BATCH ADSORPTION OF *p*-NITROPHENOL AND *p*-CHLOROPHENOL ON ANION EXCHANGE RESIN

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A model was proposed by simplifying the surface diffusion model. In addition, three models—the simplified model, the quadratic driving force model and the surface diffusion model—were used to analyse experimental data of the adsorption of *p*-nitrophenol and *p*-chlorophenol on anion exchange resin (Ionac AFP-329) in a batch adsorber. The simplified model gives a better approximation to the surface diffusion model than does the quadratic driving force model. Moreover, from the experimental data the result also shows that the surface diffusion coefficient varies linearly with $q_{\infty}^{1/n}$.

Introduction

The adsorption of organic substances with activated carbon is an important process in the purification of domestic and industrial effluents. Many experimental and theoretical works^{4,7,8,10,14} have been reported on the prediction of adsorption capacity and the design of adsorption processes. The basic data required for adsorption operation are the parameters pertaining to the kinetics of adsorption (rate parameters) and to the adsorption equilibrium. The adsorption equilibria data, in principle, can be determined experimentally. The rate parameters, the intraparticle diffusion coefficient for example, cannot be obtained from experimental data directly. Thus a suitable mathematical model is needed. The two most widely used intraparticle diffusion models are the pore diffusion model (PDM) and the surface diffusion model (SDM). However, they are expressed by the equation of continuity, so it is tedious and time-consuming to solve these two models, especially for fixed-bed calculation. Consequently, some models have been proposed to simplify the surface diffusion model, such as the linear driving force (LDF)⁵ model and the quadratic driving force (QDF)¹⁵ model.

In this work, a simplified model was proposed and used to analyse data of the adsorption of *p*-nitrophenol (PNP) and *p*-chlorophenol (PCP) on anion exchange resin (Ionac AFP-329). Moreover, the dependence of the effective surface diffusion coefficient on the concentration of adsorbates was also studied.

1. Theory

1.1 Surface diffusion model

The mathematical model presented below pertains to a constant-temperature batch process.^{7,10} A fixed quantity of liquid solution with initial concentration C_0 of adsorbate is contacted with a given mass of adsorbent particles. Mass transfer occurs in series: first, diffusion through the liquid film, followed by intraparticle mass transfer controlled by surface diffusion. The adsorbent particles are assumed to be spherical and uniform in size.

The average concentration $\bar{q}$ is related to solid-phase concentration distribution by

$$\bar{q} = \frac{3}{R^3} \int_0^R q(r, t) \cdot r^2 dr \quad (1)$$

where q is given by the surface diffusion equation, i.e.

$$\frac{\partial q}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial q}{\partial r} \right) \quad (2)$$

with the initial and boundary conditions

$$q = 0 \quad \text{for } 0 \leq r \leq R, t \leq 0 \quad (3)$$

$$q = q_i \quad \text{for } r = R, t > 0 \quad (4)$$

and

$$\frac{\partial q}{\partial r} = 0 \quad \text{for } r = 0, t > 0 \quad (5)$$

where q_i is the solid-phase concentration at the liquid-particle interface. The macroscopic mass balance can be written as

$$C_b = C_0 - M\bar{q}/V \quad (6)$$

where C_b is the bulk concentration of adsorbate. The

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relation of C_i and q_i at the liquid-particle interface is expressed by an equilibrium isotherm. In this paper the Freundlich equation is considered, i.e.

$$q_i = k \cdot C_i^n \quad (7)$$

When the external diffusion resistance at the particle surface is negligible, the bulk concentration C_b is equal to C_i and in equilibrium with q_i , and the boundary condition at $r=R$ can be written as

$$\frac{\partial q}{\partial r} = \frac{-RV}{3D_s M} \frac{dC_b}{dt} \quad \text{for } r=R, t>0 \quad (4')$$

Generally, Eqs. (1)–(3), (4') and (5)–(7) can be solved by the numerical method. However, when the isotherm is linear, the analytical solutions can be expressed as follows:²⁾

$$Y = \frac{1}{1+\alpha} \left[1 + \sum_{m=1}^{\infty} \frac{6\alpha(1+\alpha) \cdot \exp(-Q_m^2 \theta)}{9\alpha^2 + 9\alpha + Q_m^2} \frac{\sin(Q_m \cdot z)}{z \sin(Q_m)} \right] \quad (8)$$

$$\bar{Y} = \frac{1}{1+\alpha} \left[1 - \sum_{m=1}^{\infty} \frac{6(1+\alpha) \cdot \exp(-Q_m^2 \theta)}{9\alpha^2 + 9\alpha + Q_m^2} \right] \quad (9)$$

and

$$Y_i = X = \frac{1}{1+\alpha} \left[1 + \sum_{m=1}^{\infty} \frac{6\alpha(1+\alpha) \cdot \exp(-Q_m^2 \theta)}{9\alpha^2 + 9\alpha + Q_m^2} \right] \quad (10)$$

where $Y = q/q_0$, $\bar{Y} = \bar{q}/q_0$, $Y_i = q_i/q_0$, $\alpha = Mq_0/VC_0$, $\theta = D_s t/R^2$, $X = C_b/C_0$, $z = r/R$ and Q_m s are the non-zero roots of

$$\tan Q_m = 3\alpha Q_m / (3\alpha + Q_m^2) \quad (11)$$

1.2 The simplified models

The rate of change of $\bar{q}$ is obtained upon differentiating Eq. (1),

$$\frac{d\bar{q}}{dt} = \frac{3}{R^3} \int_0^R \frac{\partial q(r, t)}{\partial t} r^2 dr \quad (12)$$

then substituting Eq. (2) into Eq. (12), we get

$$\frac{d\bar{q}}{dt} = \frac{3D_s}{R} \left. \frac{\partial q}{\partial r} \right|_{r=R} \quad (13)$$

Let concentration q be approximated by a polynomial, but only the first three terms are considered here, i.e.

$$q = a_0 + a_2 r^2 + a_4 r^4 \quad (14)$$

where a_i s are a function of time, but not of r . The terms of odd order have been omitted from Eq. (14) on account of spherical symmetry. From Eq. (14), the amount adsorbed at the interface can be expressed as

$$q_i = a_0 + a_2 R^2 + a_4 R^4 \quad (15)$$

the average amount adsorbed in particles can be calculated by Eq. (1) and expressed as

$$\bar{q} = a_0 + 3/5 a_2 R^2 + 3/7 a_4 R^4 \quad (16)$$

and the molar flux at the surface can be expressed as

$$D_s \left(\frac{\partial q}{\partial r} \right) \bigg|_{r=R} = D_s (2a_2 R + 4a_4 R^3) \quad (17)$$

Here, $\bar{r}$ is defined as a parameter which is a position in particle where $q = \bar{q}$, i.e.

$$a_0 + a_2 \bar{r}^2 + a_4 \bar{r}^4 = a_0 + 3/5 a_2 R^2 + 3/7 a_4 R^4 \quad (18)$$

Solving Eqs. (15), (16) and (18) simultaneously yields

$$a_2 R^2 = \frac{(q_i - \bar{q})(35\bar{z}^4 - 15)}{(14\bar{z}^4 - 20\bar{z}^2 + 6)} \quad (19)$$

and

$$a_4 R^4 = \frac{(q_i - \bar{q})(21 - 35\bar{z}^2)}{(14\bar{z}^4 - 20\bar{z}^2 + 6)} \quad (20)$$

where $\bar{z} = (\bar{r}/R)$. Substituting Eqs. (19) and (20) into Eq. (17), and then combining Eqs. (17) with (13), yields

$$\frac{d\bar{q}}{dt} = \frac{15D_s}{R^2} (q_i - \bar{q}) \frac{35\bar{z}^4 - 70\bar{z}^2 + 27}{35\bar{z}^4 - 50\bar{z}^2 + 15} \quad (21)$$

Equation (21) is a model obtained by simplifying Eqs. (2), (4) and (5) when the intraparticle concentration distribution can be approximated by Eq. (14). However, Eq. (21) cannot be directly applied, and the dependence of $\bar{z}$ on t or on $\bar{q}$ and q_i is also needed.

When Eq. (21) is compared with the linear driving force model, i.e.

$$\frac{d\bar{q}}{dt} = \frac{15D_s}{R^2} (q_i - \bar{q}) \quad (22)$$

it can be found that

$$\bar{z}^2 = 0.6 \quad (23)$$

That is, the value of $a_4 R^4$ as given in Eq. (20) must be equal to zero. This is consistent with the result obtained by Liaw *et al.*,⁹⁾ who assumed an intraparticle concentration distribution with the first two terms as given in Eq. (14) to derive the linear driving force model.

When Eq. (21) is compared with the quadratic driving force model, i.e.

$$\frac{d\bar{q}}{dt} = \frac{15D_s}{R^2} \frac{(q_i^2 - \bar{q}^2)}{2\bar{q}} \quad (24)$$

the relationship among z , $\bar{q}$ and q_i can be expressed as

$$\frac{\bar{q}}{q_i} = \frac{35\bar{z}^4 - 50\bar{z}^2 + 15}{35\bar{z}^4 - 90\bar{z}^2 + 39} \quad (25)$$

Originally, the LDF model was proposed by Glueckauf and Coates,⁵⁾ and the QDF model was

proposed by Vermeulen.¹⁵⁾ In general, the latter gives a better approximation to the surface diffusion model than the former.¹²⁾

2. Numerical Method

For the solution of the boundary value problem, Eqs. (1)–(3), Eq. (4') and Eqs. (5)–(7), the method of orthogonal collocation,¹⁶⁾ which has been widely used for finite-bath single component adsorption,^{1,11)} was used. In this method, the precision depends on the number of collocation points. Consequently, the number of collocation points N_c was tested with $N_c=4, 6$ and 8 . $N_c=6$ was proved to be sufficient to obtain a difference in only the 4th digit as compared to higher approximation. Moreover, the surface diffusion model with a linear isotherm was also used to test the method, since the analytical solution²⁾ is known in this case.

The collocation equations and the ordinary differential equations, e.g. Eqs. (21) and (24), were solved by the 4th-order Runge-Kutta method.³⁾ Then the surface diffusion coefficients were determined by a nonlinear regression method. The mean deviation between experimental data and predicted value as expressed below was minimized.

$$\delta = \frac{1}{N} \sqrt{\sum_{j=1}^N (X_{ej} - X_j)^2} \quad (26)$$

where X_{ej} is the value calculated by the model equations, and X_j is the experimental datum.

3. Experimental

3.1 Materials

The adsorbent is a commercial anion exchange resin (Ionac AFP-329). It has been used as adsorbent in the studies of Huang *et al.*,⁷⁾ and Huang and Chung.⁶⁾ PNP and PCP are guaranteed reagents obtained from Hayashi Pure Chemical Ind. Ltd., Japan.

3.2 Batch adsorption

The adsorption rate of PNP and PCP on the resins was measured by adding an amount of resins with 0.0707 cm (25 U.S. mesh) in diameter into a well stirred vessel.⁷⁾ The agitation rate is increased until that the concentration-time curve of adsorption is not obviously affected by the increment of agitation rate, and the film mass transfer resistance is assumed to be neglected.

The amount of resins is 1.000 g for PNP and 1.500 g for PCP. The vessel contains 400 ml aqueous solution with a given concentration, and was immersed in a thermostat. The temperature is controlled within ± 0.1 K of 298.1 K. At each pre-set time interval, samples were taken out for analysis. The concentrations of solutions were determined with a ultraviolet spectrophotometer (Hitachi, UV-300). The

Fig. 1. Intraparticle concentration distribution

wave length is 317 and 280 nm for PNP and PCP, respectively.

4. Results and Discussion

4.1 The relationship among $\bar{z}$, $\bar{q}$ and q_i

The dimensionless concentration distributions in the particle are calculated by the orthogonal collocation method from the model equations, Eqs. (1)–(3), Eq. (4') and Eqs. (5)–(7), for various values of α and n . A typical example in the plot of Y against z^2 for $\alpha=1$ and $n=1$ with θ as model parameter is shown in Fig. 1. Moreover, in Fig. 1, the numerical solution is also compared with the analytical solution as given in Eq. (8). It shows that the numerical solution is highly consistent with the analytical solution at $z=1$, so the concentration-time curve calculated by the numerical method should show good agreement with the analytical solution given in Eq. (10), since the bulk concentration in liquid phase is in equilibrium with q_i . For other values of α , the results, not shown here, are similar to those shown in Fig. 1.

When the relationship among $\bar{q}$, q_i and $\bar{z}$ can be approximately expressed by Eq. (25), Eq. (21) can be reduced to the quadratic driving force model. However, the real relationship among $\bar{q}$, q_i and $\bar{z}$ is desired. For a nonlinear isotherm, the value of q_i is obtained by the numerical solution at $r=R$. The value of $\bar{q}$ can be calculated by Eq. (6), since C_b , which is in equilibrium with q_i , is known. The value of $\bar{z}$ at each time is obtained from the plots of Y vs. z^2 as shown in Fig. 1, since the value of $\bar{q}$ is known. For a linear isotherm, $\bar{q}$ and q_i can be respectively calculated by Eqs. (9) and (10), and $\bar{z}$ can be obtained by solving Eqs. (8) and (9) simultaneously. The plots of $\bar{z}^2$ vs. $(\bar{q}/q_i)$ for α in the range of 0.25 to 4, and $n=0.2, 0.41, 0.65$ and 1 are shown in Fig. 2. It is seen that the plots of $\bar{z}^2$ vs. $(\bar{q}/q_i)$ are nearly on a curve for various values of α and n . The curve can be correlated with a simple equation,

$$\bar{z}^2 = \frac{1 + 0.856(\bar{q}/q_i)}{1 + 2.57(\bar{q}/q_i)} \quad (27)$$

Fig. 2. Plots of $\bar{z}^2$ vs. $(\bar{q}/q_i)$ for various α and n

Combining Eqs. (27) with (21), a new simplified model is obtained. It should give a good approximation to the surface diffusion model.

Figure 2 also shows that Eq. (25) gives a better approximation to represent the relationship between $\bar{z}^2$ and $(\bar{q}/q_i)$ than does Eq. (23), so the QDF model gives a better approximation to the surface diffusion model than does the LDF model.¹²⁾

4.2 Adsorption isotherm

The relationship between the equilibrium concentration and the amount adsorbed have been studied at 288.1, 298.1 and 308.1 K by Huang and Chung.⁶⁾ The adsorption isotherms of PNP and PCP at various temperatures can be expressed by the Freundlich equation for equilibrium concentrations in the range of 0.2 to 12.5 mol/m³. The experimental results of the adsorption at 298.1 K are as follows:

$$\text{PNP} \quad q = 1.98C^{0.407} \quad (28)$$

and

$$\text{PCP} \quad q = 1.65C^{0.312} \quad (29)$$

As given in Eqs. (28) and (29), PNP is more favorable than PCP, since the amount adsorbed of PNP is greater than that of PCP at a given concentration.

4.3 Analysis of experimental data

Typical concentration-time curves are shown in Figs. 3 and 4 respectively for PNP and PCP. In Fig. 3, the solid line is the solution of the surface diffusion model with $D_s = 2.6 \times 10^{-13}$ m²/s and the equilibrium constants as given in Eq. (28). The value of D_s is determined by minimization of the mean deviation as given in Eq. (26). It shows that the solution of the surface diffusion model agrees well with experimental data, although the value of D_s is calculated from the unsteady-state analysis with the assumption that it is constant during adsorption. Moreover, both the results calculated by Eqs. (21) and (27) and by the quadratic driving force model with the same value of

Fig. 3. Concentration-time curves of PNP calculated by three models with the same value of surface diffusion coefficient. $D_s = 2.6 \times 10^{-13}$ m²/sec, $C_0 = 4.54$ mol/m³

Fig. 4. Concentration-time curves of PCP calculated by three models with the same value of surface diffusion coefficient. $D_s = 2.9 \times 10^{-13}$ m²/sec, $C_0 = 6.84$ mol/m³

D_s are also compared with the solution of the surface diffusion model. It indicates that the solution of the simplified model, Eqs. (21) and (27), gives a much better approximation to the surface diffusion model than does that of the quadratic driving force model. In addition, the result of PCP as given in Fig. 4 is similar to that of PNP as given in Fig. 3.

4.4 Surface diffusion coefficient

For the batch adsorption of PNP and PCP on anion exchange resin Ionac AFP-329 at 298.1 K, the surface diffusion coefficients D_s of PNP and PCP at various initial concentrations are determined by the surface diffusion model, concentration-time curve and the adsorption isotherms as given in Eqs. (28) and (29), and the results are listed in Table 1. The surface diffusion coefficients estimated by the simplified model, Eqs. (21) and (27), are also listed in Table 1. It indicates that the D_s estimated by Eqs. (21) and (27) is only about 15% smaller than that determined by the surface diffusion model. The simplified model, Eqs. (21) and (27), gives a good estimation of the surface diffusion coefficient, and can save much calculating time since Eq. (21) is expressed by an ordinary

Table 1. Surface diffusivities for the adsorption of PCP and PNP on anion exchange resin Ionac AFP-329 at 298.1 K

Comp.	$M \times 10^3$ [kg]	C_0 [mol/m ³]	$D_s \times 10^{13}$ [m ² /s]	
			Eqs. (21) and (27)	SDM
PNP	1.000	1.43	1.6	2.1
	1.000	2.92	2.0	2.2
	1.000	4.54	2.2	2.6
	1.000	6.98	2.7	3.3
	1.500	11.3	3.6	4.0
PCP	1.500	5.43	1.9	2.3
	1.500	6.84	2.6	2.9
	1.500	8.95	3.2	3.7
	1.500	10.5	3.6	4.0
	1.500	11.8	4.4	5.0

differential equation.

In Fig. 5, the surface diffusivities of PNP and PCP determined by the surface diffusion model are correlated as functions of the final equilibrium amount adsorbed, q_∞ .¹³⁾ It shows that D_s varies linearly with $q_\infty^{1/n}$ for both adsorbates. Such a result is similar to that obtained by Suzuki and Fujii,¹⁴⁾ who assumed that the activation energy of surface diffusion can be approximated by the isosteric heat of adsorption. However, the intercept in the plot of D_s vs. $q_\infty^{1/n}$ is not equal to zero for each adsorbate, as shown in Fig. 5. This is inconsistent with the results obtained by Suzuki and Fujii.¹⁴⁾ They showed that the surface diffusion coefficient should be equal to zero when the amount adsorbed is equal to zero.

Conclusion

The analysis of data of the adsorption of PNP and PCP on synthetic resin Ionac AFP-329 in a batch adsorber suggests the following conclusions:

- (1) Equations (21) and (27) give a good approximation to the surface diffusion model, and can be used to estimate the surface diffusion coefficient.
- (2) The surface diffusion model with the surface diffusion coefficients as model parameters gives fairly good agreement with experimental data.
- (3) The surface diffusion coefficient varies linearly with $q_\infty^{1/n}$.

Nomenclature

a_i	= constants as defined in Eq. (14)	[mol/kg·m ³]
C_b	= concentration in aqueous phase	[mol/m ³]
C_0	= initial concentration in aqueous phase	[mol/m ³]
D_s	= surface diffusion coefficient	[m ² /s]
k	= constant of the Freundlich equation	[m ³ⁿ /kg·mol ⁿ⁻¹]
M	= resin dosage	[kg]
N	= number of data points	[—]
N_c	= number of collocation points	[—]
n	= exponent of the Freundlich equation	[—]
q	= amount adsorbed	[mol/kg]

Fig. 5. Dependence of surface diffusivity on the final equilibrium amount adsorbed for adsorption of PNP and PCP on anion exchange resin Ionac AFP-329

q_0	= amount adsorbed in equilibrium with C_0	[mol/kg]
q_∞	= final equilibrium amount adsorbed	[mol/kg]
r	= radius position within particle	[m]
R	= particle radius	[m]
t	= time	[s] or [min]
V	= volume of aqueous solution	[m ³]
X	= C_b/C_0	[—]
Y	= q/q_0	[—]
z	= r/R	[—]
α	= Mq_0/VC_0	[—]
θ	= $D_s t/R^2$	[—]
δ	= mean deviation	[—]

<Subscripts>

b	= bulk phase
c	= calculated
i	= interface

<Superscripts>

—	= average value
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Abbreviation

LDFM	= linear driving force model
QDFM	= quadratic driving force model
PCP	= <i>p</i> -chlorophenol
PDM	= pore diffusion model
PNP	= <i>p</i> -nitrophenol
SDM	= surface diffusion model

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PATTERN RECOGNITION IN FLOW VISUALIZATION AROUND A PADDLE IMPELLER

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Key Words: Mixing, Paddle Impeller, Visualization, Flow Recognition, Impeller Stream, Conditional Sampling, Velocity Distributions, Torque Fluctuations

Very low frequency fluctuations in the velocity signal from several seconds to several minutes in scale are usually observed in agitated vessels. It is shown in this work that these fluctuations result from the abrupt replacement of the flow pattern in the vessel, even in part. Pattern recognition studies of the flow in the impeller region of a paddle were carried out, using high-speed VTR. The results showed that the flow between blades is characterized into five patterns which are replaced one after another. They are classified into the discharge and the cross-pass types of flow. The latter means that flow passes between impeller blades, upwardly or downwardly. The lifetime of the discharge flow type was three times that of the cross-pass flow type. The velocity distributions of the discharge and cross-pass flow types estimated from visualized pictures were quite different from each other and were different from the average distributions obtained by LDV. When the cross-pass pattern had developed over the whole region between blades, a horizontal figure-eight pattern of flow developed in the entire vessel with abrupt reduction of the torque.

Introduction

Most measurements of turbulence in a mixing vessel have shown that the relative intensities were higher than 50%.^{2,3,7,9,13-15} Rao and Brodkey¹³ pointed out that a flat-blade impeller caused random movement of the impeller stream. Mujumdar *et al.*⁷ and Gunkel *et al.*³ attempted to separate the velocity fluctuations into random and periodic components. Van't Riet and Smith¹⁶ found a trailing vortex that originated in the region behind the upper and lower edges of the blade of the turbine impeller. They introduced the pseudo-turbulence concept, which is that most of the velocity fluctuations detected by a stationary probe in the discharge stream are largely dependent on the trailing vortex.¹⁷ Subsequent works have extensively investigated the trailing vortex flow.^{1,5,6,15} Recently, Yianneskis *et al.*¹⁸ determined experimentally the structure of the trailing vortex produced by a disc turbine, using LDV technique.

However, there are a few measurements of the discharge flow from a paddle impeller. One of the present authors found cross-pass flow, in which flow passes axially through the region between the blades of the paddle, together with the usual discharge flow.^{9,10} A similar observation was reported by Oldshue.¹² Thus the real flow in the vessel is very unstable in the sense of the combination of the cross-pass patterns and the discharge patterns including trailing vortex. In fact, the flow in the vessel could be said to be a kind of unstable turbulent flow, in that several kinds of turbulent flows are distributed in the vessel locally at the same time, and the distribution changes continuously with time.

The paddle impeller is more often used in practice than the turbine impeller. Therefore, for further advancement of mixing research it is interesting to recognize unstable turbulent flow phenomena in the vessel before making a turbulence analysis. This work is a first attempt at flow recognition as a means of simplifying the study of the real flow.

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