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Adsorption Rate of Orthophosphate Ion during Its Adsorptive Removal from Solution by Activated Carbon

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In order to ensure the effective adsorptive removal of orthophosphate ion from solution, the adsorption equilibrium and adsorption rate of orthophosphate ion on activated carbon were measured at 30 °C. The Freundlich equation was applicable to the adsorption isotherms, but an inflection was observed in the Freundlich plots of the isotherms. It was concluded that the inflection is a consequence of the pore size distribution of the porous activated carbon. The amounts of orthophosphate ion adsorbed at low concentration and at high concentration seemed to be affected by pH and pore volume, respectively. The adsorption rate of orthophosphate ion into the pores of activated carbon was investigated on the basis of the intraparticle diffusivity (D_i') determined by a batch method. The value of D_i' changed with the adsorption ratio (F). In the range of constant D_i', regardless of F, intraparticle diffusivity was affected by the surface diffusivity rather than the pore diffusivity. The transitional pore volume of activated carbon contributed predominantly to the intraparticle diffusivity of orthophosphate ion.

Keywords——adsorption rate; orthophosphate ion; activated carbon; intraparticle diffusivity; adsorptive removal

The essential nutritive elements for the breeding and growth of harmful animals and plants in marine and enclosed water areas are mainly phosphorus and nitrogen. It is possible to prevent eutrophication by varying the balance of phosphorus and nitrogen. Since it is technically very difficult to remove most of the nitrogen,1) the removal of phosphorus is necessary to provide unfavorable conditions for the growth of phytoplankton. Coagulation, crystallization, and biological methods have been utilized to remove phosphate from aqueous solution. Adsorption equilibria of phosphate on synthetic silica-alumina,2,3) ion-exchange resin,4,5) hydroxyapatite,6) and activated carbon loaded with zirconium oxide,7) or molybdenum8) have been investigated. The primary interest of these studies2-8) was the mechanism of chemical adsorption of phosphate ion as an adsorbate at the active site of the adsorbent.

The adsorption rate of phosphate on nonporous adsorbents such as iron oxides9) and laterite soil cores10) has been studied with the use of second-order rate equations. As far as we know, there are few fundamental studies on the adsorption rate during the removal of phosphate by physical adsorption on porous adsorbents such as activated carbon. The forms of phosphorus contained in municipal sewage and liquidwaste discharged from cotton-dyeing and food-processing factories and slaughterhouses are orthophosphate, triphosphate, and pyrophosphate ions.11) Most of the organic phosphorus and polyphosphate are decomposed into orthophosphate by biological treatment, and orthophosphate is available as a food source for algae in lakes, marshes, and rivers.12) Therefore, removal of orthophosphate by a

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third sewage treatment process has become necessary.

The purpose of this work was mainly to clarify the adsorption rate of orthophosphate ion during its adsorptive removal by activated carbon on the basis of the values of intraparticle diffusivity obtained by a batch method.

Experimental

Materials——Orthophosphoric acid was an extra-pure reagent (Wako Pure Chemical Inds., Ltd.) and was used without further purification. Activated carbons used were obtained from commercial sources, that is, activated carbon No. 1, Bamberg Co., Technicoal; activated carbon No. 2, Calgon Co., Pittsburgh PCB; activated carbon No. 3, Wako Pure Chemical Inds., Ltd., WTF0050; activated carbon No. 4, Nakarai Chemicals, Ltd., MOR5008. The particle sizes ranged from 4 to 7 mesh. The physical properties are shown in Table I.

Procedure for Equilibrium Isotherm——Orthophosphoric acid solution was prepared by dissolving a given amount of orthophosphoric acid into distilled water. A weighed amount of activated carbon, 0.5 g, was shaken with 100 ml of orthophosphoric acid solution of *ca.* 10 to 2000 ppm at a constant temperature, 30 °C. It took 4 d to attain equilibrium adsorption. After equilibration, the orthophosphate ion concentration in the supernatant solution was determined by the molybdenum blue method.[13)]

Adsorption Rate——The adsorption rate of orthophosphate ion was measured according to the method of Urano and Nakai.[14)] A weighed amount of activated carbon, 4.0 g, was placed in a flask containing distilled water, and the suspension was boiled for 1 h to displace the air in the pores of activated carbon with water. The activated carbon impregnated with water was placed in a stirred solution of 800 ml of orthophosphoric acid solution (PO_4^{3-}, *ca.* 100 ppm). A solution of orthophosphoric acid solution (*ca.* 1000 ppm) and distilled water were added to the suspension until its concentration and its volume became *ca.* 100 ppm and 800 ml, respectively. The amount of orthophosphate ion adsorbed was determined by the isotherm method. The adsorption rate experiments were repeated three times to check the reproducibility.

Pore Size Distribution and Specific Surface Area——The pore size distibution of activated carbon was measured by the method described previously.[15)] The specific surface area of activated carbon was measured by means of the BET method.[15)]

Surface pH——The method for measuring the surface pH of activated carbon was that described by Urano *et al.*[16)]

Results and Discussion

Adsorption Isotherm for Orthophosphate Ion

Adsorption isotherms of orthophosphate ion on activated carbon at 30 °C are shown in Fig. 1. The logarithm of the amount adsorbed is plotted linearly against the logarithm of the equilibrium concentration. The linear relationship indicates that the adsorption of orthophosphate ion on activated carbon is of Freundlich type. The Freundlich equation can be expressed in the following form,

$$\log V = 1/n \log C + \log k \qquad (1)$$

where V is the amount adsorbed, C is the equilibrium concentration, and n and k are constants.

TABLE I. Properties of Activated Carbon

Activated carbon No.	Specific surface area (m^2/g)	Particle diameter (mm)[a)]	Equilibrium amount adsorbed (mg/g) at 100 ppm[b)]
1	1384.5	4.53	11.00
2	866.4	4.08	3.33
3	906.0	4.65	15.11
4	828.8	4.61	10.84

a) Geometric particle diameter was measured by using a reading microscope. *b)* Equilibrium amount of orthophosphate ion adsorbed at 100 rpm was obtained from the adsorption isotherm at 30 °C.

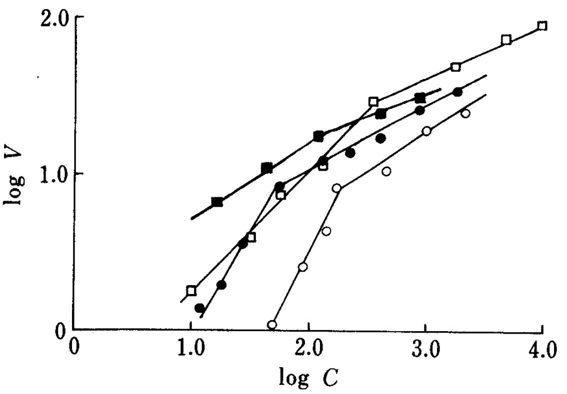

Fig. 1. Adsorption Isotherms of Orthophosphate Ion on Activated Carbon

V, amount adsorbed (mg/g); C, equilibrium concentration (ppm); ●, No. 1; ○, No. 2; ■, No. 3; □, No. 4.

There was an inflection at an orthophosphate ion concentration of 50 to 370 ppm, as shown in Fig. 1. The inflection in the isotherms of orthophosphate on a synthetic silica-alumina was proposed to be due to a difference in the adsorption mechanism at low and high phosphate concentrations.[3)] The inflection in each isotherm obtained in the range of initial pH 2 to 10[3)] seems to originate from the pore structures of silica-alumina rather than pH variation. The inflection in the Freundlich plots of isotherms of phosphate ion on zirconium oxide hydrate-activated carbon complex could be found in the range of phosphate ion concentration 10 to 50 ppm, but no inflection could be found in the case of zirconium oxide hydrate itself.[7)] This result[7)] clearly indicates that the pore structures of activated carbon are important in producing the inflection. A study on the adsorption of sodium dodecylbenzene sulfonate on activated carbon[17)] indicated that the adsorption isotherm at low equilibrium concentration represents the adsorption mainly in small pores and the isotherm at high concentration represents that in large pores. Kawazoe *et al.*[18)] found that sodium dodecylbenzene sulfonate was adsorbed consecutively from the smallest pores to the large pores of activated carbon. These findings and our results on the adsorption isotherm of phosphate ion support the view that the inflection in the isotherm originates from the pore size distribution of the porous activated carbon.

Effect of Pore Volume and pH of Activated Carbon on the Amount Adsorbed

At low concentrations of orthophosphate ion (less than approximately 200 ppm), the amount adsorbed depends markedly on the batch of activated carbon used, but at high concentration (200 ppm) such a variation was not seen. Activated carbon No. 3 had a high adsorption capacity for orthophosphate ion at both low and high concentrations. It was concluded that activated carbon No. 3 is the preferred adsorbent for removing orthophosphate ion. Figure 2 shows the pore size distribution of activated carbon. The adsorption isotherm and pore size distribution data indicate that the amount adsorbed at concentrations of less than approximately 200 ppm was to some degree determined by the micropore volume up to a pore radius of 9.5 Å and that the amount adsorbed at concentrations higher than 200 ppm was clearly determined by transitional pore volume at pore radii of larger than 14.5 Å. Activated carbon No. 2, in spite of having the largest micropore volume, gave the smallest adsorption because of its high basicity (pH = 9.91). It has been reported that acidic conditions, particularly at pH 2 to 4, seem to favor the adsorption of phosphate.[3−5,7,8)]

Table II shows the pH values of activated carbon and the final pH values of the solution. The initial pH values of orthophosphate solution of various concentrations were 3.77—2.62. The pH of solutions varied during the course of adsorption but finally increased to the pH values shown in Table II. Remarkable increases in pH value at low equilibrium concentrations were observed. This can be explained in terms of desorption of hydroxide ions from activated carbon in solutions of low concentration. From the results of pore size

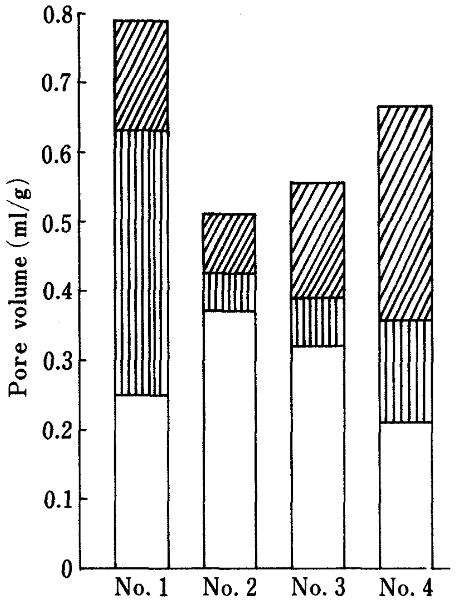

Fig. 2. Pore Size Distribution of Activated Carbon

□, radius < 9.5 Å; ▥, 9.5 Å < radius < 14.5 Å; ▨, radius > 14.5 Å.

TABLE II. Values of pH of Activated Carbon and Final pH of Orthophosphate Solution

Activated carbon No.	pH of activated carbon	Final pH of various concentration of orthophosphate solution
1	6.53	5.50—2.68
2	9.91	8.74—4.23
3	6.95	5.92—3.10
4	8.74	7.57—3.06

Initial pH of orthophosphate solution of various concentrations was in the range of 3.77 to 2.62.

distribution and final pH of the solution, it was concluded that the amount of orthophosphate ion adsorbed on activated carbon was affected by the pore volume and the pH of the adsorbent. Amounts adsorbed at low concentrations (less than approximately 200 ppm) seemed to be affected by the pH rather than the pore volume of the adsorbent. Since an adequate correlation exists between amount adsorbed at high concentration and transitional pore volume, it appeared that the amount adsorbed at high concentration was affected by pore volume rather than pH.

Adsorption Rate of Orthophosphate Ion on Activated Carbon

Particularly in the case of liquid-phase adsorption, intraparticle diffusivity is of major importance since it is the rate-determining step in the adsorption process. The intraparticle diffusivity (D_i') can be evaluated from Keii's formula[19] as,

$$\log(1-F^2) = -\Pi^2(D_i'/2.303R^2)t \qquad (2)$$

$$F = Q_t/Q_\infty \qquad (3)$$

where F is the adsorption ratio, R is the particle radius of the adsorbent, t is the adsorption time, Π is the ratio of the circumference of a circle to its diameter, Q_t is the amount of orthophosphate ion adsorbed onto activated carbon at adsorption time, t, and Q_∞ is the equilibrium amount adsorbed.

In order to calculate the value of D_i' by using Eq. 2, the amount adsorbed must be measured at regular intervals at a fixed concentration. In this case, the amount adsorbed (Q_t)

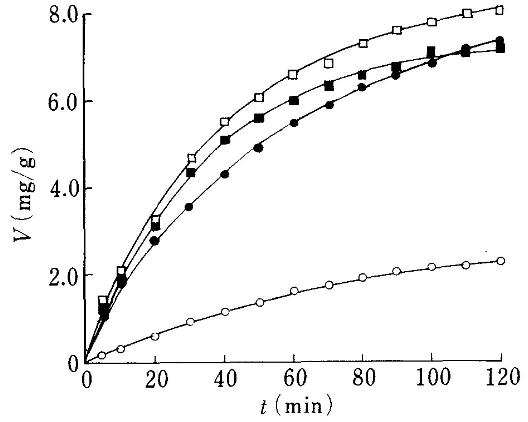

Fig. 3. Adsorption Rate of Orthophosphate Ion on Activated Carbon

V, amount adsorbed; t, adsorption time; ●, No. 1; ○, No. 2; ■, No. 3; □, No. 4. The pH values of the solution during the adsorption run were as follows, No. 1, pH = 3.43; No. 2, pH = 7.64; No. 3, pH = 3.85; No. 4, pH = 6.57.

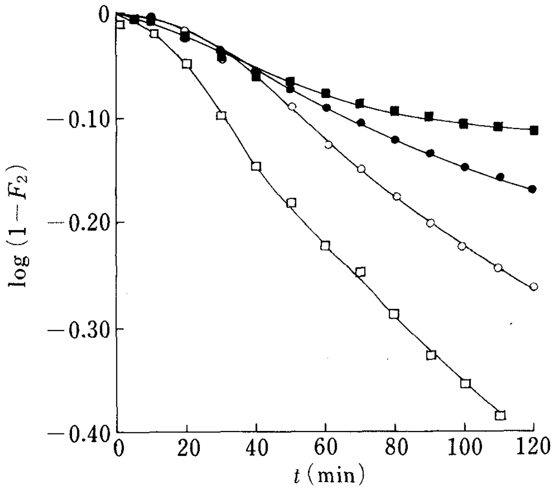

Fig. 4. Relationship between $\log(1-F^2)$ and Adsorption Time for Orthophosphate Ion on Activated Carbon

F, adsorption ratio; t, adsorption time; ●, No. 1; ○, No. 2; ■, No. 3; □, No. 4.

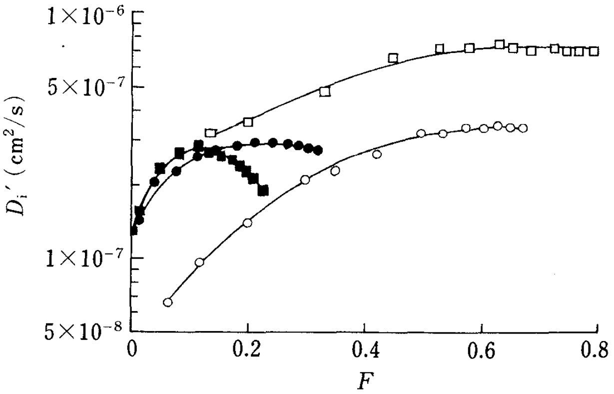

Fig. 5. Change in Intraparticle Diffusivity with Adsorption Ratio for Adsorption of Orthophosphate Ion on Activated Carbon

D_i', intraparticle diffusivity; F, adsorption ratio; ●, No. 1; ○, No. 2; ■, No. 3; □, No. 4.

at elapsed time t was measured at a fixed concentration of 100 ppm and the equilibrium amount adsorbed (Q_∞) was obtained from the adsorption isotherm at an equilibrium concentration of 100 ppm. Figure 3 shows the relation between amount adsorbed and adsorption time. The amount adsorbed increased convexly with increasing adsorption time. Figure 4 shows the relationship between $\log(1-F^2)$ and adsorption time. The plots of $\log(1-F^2)$ *vs.* t are somewhat curved over the whole range of adsorption time. The results imply that the value of intraparticle diffusivity changes with the adsorption time, that is, adsorption ratio. Since the values of D_i' at different adsorption ratios can be considered to be constant over a small range of adsorption ratios, they can be calculated from the slopes of the gentle curves between $\log(1-F^2)$ and t. Figure 5 shows the change in intraparticle diffusivity with adsorption ratio.

According to the study of Masamune and Smith,[20] 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

$$D_i' = D_p/\rho_p(dQ_{p\infty}/dC_p) + D_s \tag{4}$$

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 $dQ_{p\infty}/dC_p$.[14)] According to the above definition, no linear equilibrium is established between $Q_{p\infty}$ and C_p in the early stage of F, though linear equilibrium is established in the range of constant D_i' regardless of F. In the latter range, the results can be explained by assuming that the intraparticle diffusivity is affected by the surface diffusivity rather than pore diffusivity.

The relationship between the intraparticle diffusivity and the pore radius was described by Hirschler and Mertes[21)] and Yagi *et al.*[22)] for the adsorption of organic solvents on silica gel. Hirschler and Mertes[21)] 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.*[22)] indicated that D_i' is proportional to the average pore radius to the third power. From the results of Figs. 2 and 5, a correlation coefficient of intraparticle diffusivity with transitional pore volume of 0.8956 ($p<0.01$) was obtained in the early stage (F less than 0.2). The present results indicate an apparent relation between D_i' and the transitional pore volume at radii above 14.5 Å, that is, the transitional pore volume of activated carbon contributes predominantly to the value of intraparticle diffusivity of phosphate ion.

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