

# ADSORPTION OF POLY(OXYETHYLENE) OF VARIOUS MOLECULAR WEIGHTS FROM AQUEOUS SOLUTIONS ON ACTIVATED CARBON

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Adsorption of poly(oxyethylene) of nine different molecular weights ranging from 194 to  $2.49 \times 10^6$  from aqueous solution of 100 mg/l on activated carbons was tried in a batch finite bath. Activated carbon of coconut shell base, which has micropores of 8 Å radius, and of lignite base activated carbon showed a reasonable capacity of adsorption of even poly(oxyethylene) of molecular weight bigger than  $10^4$  which has Flory's dimension of 84 Å radius. This suggests that shrinkage of a polymer molecule occurs when it is adsorbed on the carbon surface. As for the rate of adsorption, surface diffusion possibly caused by migration of monomer units is considered dominant, and the effective surface diffusion coefficient was determined for each system by applying the concentration diagrams previously presented by the authors. The effective surface diffusion coefficient on each carbon decreased in proportion to the square root of molecular weight of the polymer.

## Introduction

For reclamation of wastewater, activated carbon has proved an effective tool for removing dissolved organic pollutants from water. Since many different types of organic pollutants are expected in ordinary wastewaters, and since activated carbon is rather expensive, a rational and effective methodology of applying activated carbon adsorption to water treatment is needed.

In the case of granular carbon adsorption in aqueous phase, adsorption rate is limited mainly by intraparticle diffusion of adsorbates and the contact time is determined from the estimation of adsorption rate.

Suzuki and Kawazoe<sup>(2)</sup> showed that the adsorption rate of volatile organics is highly dependent on properties of organics, and the effective surface diffusion coefficients for fifteen organics were correlated against boiling point of the organics. Those organics were of relatively low molecular weight. Another type of organics frequently met in industrial wastewater treatment is high molecular weight organics, such as natural or synthetic polymers. From the standpoint of water treatment, most natural soluble polymers are reasonably biodegradable. Some synthetic soluble high polymers, however, are biorefractory and need some physicochemical treatment to be removed from wastewaters. Polymers included in this category are

poly(oxyethylene) known as PEG or PEO, poly(vinylalcohol), poly(acrylic acid), etc.

This work has focused on clarifying the adsorption phenomena of poly(oxyethylene) of molecular weight ranging from 194 to  $2.5 \times 10^6$  on activated carbon. Since no information is available on adsorption rate of soluble high polymers, special attention was given to intraparticle diffusion coefficients, which are determined here by using the concentration change diagrams presented by Suzuki and Kawazoe<sup>(1,2)</sup>.

## Experimental

### Activated carbons

Two types of granular activated carbons were employed. Carbon A is of coconut shell origin and manufactured for use in water treatment by Takeda Chemical Co. (Type 911). Carbon B is of lignite basis and a product of Atlantic Chemicals Co. (Darco Granular). This carbon has a larger porosity and is known to have a large micropore size. The properties of these adsorbents are listed in **Table 1**. Also, the pore size distributions determined from nitrogen adsorption and mercury penetration are shown in **Fig. 1**. Both carbons were crushed and screened to give 48/65 mesh samples. The samples were washed in boiling distilled water to remove fine dust from the surface. The samples were dried overnight in a 110°C thermostat and then cooled and kept in a desiccator until taken out for use.

### Adsorbates

Polymers of ethylene oxide of nine different mole-

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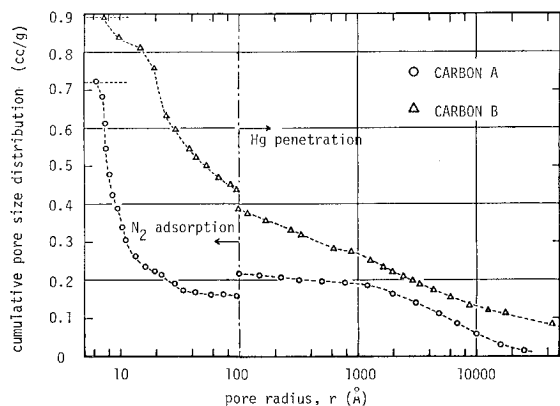
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**Table 1 Properties of activated carbons**

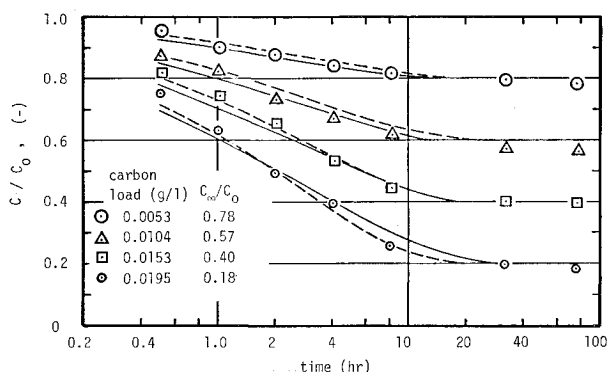
Origin	Carbon A Coconut shell base Takeda 911	Carbon B Lignite base Darco Granular
Sieve openings [mesh]	48/65	48/65
Average radius $R_p$ [mm]	0.127	0.127
Particle density $\rho_p$ [g/cm <sup>3</sup> ]	0.82	0.67
True density* $\rho_t$ [g/cm <sup>3</sup> ]	2.02	1.66
Surface area $S$ [m <sup>2</sup> /g]	1200	530
Pore volume** $V_p$ [cm <sup>3</sup> /g]	0.72	0.89
Macropore fraction $\varepsilon_a$ [—]	0.18	0.25
Most probable micropore radius [Å]	8	22
Micropore fraction $\varepsilon_i$ [—]	0.37	0.30

\* determined by helium pycnometer

\*\* calculated from  $\rho_t$  and  $\rho_p$



**Fig. 1 Cumulative pore size distributions of Carbon A and Carbon B**



**Fig. 2 Typical concentration change (PEG 1000 with Carbon B,  $C_0=100$  mg/l) compared with pore diffusion kinetics curves (—) and surface diffusion kinetics curves (---) both for  $t_{\tau=1}=t_{\tau_s=1}=50$  hr and  $C_{\infty}/C_0=0.8, 0.6, 0.4$  and  $0.2$**

cular weights were used. Tetraethyleneglycol ( $M=194$ ) is a product of Tokyo Kasei Co. (Special grade). Polyethylene glycol (PEG) of nominal molecular weights 400, 600, 1000, 1500 and 20 M ( $=20,000$ ) were provided by Gas-Chro. Kogyo Ltd. PEO 1Y, 3Y, and 15Y were manufactured by Seitetsu Kagaku Co. Their average molecular weights were determined to be 258,000, 579,000 and 2,490,000, respec-

tively, by viscosity measurement.

Since these polymers are produced by polymerization of ethylene oxide, molecular weight distribution should be broad to a certain extent. So the molecular weight adopted here must be considered an approximate measure of characteristic effective molecular size of the polymers employed.

### Apparatus

Since adsorption rates of these polymers are expected to be not so rapid as volatile organics tested before<sup>12)</sup>, fluid-to-particle mass transfer resistance was expected to be negligible. Then conventional suspension-type batch adsorption was performed for measurement of concentration changes<sup>10)</sup>. As a reactor, a 300-ml glass flask was used with a shaker in a 30°C constant-temperature bath. 200 ml of 100 mg/l aqueous solution of each polymer was put in a flask and then a known quantity (0.025 g—0.15 g) of carbon particles was added. At least four different carbon loads (carbon weight per liquid volume) were employed for each combination of a polymer and a carbon. Concentration change in each flask was followed by periodical sampling and analysis of total organic carbon content using Shimadzu TOCA. Three or more injections were made to determine the TOC concentration of each sample with reasonable accuracy. Typical concentration change data obtained by PEG 1000 and Carbon B are shown in Fig. 2.

### Results

#### Amount adsorbed

From the equilibrium concentrations, isotherm relation for each system was determined. Freundlich equation ( $q/q_0=(C/C_0)^{1/n}$ ) was applied and the exponent  $1/n$ , together with amount adsorbed  $q$  extrapolated or interpolated to  $C=10$  and 100 mg/l are shown in Fig. 3. Exponent  $1/n$  decreased rapidly when molecular weight of poly(oxyethylene) increased to 400 (carbon A) or 1000 (carbon B). This can be attributed to the diminishing effect of the strongly hydrophilic  $-OH$  group at the ends of the long chain polymers.

Regarding the amount adsorbed, molecular sieving effect in the high molecular weight range was expected. Poly(oxyethylene) is a long-chain polymer and is expected to exist in water as a random coil or "pearl-string-like" fragment<sup>1)</sup>. As the effective radius of this random coil molecule in bulk water, Flory's equation<sup>1)</sup> can be used. The mean square distance of a monomer unit  $[-CH_2-CH_2-O-]$  and the center of gravity is given as

$$\langle r^2 \rangle^{1/2} = 7.8 \times 10^{-8} \{ [\eta] \cdot M \}^{1/3} \quad (1)$$

The intrinsic viscosity  $[\eta]$  is a function of molecular weight  $M$  and the Sakurada-Houwink equation is

applicable<sup>7</sup>).

$$[\eta] = KM^a \text{ [cc/g]} \quad (2)$$

For poly(oxyethylene) in water,  $K$  and  $a$  were already measured as

$$K = 156 \times 10^{-3}, a = 0.5 \text{ for } M = 194 - 1000 \quad (3)$$

$$K = 6.4 \times 10^{-3}, a = 0.82 \text{ for } M = 3 \times 10^4 - 7 \times 10^6 \quad (4)$$

Then the effective radius,  $\langle \bar{r}^2 \rangle^{1/2}$ , is calculated as a function of  $M$  and is shown by solid lines in Fig. 4. The most probable micropore radii of Carbon A and B are also shown in the figure.

In the case of carbon A, the amount adsorbed,  $q$ , decreases slowly as the molecular weight of the polymer increases above  $M = 1500$ . But by comparison of Figs. 3 and 4, molecular sieving effect is not so apparent as was expected, since even poly(oxyethylene) of molecular weight 258,000 which has  $\langle \bar{r}^2 \rangle^{1/2} \approx 500 \text{ \AA}$  obviously is able to get into the micropores that are far smaller than  $100 \text{ \AA}$ . This fact suggests that since a long-chain polymer such as poly(oxyethylene) easily deforms, it shrinks when adsorbed on the carbon surface and enters the micropore, which is considered slit-like.

If a long-chain polymer shrinks to a rigid spherical particle, the radius of this particle can be estimated by assuming the density of the polymer particle to be equal to that of liquid polymer. The density of PEG 600,  $\rho_e$ , was measured by a glass pycnometer at  $30^\circ\text{C}$  to be  $1.28 \text{ g/cm}^3$ . Then the radius of the imaginary spherical ball of a polymer molecule  $r_b$  is given as

$$r_b = [(M/N\rho_e)3/4\pi]^{1/3} \quad (5)$$

where  $N$  denotes Avogadro number. Thus calculated  $r_b$  is shown as a function of  $M$  by a dotted line in Fig. 4. By comparison of this size with the micropore radii, decrease of  $q$  above  $M = 1500$  for Carbon A may seem to be partially explainable. However, since Carbon B has a large capacity of adsorption even for  $M > 10^5$ , the rigid sphere model is not sufficient to explain complete adsorption equilibrium characteristics of long-chain polymers on activated carbon.

Regarding the nature of adsorbed long-chain polymers, little is known, especially about adsorption from aqueous phase on activated carbon<sup>3</sup>. The area occupied by one polymer molecule at  $C = 10 \text{ mg/l}$  can be calculated by assuming, as a first approximation, that polymers were adsorbed in single layers.

$$s = S/(q_{10}/M) \cdot N \quad (6)$$

Also, by assuming approximately that each adsorbed molecule forms an equivalent spherical disc of radius  $R$ ,  $R$  is obtained from  $s$  as

$$R = (s/\pi)^{1/2} \quad (7)$$

This calculation was tried for poly(oxyethylene) of  $M = 10^3, 2 \times 10^4, 2.58 \times 10^5$  and  $2.49 \times 10^6$  and the resultant  $R$  values are included in Fig. 4.  $R$  deter-

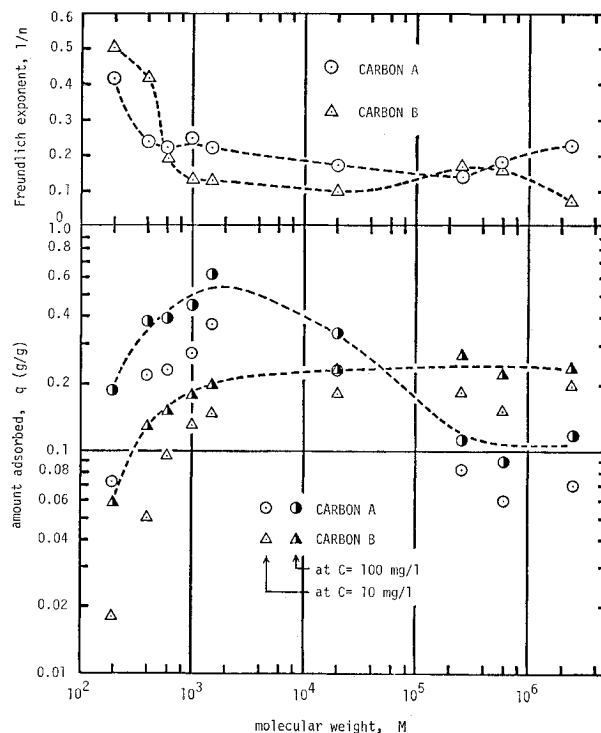


Fig. 3 Freundlich constant ( $1/n$ ) and amount adsorbed at  $C = 10$  and  $100 \text{ mg/l}$

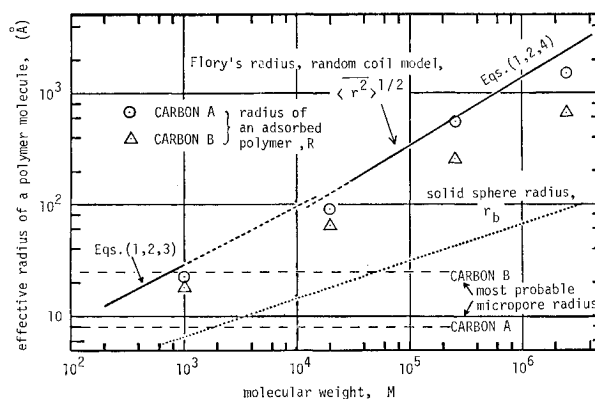


Fig. 4 Comparison of the effective radius of the adsorbed polymer molecule,  $R$ , Flory's radius (the mean square distance of the segments from the center of gravity) of a long chain polymer in water,  $\langle \bar{r}^2 \rangle^{1/2}$ , and the radius of an imaginary solid sphere of a polymer molecule,  $r_b$

mined for Carbon A and B lie fairly close to each other. It is interesting to see that thus-obtained  $R$  values are relatively close to Flory's dimension  $\langle \bar{r}^2 \rangle^{1/2}$ , suggesting that a random coil of a high polymer may be adsorbed to form a disc of the radius of the same order of magnitude as that of the random coil. There is no evidence that maximum single-layer adsorption is attained at  $C = 10 \text{ mg/l}$ . With increase of equilibrium concentration  $C$ ,  $R$  decreases due to a slight increase of  $q$ , suggesting the possibility of entanglement or compression of polymer coils at high surface coverage<sup>3</sup>.

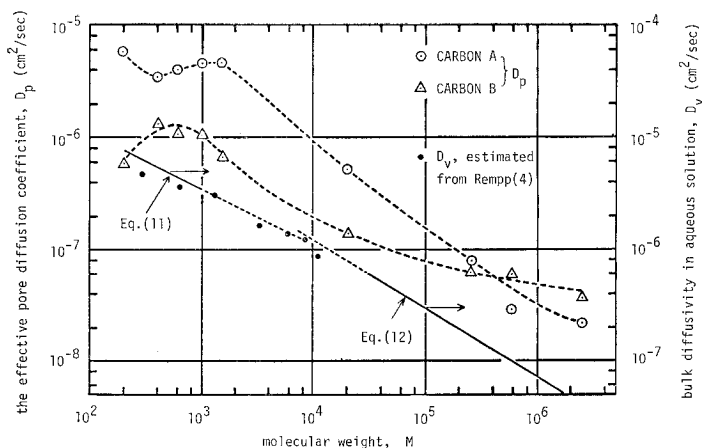


Fig. 5 The apparent pore diffusion coefficient,  $D_p$ , determined by assuming pore diffusion kinetics and bulk diffusivity,  $D_v$ , estimated from Flory's equation (solid lines) and Remp's measurement (solid circles)

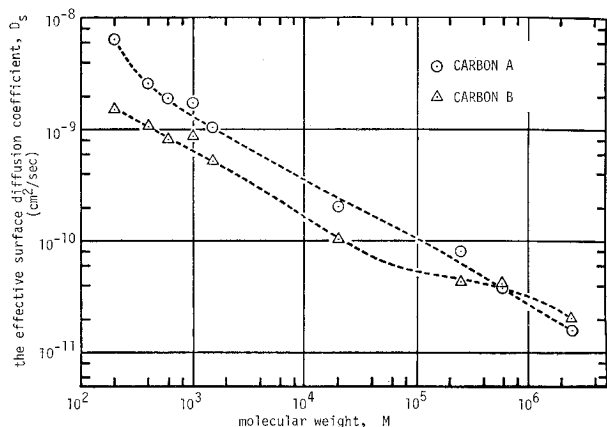


Fig. 6 The effective surface diffusion coefficient,  $D_s$ , determined by assuming surface diffusion kinetics

### Rate of adsorption

Intraparticle diffusion is assumed to be rate-controlling. The authors presented concentration change diagrams in a batch adsorption vessel based on Freundlich isotherm ( $n=1, 1.25, 1.5, 2, 3, 5, 10$  and  $\infty$ ) for both the case of surface diffusion kinetics and the case of pore diffusion kinetics<sup>10,11</sup>. Surface diffusion was considered to be dominant in the adsorption of volatile organics<sup>12</sup>. Then it was first assumed that pore diffusion kinetics is controlling in the case of such a high molecular weight substance as the poly(oxyethylene) tested here.

The effective pore diffusion coefficient,  $D_p$ , obtained by applying the concentration diagrams based on Freundlich isotherm and pore diffusion kinetics, are shown in Fig. 5 for both Carbon A and B. Those values of  $D_p$  should be considered to include maximum 20% error. When pore diffusion kinetics is dominant inside the particle, the following relation is expected to hold<sup>8,10</sup>.

$$D_p = \frac{\varepsilon_a}{k^2} D_v \quad (8)$$

Regarding the molecular diffusivity  $D_v$  of poly(oxyethylene) in water, there have been some measure-

ments for  $M=290-11000$  at  $25^\circ\text{C}$ <sup>5</sup>. Theoretical estimation from Flory's theory is also possible.  $D_v$  values measured by Remp at  $25^\circ\text{C}$ <sup>5</sup> are converted to  $30^\circ\text{C}$  by assuming  $D_v\eta_0/T=\text{constant}$  and are plotted in Fig. 5 (solid circles).

Also, Flory's equation gives

$$D_v\eta_0/T = kP^{-1}\phi^{1/3}[[\eta]M]^{-1/3} \quad (9)$$

where  $[P^{-1}\phi^{1/3}]$  is given as  $2.5 \times 10^6$ <sup>4</sup> and  $k$  is Boltzmann constant,  $1.38 \times 10^{-16}$  erg/deg. By introducing the relations between  $[\eta]$  and  $M$  (Eqs. (2-4)), Eq. (9) gives the relations between  $D_v$  and  $M$  at  $30^\circ\text{C}$  as

$$\left. \begin{aligned} D_v &= 1.12 \times 10^{-4} M^{-0.5} \quad (M=190-1000) \\ &3.24 \times 10^{-4} M^{-0.61} \quad (M=3 \times 10^4-7 \times 10^6) \end{aligned} \right\} \quad (10)$$

Those equations are shown in Fig. 5 by solid lines.

Since the macropore fractions  $\varepsilon_a$  for Carbon A and Carbon B are respectively 0.18 and 0.25 and  $k^2$  is reported to be 2-4 or higher<sup>8,10</sup>,  $D_p$  calculated from Eq. (8) is expected to be less than one tenth of  $D_v$ .  $D_p$  estimated from the experiment for Carbon A and B, however, are far larger than this estimation except for tetraethyleneglycol for Carbon B (Fig. 5). This suggests that a major contribution of another type of diffusion in addition to pore diffusion exists in the carbon particles. This diffusion is considered to be surface or solid diffusion, induced by the gradient of amount adsorbed inside the particle.

The concentration change diagrams presented for batch adsorption and surface diffusion kinetics are then used to determine the effective surface diffusion coefficient for each system. Fig. 2 shows one typical example of experimental concentration changes together with the calculated diagram for both pore diffusion kinetics and surface diffusion kinetics for Freundlich isotherm of the nearest  $n(n=10)$ . Obviously surface diffusion kinetics explain the change of concentration better than pore diffusion kinetics. The effective surface diffusion coefficients,  $D_s$ , obtained from curve fitting are given in Fig. 6, which shows that  $D_s$  monotonously decreases with the molecular weight,  $M$ .

Surface migration of such a high molecular weight polymer on active sites of the carbon surface may be difficult to realize. In the case of a long-chain polymer such as poly(oxyethylene), however, there are intramolecular freedoms to deform itself. Contrary to the case of small molecules whose thermal motion is a vibration-translation motion of the center of gravity, the main feature of the thermal motion is expected to be a rotation of the consecutive links in the case of a long-chain macromolecule. Then surface migration of monomer unit  $[-CH_2-CH_2-O-]$  may possibly contribute to the migration of the whole polymer molecule on the carbon surface.

The dependence of  $D_s$  on molecular weight can be expressed in a similar form as the Sakurada-Houwink equation of viscosity-molecular weight relationship:

$$D_s = K_D M^b \quad b \simeq -0.5 \quad (11)$$

Thus the effective surface diffusion coefficient decreases in proportion to the square root of the chain length, in the case of such a long-chain polymer as the poly(oxyethylene) tested here.

In the practical operation of a packed-bed adsorption column for water treatment, residence time of water in the column is usually of the order of 10 minutes. On the other hand,  $(R_p^2/D_s) (1/15) (C_0/\rho_p q_0)$  is a time constant of adsorption in a spherical particle when intraparticle diffusion is rate-determining (**Appendix**). Minimum requirement for adsorption to be effective is that the residence time should be larger than this time constant for adsorption, that is,

$$\left(\frac{R_p^2}{D_s}\right) \frac{1}{15} \cdot \left(\frac{C_0}{\rho_p q_0}\right) \ll 10 \text{ [min]} \quad (12)$$

In the ordinary adsorption column, 14–20 mesh activated carbon particles are used and  $\rho_p q_0/C_0 \simeq 10^3$  is expected. Then Eq. (12) gives

$$D_s \gg (2.6 \times 10^{-3}) / (10 \times 60 \times 15 \times 10^3) = 3 \times 10^{-10} \text{ cm}^2/\text{sec}.$$

This is, when  $D_s$  of an adsorbate is far smaller than this value, it passes through the column without a chance to reach the active sites in the carbon particles. This inequality corresponds to  $M \ll 10^4$  in the present case of poly(oxyethylene). This may be a partial explanation of the finding of Zuckerman and Molof<sup>13)</sup> in the experiment of municipal wastewater treatment. They showed that TOC material of molecular weight bigger than 1400 in municipal wastewater was not removed in a packed bed of activated carbon.

For removing high molecular weight organics in wastewater by activated carbon, longer contact time has to be accomplished or chemical degradation of polymer by oxidizing agent or alkali hydrolysis may be effective as pretreatment to carbon adsorption.

## Conclusion

Adsorption of poly(oxyethylene) of molecular

weights ranging from 194 to  $2.5 \times 10^6$  by two different activated carbons from aqueous solution was tested. Even polymers of molecular weight higher than  $10^4$  are adsorbed on activated carbons. For higher molecules, activated carbon of larger micropore sizes has more capacity of adsorption.

Regarding the rate of adsorption, surface diffusion seems to be dominant and the effective surface diffusion coefficient was found to decrease in proportion to the fractional power (square root) of molecular weight of the adsorbates.

## Appendix

Eq. (12) is derived in a more rigorous form from (I) the theory of non-equilibrium chromatography for linear isotherm system or (II) the requirement of column length to be greater than mass transfer zone in non-linear isotherm systems.

### (I) Linear isotherm systems

Moment equations for chromatographic elution curves gives HETP for a large adsorption equilibrium constant as<sup>9)</sup>

$$HETP = \frac{t_{20}/Z}{(\nu_1/Z)^2} = \left[ \frac{2u \cdot \varepsilon}{1-\varepsilon} \left[ \frac{1}{\rho_p K_a} + R^2 \left\{ \frac{1}{15D_e} + \frac{1}{3k_f R} \right\} \right] + \frac{E_A}{\varepsilon} \frac{1}{u^2} \right] \quad (A-1)$$

which reduces to a simple form when intraparticle diffusion ( $D_e = D_s(\rho_p q_0/C_0)$ ) is rate-determining:

$$HETP = \frac{2u \cdot \varepsilon}{1-\varepsilon} \cdot \frac{R^2}{15D_e} \quad (A-2)$$

Requirement of  $HETP \ll L$  gives

$$\frac{R_p^2}{15D_e} \ll \frac{1-\varepsilon}{2 \cdot \varepsilon} \cdot \frac{L}{u} \quad (A-3)$$

which corresponds to

$$\frac{1}{15} \cdot \frac{R_p^2}{D_s} \cdot \frac{C_0}{\rho_p q_0} \ll \alpha_i \cdot \theta \quad (A-4)$$

where  $\alpha_i = (1-\varepsilon)/2\varepsilon = 0.6-0.8$ ,  $\theta = L/u$  (residence time of water)  $= \varepsilon/SV$ .

Eq. (A-4) corresponds to Eq. (12).

### (II) Non-linear systems

Mass transfer zone defined by the length between  $C=0.05$  and  $0.95$  is given by an approximate treatment<sup>2)</sup> as

$$MTZ = \frac{\varepsilon \cdot u}{K_F a_v} \cdot NTU \quad (A-5)$$

$$NTU = \int_{0.05}^{0.95} \frac{dc}{C-C^*} \quad (A-6)$$

for the case of intraparticle diffusion-controlling  $K_F a_v$  is given as

$$K_F a_v = (15D_e/R^2)(1-\varepsilon) \quad (A-7)$$

Requirement of  $MTZ \ll L$  gives

$$\frac{1}{15} \cdot \frac{R^2}{D_e} \ll \frac{1-\varepsilon}{\varepsilon} \cdot \frac{L}{NTU \cdot u} \quad (A-8)$$

$$\frac{1}{15} \cdot \frac{R^2}{D_s} \cdot \frac{C_0}{\rho_p q_0} \ll \alpha_{n.l.} \cdot \theta \quad (A-9)$$

Where  $\alpha_{n.l.} = (1-\varepsilon)/\varepsilon \cdot NTU$ ,  $NTU$  is 2.94 for rectangular isotherm and larger for other non-linear isotherm systems. Eq. (12) is again a requirement for Eq. (A-9).

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### Nomenclature

$a$	= constant defined by Eq. (2)	[—]
$b$	= constant defined by Eq. (13)	[—]
$C$	= concentration in aqueous phase	[mg/l]
$C_0$	= initial concentration	[mg/l]
$D_p$	= the effective pore diffusion coefficient	[cm <sup>2</sup> /s]
$D_s$	= the effective surface diffusion coefficient	[cm <sup>2</sup> /s]
$D_0$	= bulk diffusivity	[cm <sup>2</sup> /s]
$K$	= constant defined by Eq. (2)	[cm <sup>3</sup> /g·(mole/g) <sup>a</sup> ]
$K_D$	= constant defined by Eq. (13)	[cm <sup>2</sup> /s·(mole/g) <sup>b</sup> ]
$k$	= Boltzman constant	[erg/deg]
$k^2$	= tortuosity factor	[—]
$M$	= molecular weight	[g/mole]
$N$	= Avogadro number	[molecules/mole]
$n$	= Freundlich constant	[—]
$P$	= universal constant introduced in a friction coefficient relation of polymers=5.11	[—]
$q$	= amount adsorbed	[g/g]
$q_0$	= amount adsorbed at $C=C_0$	[g/g]
$q_{10,100}$	= amount adsorbed at $C=10, 100$ mg/l respectively	[g/g]
$R$	= the effective radius of a polymer adsorbed	[Å]
$R_p$	= particle radius	[cm]
$r_b$	= radius of a rigid spherical polymer	[Å]
$\langle \bar{r}^2 \rangle$	= Flory's size, the mean square distance of a monomer unit and the center of gravity of the polymer	[Å]
$S$	= internal surface area of adsorbent	[m <sup>2</sup> /g]
$s$	= the area occupied by a polymer adsorbed	[Å <sup>2</sup> ]
$T$	= temperature	[°K]
$t$	= the thickness of the adsorbed phase	[Å]

$\epsilon_a$	= macropore fraction	[—]
$\eta_0$	= viscosity of water	[g·cm/sec <sup>2</sup> ]
$[\eta]$	= intrinsic viscosity	[cm <sup>3</sup> /g]
$\rho$	= density of adsorbed phase	[g/cm <sup>3</sup> ]
$\rho_l$	= density of liquid polymer	[g/cm <sup>3</sup> ]
$\rho_p$	= particle density	[g/cm <sup>3</sup> ]
$\rho_t$	= true density of particle	[g/cm <sup>3</sup> ]
$\phi$	= universal constant introduced in defining intrinsic viscosity of a polymer solution	[—]
	= $2.1 \times 10^{21}$	[—]

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