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Intraparticle Diffusivity of Methylene Blue into Porous Activated Carbon

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The problem of adsorption rate in liquid systems is often encountered in the control of water pollution. When the transition from a batch adsorption system to a column adsorption system is attempted, the rate parameters such as the intraparticle diffusivity are essential. URANO and NAKAI (1976) succeeded in very accurately describing the change in the intraparticle diffusivity with adsorption ratio 0.1 to 0.9 for sodium p-methylbenzenesulfonate adsorption under non-linear equilibrium. Little work on the relationship between intraparticle diffusivity and adsorption ratio at early stage of the adsorption has been done so far.

The purpose of this work is to clarify the mechanism of adsorption and to obtain the intraparticle diffusivity accuracy by the experiment of the batch adsorption. In this work Methylene Blue was selected as an adsorbate because that it is an indicator to predict the treatment capacity of activated sludge with activated carbon added (SUZUKI 1978) and the intraparticle diffusivity was determined by the use of the equation suggested by KEII (1970). The variation of the intraparticle diffusivities with the adsorption ratio up to about 0.2 and the relationship between the intraparticle diffusivity and the pore size distribution of activated carbon were investigated.

EXPERIMENTAL

Materials: Methylene Blue was of reagent grade quality (Wako Chemicals Co., Ltd., Osaka) and used without further purification. Activated carbon used was a commercial product, and its particle size was 4 - 7 mesh. Its physical properties are shown in TABLE 1.

Procedure for Equilibrium Isotherm: It took 8 days to attain equilibrium adsorption at 25°C with constant shaking, and the equilibrium amount of Methylene Blue adsorbed on activated carbon was measured at 665 nm with a spectrophotometer (Hitachi model 101).

Measurement of Adsorption Rate: A weighed activated carbon (4.000 to 8.000 g) was placed in a flask containing water, and the suspension was boiled for 1 hr to displace the air in the pores of activated carbon by water. The activated carbon impregnated with water was placed in a stirring solution of 800 mL of Methylene Blue (100 ppm) contained in a 1-L graduated cylinder. As the stirring rate above 350 rpm was confirmed experimentally

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to be the intraparticle diffusion-determing step, the suspension was stirred under the conditions of 400 rpm. The temperature of the graduated cylinder was adjusted to that of the equilibrium adsorption. A solution of 20 mL was sucked up from the suspension by means of a 20-mL pipette at regular intervals of elapsed time, and immediately a solution of Methylene Blue (*ca*, 1000 ppm) and distilled 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 the method of the isotherm run. The experiments of the adsorption rate were repeated three times to check the reproducibility.

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

RESULTS AND DISCUSSION

Figure 1 shows the Freundlich plots of the adsorption isotherms of Methylene Blue on activated carbon at 25°C. The Freundlich equation was applicable to the adsorption isotherms on activated carbon. Activated carbon No. 1 and No. 5 adsorbed the largest amount of Methylene Blue and the smallest amount, respectively, over the whole range of less than Log C = 4.0. The Freundlich constants k and n obtained are shown in TABLE 1.

TABLE 1

Properties of Activated Carbon Used

Activated Carbon No.	Surface Area^a) (m²/g)	pH^b)	Particle Diameter^c) (mm)	Q_∞^d) at 100 ppm (mg/g)	Freundlich Constant^e) k (mg/g)	n
1	1384.5	6.68	4.53	360.4	176.60	6.46
2	866.4	9.91	4.08	139.2	34.91	3.33
3	906.0	6.95	4.65	180.3	77.86	5.49
4	378.0	4.68	4.63	152.9	35.76	3.17
5	642.9	6.32	4.61	52.1	19.12	4.59

a) By N_2 BET method.

b) By the method of URANO et al. (URANO,K., M.SONAI, R.NAKAYAMA, & Y.KOBAYASHI: Nippon Kagaku Kaishi, 1773 (1976).).

c) Geometric particle radius was measured by using a reading microscope.

d) Equilibrium amount of Methylene Blue adsorbed at equilibrium concentration 100 ppm and at 25°C.

e) $V = k \cdot C^{\frac{1}{n}}$.

KEII (1970) reported the following equation to calculate the intraparticle diffusivity which refers to the concentrations of adsorbate in solid adsorbent (D_i') for the liquid phase adsorption under nonlinear equilibrium,

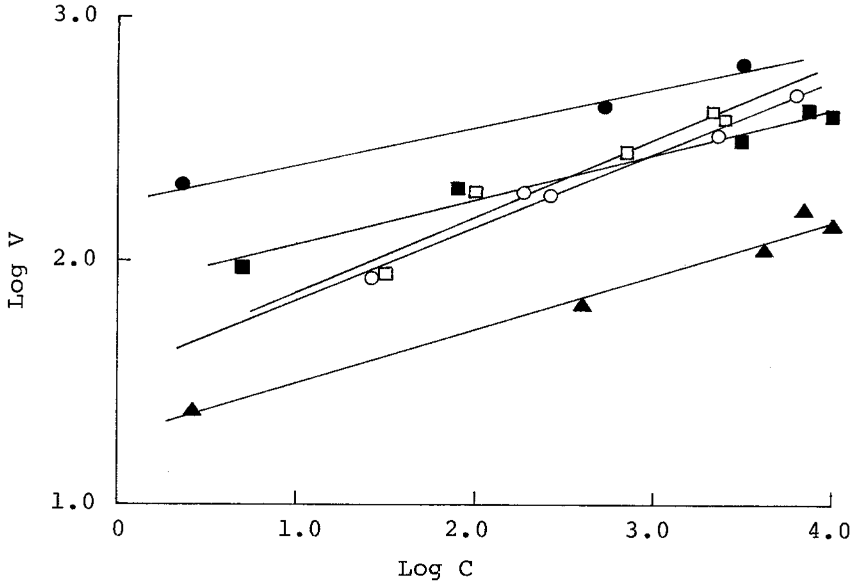

Fig. 1. Adsorption Isotherms of Methylene Blue on Activated Carbon at 25°C. ●:No. 1, ○:No. 2, ■:No. 3, □:No. 4, ▲:No. 5, V: amount adsorbed(mg/g), C: equilibrium concentration(ppm).

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

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

where F is the adsorption ratio, R is the particle radius of adsorbent, t is the adsorption time, Q_t is the amount of adsorbate adsorbed in solid adsorbent at elapsed time, and Q_∞ is the equilibrium amount of adsorbate adsorbed in solid adsorbent. The intraparticle diffusivity can be easily obtained by the application of single equation (1) to the experimental data. Figure 2 shows the relationship between $\mathrm{Log}(1-F^2)$ and adsorption time. The plots of $\mathrm{Log}(1-F^2)$ vs. t were somewhat curved in the range of t 0 - 1 hr. The results imply that the intraparticle diffusivities change with the adsorption ratio. In order to clarify in detail the relationship between D_i' and F, their plots were calculated by the use of equations (1) and (2) and shown in Fig. 3. The curves of logarithms of D_i' against F became concave towards F, and steadily approached their constant values.

According to the study of MASAMUNE and SMITH (1964), the intraparticle diffusivity is equal to the sum of the pore diffusivity(D_p) and the surface diffusivity(D_s), and the intraparticle diffusivity in adsorption under nonlinear equilibrium is given by

$$D_i'=D_p/\rho_p(dQ_{p\infty}/dC_p)+D_s \qquad (3)$$

where ρ_p is the apparent density of adsorbent, $Q_{p\infty}$ is the equilibrium amount of adsorbate adsorbed in pores and C_p is the concentration of adsorbate in pores. If no linear equilibrium of Henry's type has been established between $Q_{p\infty}$ and C_p, the intraparticle diffusivity has been reported to change because of the variation of $dQ_{p\infty}/dC_p$ (URANO & NAKAI 1976). According to the above definition, no linear equilibrium is established between $Q_{p\infty}$ and C_p in the early stage of F, but the linear equilibrium is established in the range of constant D_i' regardless of F.

ABE et al. (1979) demonstrated that the potential theory of Polanyi is capable of being applied to the liquid phase adsorption of anisole on activated carbon. According to the potential theory of Polanyi, the pores of

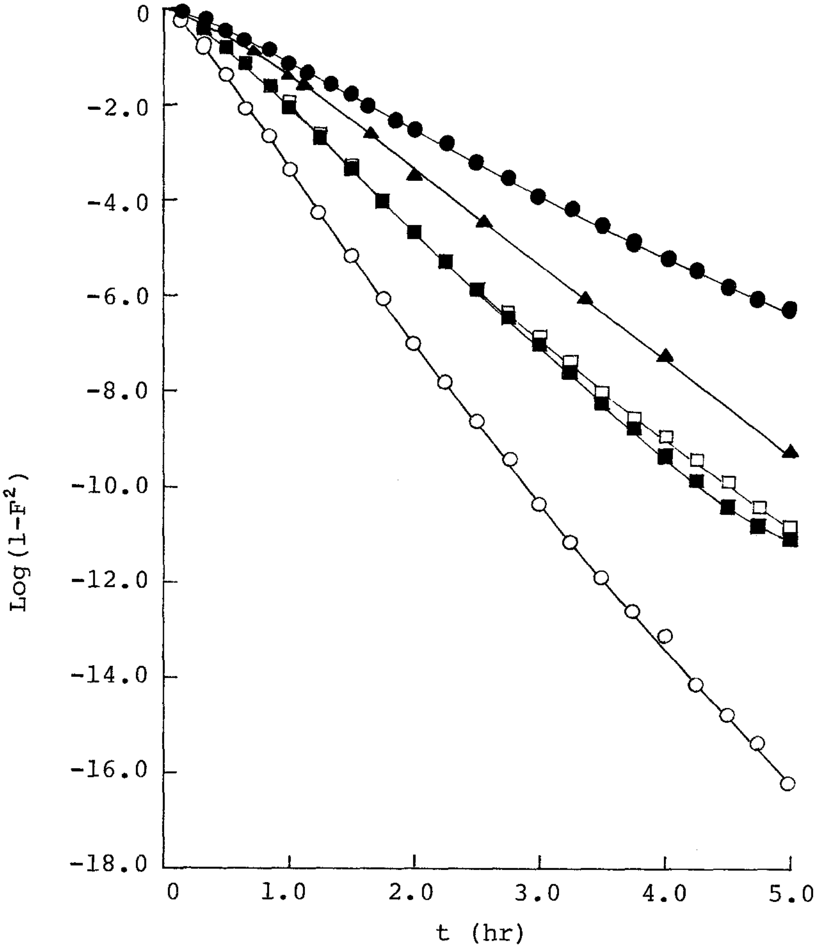

Fig. 2. Relationships between $\mathrm{Log}(1-F^2)$ and Adsorption Time for Methylene Blue on Activated Carbon. ●:No. 1, ○:No. 2, ■:No. 3, □:No. 4, ▲:No. 5, F: adsorption ratio(dimensionless parameter), t: adsorption time.

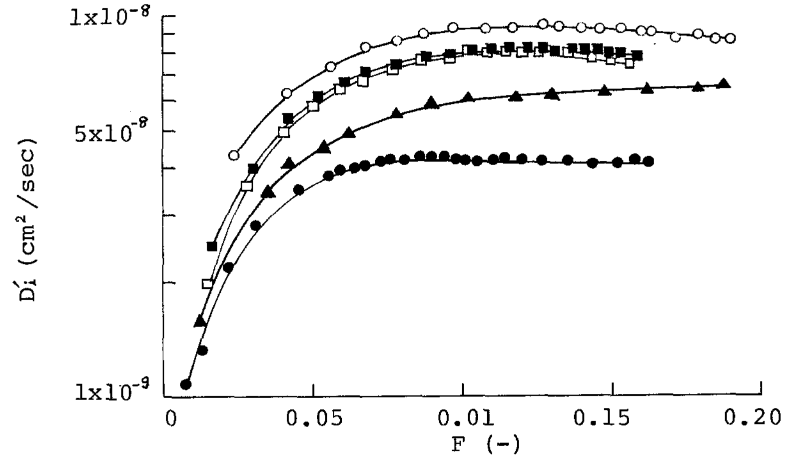

Fig. 3. Change in Intraparticle Diffusivity with Adsorption Ratio for Adsorption of Methylene Blue on Activated Carbon. ●:No. 1, ○:No. 2, ■:No. 3, □:No. 4, ▲:No. 5, D_i': intraparticle diffusivity, F: adsorption ratio.

adsorbent will be filled with adsorbate from the smallest pore up to pores of a certain dimension (PONEC et al.1974). KAWAZOE et al.(1975) found that sodium dodecylbenzene sulfonate was adsorbed consecutively from the smallest pore to the large pores of activated carbon. These information gave the following conclusion that Methylene Blue was mainly adsorbed in the micropores of activated carbon in the early stage of the adsorption. In the early stage of F, that is, in the range where D_i' increases with the increase of F, D_i' is affected by the pore diffusivity rather than the surface diffusivity, while the predominant contribution of the surface diffusivity to D_i' is observed in the range of constant D_i' regardless of F.

Figure 4 shows the pore size distribution curves of activated carbon to clarify the relationship between D_i' and pore size distibution. The relationship between the intraparticle diffusivity which refers to the concentration of adsorbate in solution (D_i) and the pore radius were described by HIRSCHLER et al. (1955) and YAGI et al. (1965) on the adsorption of organic solvents on silica gel. HIRSCHLER et al. (1955) have pointed out that a relatively small increase in pore diameter can greatly increase the rate of adsorption. The result obtained by YAGI et al.(1965) indicated that D_i' is proportional to the average pore radius to the third power. The results reported here were somewhat different from those reported by HIRSCHLER et al.(1955) and YAGI et al.(1965). The present results indicated an apparent interaction between D_i' and the micropore volume of less than radius 9 Å. The minimum of pore radius into which Methylene Blue molecule can enter is about 6.5 Å(GLEYSTEEN et al. 1960), and ABE et al.(1977) reported that the adsorption at low equilibrium concentrations as utilized in this work is mainly affected by the micropores rather than the large pores. The results that there was an interaction between D_i' and micropore volume can be consistently explained on the basis of the information described above.

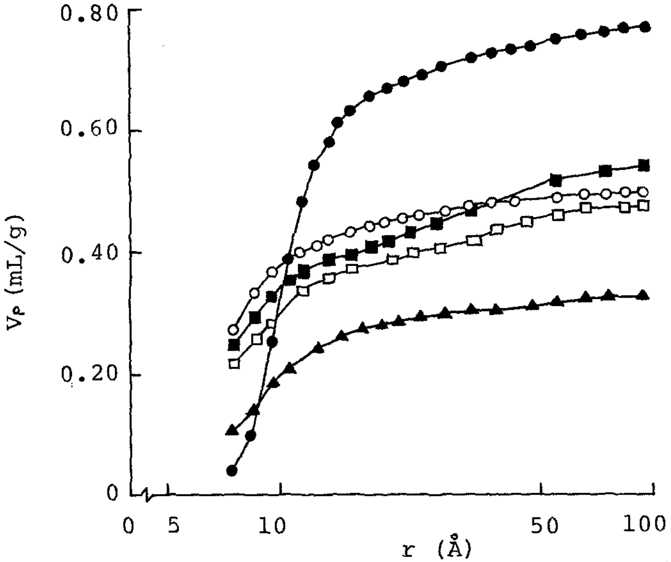

Fig. 4. Pore Size Distribution Curves of Activated Carbon. ●:No. 1, ○:No. 2, ■:No. 3, □:No. 4, ▲:No. 5, V_P: integral pore volume, r: pore radius.

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