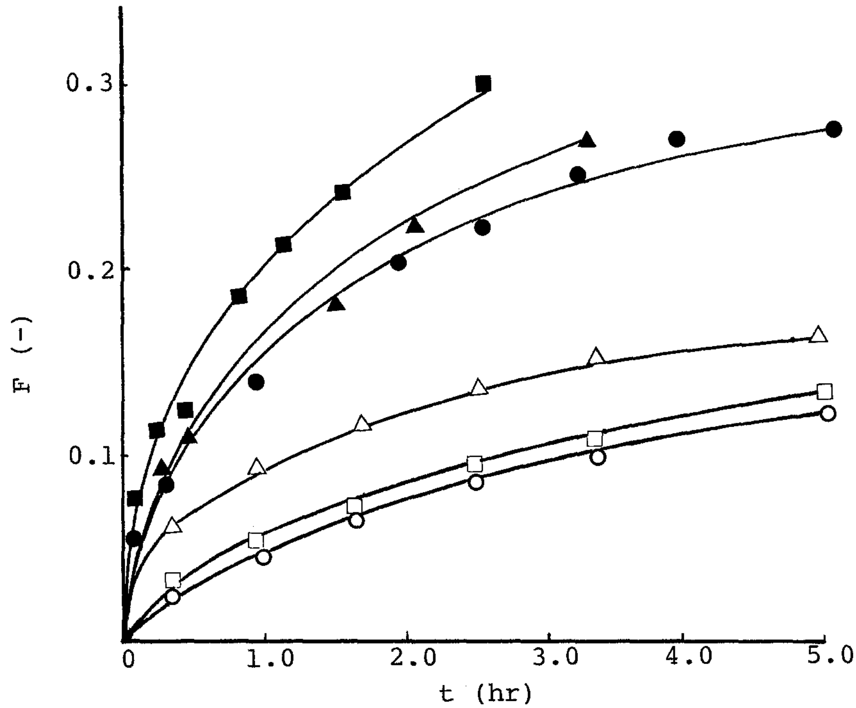

Fig. 3. Relationships between Adsorption Ratio and Adsorption Time for Methylene Blue on Activated Carbon and Pyrolysis Ash. F: adsorption ratio (dimensionless parameter); t: adsorption time; ○:No.1; □:No.2; △:No.3; ●:No.4; ■:No.5; ▲:No.6.

When the transition from a batch adsorption system to a column adsorption system is attemped, the rate parameters such as the intraparticle diffusivity are essential. The intraparticle diffusivity can be evaluated by the KEII's formula (1970) as,

$$\mathrm{Log}(1-F^2) = -(\pi^2 D'i/2.303R^2)t \qquad (1)$$

$$F = Qt/Q_\infty \qquad (2)$$

where F is the adsorption ratio, R, the particle radius of adsorbent, t, the adsorption time, Q_t, the amount of adsorbate adsorbed onto solid adsorbent with time, and Q_∞, the equilibrium amount of adsorbate adsorbed onto solid adsorbent. Figure 4 shows the relationship between the intraparticle diffusivity (D'i) and adsorption ratio. The curves (Nos.1-3) of logarithms of D'i against F became concave towards F and then approached their constant values, while the curves (Nos.4-6) showed their constant D'i regardless of F. The intraparticle diffusivity value of pyrolysis ash was 2-10 times larger than that of activated carbon.

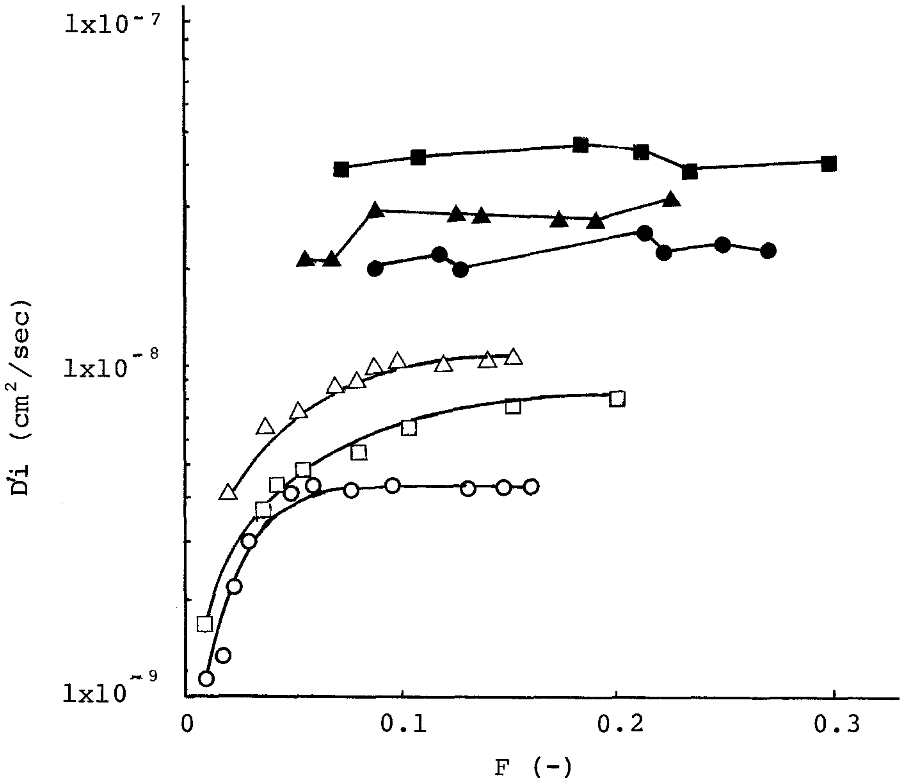

Fig. 4. Change in Intraparticle Diffusivity with Adsorption Ratio for Adsorption of Methylene Blue on Activated Carbon and Pyrolysis Ash. D'i: intraparticle diffusivity (cm^2/sec); F: adsorption ratio; ○:No.1; □:No.2; △:No.3; ●:No.4; ■:No.5; ▲:No.6.

The difference of D'i of methylene blue for activated carbon and pyrolysis ash can best be explained by the adsorption into the micropores and that into the transitional pores, respectively.

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