BATCH MEASUREMENT OF ADSORPTION RATE IN AN AGITATED TANK — PORE DIFFUSION KINETICS WITH IRREVERSIBLE ISOTHERM* —

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A simple technique is proposed to determine the intraparticle diffusivities of adsorbents from concentration change in an agitated tank. Pore diffusion and rectangular isotherm are assumed to derive the theoretical solutions, which are then compared with the experimental results. The theory gave a good prediction for the transient concentration profile in the tank. The effective diffusivities of 2-dodecylbenzene sulfonate in four different activated carbon particles are determined by the proposed technique.

Introduction

Adsorption from a solution by a solid adsorbent has attracted considerable attention in connection with advanced treatment of waste water. One of the important problems met in the course of designing adsorption systems is the determination of contact time in adsorption equipment. In the case of aqueous systems, the rate of adsorption is controlled by diffusion of the solute into adsorbent particles. For adsorption in aqueous solutions, we frequently meet strongly non-linear isotherms such as a rectangular one which means strong adsorption and limited adsorption capacity. For determination of intraparticle diffusivity in such a case, the most common method is to apply the theories developed by Kawanabe6) or Vermeulen et al.5) to the concentration breakthrough for flow through a packed bed of adsorbent. However, this type of experiment sometimes requires a long time to finish and then the difficulty lies in getting data for different conditions such as different samples, particle sizes or temperatures.

Batch measurements seem to solve these difficulties. In the case when isotherm is given by Henry's relation, the theories developed by the previous investigators4)-7) are applicable, but no available theory has been presented for non-linear isotherm systems with pore diffusion kinetics.

The purpose of this note is to show a way to rapidly estimate the intraparticle diffusivity by batch measurement for a rectangular isotherm system which, as mentioned before, is common in adsorption from aqueous solutions. Adsorption rates of 2-dodecylbenzene sulfonate on four different activated carbons were measured and the proposed technique was applied to the estimation of the intraparticle diffusivities.

Development of a Model

The following assumptions are made:

(1) Isotherm is rectangular. Then the adsorption site is either vacant or saturated with the adsorbate, depending on whether the liquid-phase concentration is zero or finite.

(2) The particle is homogeneous.

(3) Accumulation of adsorbate in the liquid phase in a particle is negligible.

The above assumptions lead to an idea similar to the shrinking-core model for the case of gas-solid reactions10). Namely, adsorption takes place only at adsorption front, \( r = r_s \), where concentration of liquid phase is considered to be zero. Solid phase in the shell between adsorption front and the external surface of the particle \( (r_s < r \leq R) \) is saturated by adsorbate, and then the velocity of movement of adsorption front toward the center of the particle is controlled by the
rate of diffusion of adsorbate in the liquid phase through the shell. The basic equations for the above model are as follows:

diffusion in the shell

\[ D_s \left( \frac{\partial c}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial c}{\partial r} \right) = 0 \quad \text{for} \quad r_t \leq r \leq R \]  

(1)

and boundary conditions at \( r=r_t \) and \( r=R \)

\[ c=0 \quad \text{at} \quad r=r_t \]

(2)

\[ -\rho_s q_s \frac{\partial c}{\partial r} = D_s \frac{\partial c}{\partial r} \quad \text{at} \quad r=r_t \]

(3)

\[ D_s \frac{\partial c}{\partial r} \quad \text{at} \quad r=R \]

(4)

If \( q_s \) is the uptake of adsorbate by a unit mass of an adsorbent particle, \( W_s \) the mass of particles introduced in a solution of volume \( V_L \), and \( C_o \) initial concentration of the solution, a global mass balance determines the equilibrium concentration \( C_w \)

\[ q_s W_s = (C_o - C_w) V_L \]  

(5)

Here it must be kept in mind that \( W_s \) is chosen so as to make \( C_w \) reasonably different from zero. Then the isotherm and the operation line given by Eq. (5) are as shown in Fig. 1.

By introducing \( \xi = r_t/R = [(C-C_w)/(C_o-C_w)]^{1/3} \), and eliminating \( c \), the above equations reduce to

\[ - \frac{d\xi}{dt} = \frac{D_s}{R^2} \left( \frac{C_o}{\rho_s q_s} \cdot \frac{1}{1+a^2} \right) \]

\[ \times \left\{ \frac{B_i}{1+B_i(1/\xi-1)} \right\} \left\{ \xi + a \cdot \frac{1}{\xi^2} \right\} \]  

(6)

where \( \rho_s \) is the density of the particles \( B_i=k_f R/D_s \), and \( a=(C_w/(C_o-C_w))^{1/3} \). Eq. (6) is solved to give

\[ \tau = \left\{ (1+a^2) \left[ 1 - (B_i)^{-1} \right] \right\} \ln \left\{ \xi + a \cdot \frac{1}{\xi^2} \right\} \]

\[ + \frac{1}{3a} \ln \left\{ \frac{\xi + a}{1+\xi^2} \right\} \frac{1}{6a} \ln \left\{ \frac{\xi^2 - a^2 + a^2}{1+a^2} \right\} \]

\[ + \frac{1}{\sqrt{3}a} \left[ \tan^{-1} \frac{2 - a}{\sqrt{3}a} - \tan^{-1} \frac{2\xi - a}{\sqrt{3}a} \right] \]  

(7)

where \( \tau = [C_o/(\rho_s q_s)] \cdot (D_t/R^2) \). Since concentration in the solution \( C \) is directly related to \( \xi \) and \( a \) by the following expression

\[ \frac{C}{C_o} = \frac{\xi^2 + a^2}{1+\xi^2} \]  

(8)

then the change of \( C/C_o \) along time parameter \( \tau \) is readily obtained from Eq. (7). Diagrams in Fig. 2 show this relation for various \( C_w/C_o (= a^3/[a^3+1]) \) in the case where external mass transfer resistance is negligible \( (Bi=\infty) \).

By comparing the diagram shown in Fig. 2 with the experimentally obtained plot of \( C/C_o \) versus time \( t \) for a sufficiently agitated system, the diffusivity \( D_s \) can be determined from the time \( t \) and the corresponding dimensionless time \( \tau \). In other words, when it is given that time \( t=t_s \) corresponds to \( \tau=1 \) by fitting the experimental curve of \( C/C_o \) vs. log \( t \) with the theoretical curve which gives the same \( C_w/C_o \) with the experimental results, then \( D_s \) is calculated by the equation

\[ D_s = \frac{\rho_s q_s \cdot R^2}{C_o (t_s)^2} \]  

(9)

The Effect of External Mass Transfer Resistance

The effect of \( Bi \) in Eq. (7) can be checked by comparing \( C/C_o \) versus \( \tau \) for a fixed \( a \) and various \( Bi \). This was done for \( a=1 \) \( (C_w/C_o=0.5) \) in Fig. 3. It is estimated that \( Bi=100 \) is necessary to neglect the effect of \( Bi \) with reasonable accuracy for the range \( (C-C_w)/(C_o-C_w)<0.9 \). In most cases the effective diffusivity \( D_e \) is about one-tenth of the molecular diffusivity \( D_v \) and then \( Bi>100 \) means \( Sh=k_f D_v/D_e>20 \), which is not difficult to attain by sufficient agitation.
Fig. 4 Diagrams of $C/C_0$ versus $r_s$ for irreversible adsorption with surface diffusion kinetics.

Fig. 5 Diagrams of $C/C_0$ versus $r_s$ for linear isotherm ($D_s=D/s_0K_a$)

Comparison with Other Cases

1) Irreversible isotherm with surface diffusion

If the diffusion into a particle is controlled by the surface concentration gradient, Eq. (1) is replaced by

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

(10)

with the boundary condition at the surface for a negligible external mass transfer resistance

$$q=q_o \quad \text{at} \quad r=R$$

(11)

Then a well known solution\(^1\) is applicable.

$$\frac{C}{C_0} = 1 - \frac{q_o}{C_o} W_s \left( \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left( -n^2 \pi^2 \tau_s \right) \right)$$

(12)

where $\tau_s=D_s t/R^2$

Eq. (12) is demonstrated in Fig. 4 in a similar manner to Fig. 2.

2) Linear isotherm systems

When the isotherm can be approximated by Henry's type, Crank\(^1\) and Huang and Li\(^3\) gave the analytical solutions for negligible and finite external mass transfer resistance cases in the same experimental systems as adopted here. The solution for the former case is given as

$$\frac{C}{C_0} = 1 - \left( 1 - \tau_s \right) \left[ 1 + \frac{6 \alpha (\alpha+1) e^{-\alpha q_s \tau_s}}{9 + 9 \alpha + q_s^2 \alpha^2} \right]$$

(13)

where $\tau_s=D_s t/R^2$ and $q_s$'s are the non-zero roots of

$$\tan q_s = 3a_0 (3 + \alpha q_s^2)$$

(14)

where $\alpha=V_s/W_s K_a$ and $K_a$ is the adsorption equilibrium constant. The diagrams are given for various final uptakes in Fig. 5.

Direct comparison between Figs. 2, 4 and 5 cannot be done since they include different parameters. However, it is possible to distinguish one from the others by comparing the diagrams with, for instance, experimental plots of $C/C_0$ versus $t$ obtained by using different amounts of adsorbent for the same volume and the same initial concentration of the solution. This will be done in the next section.

Experimental

Adsorption of 2-dodecylbenzene sulfonate (Wako Chemicals) on four different activated carbons was employed as an example of applying the technique developed here.

The isotherm of this system is known to be almost rectangular for the range of liquid concentration above 10 ppm\(^4\).

A small amount of activated carbon particles was thrown into a flask which contained an aqueous solution of DBS. The flask was equipped with an agitator whose speed was about 115 rpm. Concentration change in the solution was detected continuously by ultraviolet beam (wave length 262 m\(\mu\)) adsorption of the solution by a Beckmann DBGT spectrophotometer furnished with a micro flow cell (Shimazu, cell volume 0.5 ml), through which a small amount of the solution was passed by a micro tube pump.

Table 1 Characteristics of activated carbon particles

<table>
<thead>
<tr>
<th>Carbon Origin</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>CAL</td>
<td>Takeda</td>
<td>Takeda*</td>
<td>Mitsui</td>
</tr>
<tr>
<td>Sieve opening (mesh)</td>
<td>48/65**</td>
<td>48/65**</td>
<td>48/65**</td>
<td>14/20</td>
</tr>
<tr>
<td>Average radius [mm]</td>
<td>0.127</td>
<td>0.127</td>
<td>0.127</td>
<td>0.508</td>
</tr>
<tr>
<td>Particle density [g/cc]</td>
<td>0.80</td>
<td>0.8</td>
<td>0.82</td>
<td>0.65</td>
</tr>
<tr>
<td>Nitrogen surface area [m²/g]</td>
<td>1140</td>
<td>1250</td>
<td>1200</td>
<td>1097</td>
</tr>
<tr>
<td>Pore volume [cc/g]</td>
<td>0.91</td>
<td>0.82</td>
<td>0.89</td>
<td>1.05****</td>
</tr>
<tr>
<td>Macropore fraction [—]</td>
<td>0.22</td>
<td>0.13</td>
<td>0.18</td>
<td>0.34</td>
</tr>
<tr>
<td>Average macro-pore radius [microns]</td>
<td>0.30</td>
<td>0.45</td>
<td>0.50</td>
<td>0.65</td>
</tr>
</tbody>
</table>

* Coconut shell base. The other carbons are made from coal.
** Fractioned after crushing
*** Determined by mercury porosimeter for the particles used.
**** Supplied by the manufacturer. Pore volume for the other carbon particles were determined from the nitrogen adsorption data (for pore radius=4-200 Å) and the mercury porosimeter data (200 Å-5 μ).

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solution was then recycled to the flask. Characteristics of the activated carbons and experimental conditions are listed in Tables 1 and 2, respectively. For larger particles (Runs D1–3), the flask was kept in a shaking bath and the concentrations were measured periodically by sampling the solution from the flask. Concentration-time plot for each run is shown in Fig. 6 where the hollow circles for Runs D1–3 show the continually measured concentration while the other curves indicate the direct measurements.

**Intraparticle Diffusivity**

Table 2 includes the amount adsorbed per unit mass of activated carbons for each run \( q_n = V_s / (C_o - C) / W_s \). The values for each activated carbon are almost constant regardless of the final concentration \( C_f \), which is a requirement of the assumption of the rectangular isotherm. The plot \( C/C_0 \) versus log \( t \) for each set of runs was compared with Figs. 2, 4, 5. Only Fig. 2 gave a consistent result between runs with different amounts of the same carbon particles, suggesting that pore diffusion is controlling in the condition adopted here. The diffusivities calculated from \( t \) which corresponds to \( \tau = 1 \) by using Eq. (9) are shown in Table 2. When liquid-phase diffusion in macro pores of activated carbon is solely responsible for the total diffusion through the particle, then \( D_e \) is estimated by the equation

\[
D_e = \varepsilon_s D_v / k^2
\]

where \( k^2 \) is the tortuosity factor. The values of \( k^2 \) calculated from \( D_e \) and \( D_v \) predicted by Weber and Rumer \(^{31} \) \( (4.5 \times 10^{-6} \text{ cm}^2/\text{sec}, \text{ at } 30^\circ) \) are listed in Table 2. Results for carbon A, B and C are comparable with \( k^2 > 4 \) suggested by Satterfield \(^{31} \), while \( k^2 \) for carbon D was far larger than this figure. This may be attributed to the existence of another diffusion resistance such as a resistance of micropore diffusion or skin effect of the particle surface.

**Conclusion**

A technique was proposed to determine the intraparticle diffusivity of adsorbents from concentration change in a batch agitated tank. Pore diffusion kinetics and the rectangular isotherm are assumed to derive the theoretical diagrams, which are then compared with the experimental results. The theory gave a better prediction for the transient concentration profile in the tank than the theory based on surface diffusion kinetics or a linear isotherm for the adsorption of 2-dodecylbenzene sulfonate on four different activated carbons.

**Acknowledgment**

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**Nomenclature**

- \( a \) = \( (C_0 / (C_0 - C_v))^{1/3} \)
- \( B_t \) = \( k_f R / D_v \)
- \( C_v \) = concentration in liquid phase [g/cm³]
- \( C_0 \) = initial concentration [g/cm³]
- \( C_e \) = equilibrium concentration [g/cm³]
- \( c \) = concentration in the pore [g/cm³]
- \( D_e \) = pore diffusivity [cm²/sec]
- \( D_s \) = surface diffusivity [cm²/sec]
- \( D_v \) = molecular diffusivity [cm²/sec]
- \( d_p \) = particle diameter [cm]
- \( K_e \) = adsorption equilibrium constant for linear isotherm [cm³/g]
- \( k_f \) = external mass transfer coefficient [cm/sec]
- \( k^2 \) = tortuosity factor of macropores [-]
- \( q \) = amount adsorbed at point \( r \) [g/g]
- \( q_n \) = \( n \)-th root of Eq. (14)
THE EFFECT OF THE INSULATION OF AN ISOLATED ELECTRODE ON MEASUREMENTS OF LOCAL MASS TRANSFER COEFFICIENTS BY ELECTRO-CHEMICAL METHOD*

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The effect of the insulation of a circular isolated electrode on the measurement of local mass transfer rates by the electrochemical method was investigated theoretically and experimentally. Three kinds of model for the velocity profile adjacent to the electrode were proposed and compared with experimental results, which were obtained with four kinds of isolated electrode in two-dimensional flow. It was found that the apparent local mass transfer coefficients for an isolated electrode with insulation coaxially around it were rather greater than the true values. The ratio between these two coefficients was a function of the outer radius of the insulation, \( r_2 \), and the relative area of the isolated electrode, \( \Delta \). The experimental results were in good agreement with the theoretical results. The results might be applicable to estimating true local mass transfer coefficients from apparent ones.

Introduction

The measurements of mass transfer coefficients by means of the electrochemical method have been studied by several groups of workers in recent years. In measuring the mass transfer rates between fluids and solid surfaces, this technique has an enormous advantage in that there is no need to measure the concentration at the surface of the body. It is enough to know the bulk concentration. Furthermore, by imbedding isolated electrodes on the surface of the body, the local mass transfer rates are obtained very easily and rapidly, even for a cylinder or a sphere. However, in the course of investigation of the mass transfer rate for a sphere in a uniform flow, it was observed that the integral average values of the local mass transfer coefficients over the whole area of the sphere were greater by 10–20% than the overall values measured under the same conditions. Recently Suzuki et al. investigated mass transfer from periodical discontinuous sources theoretically and experimentally, and suggested an interesting conclusion that the apparent mass transfer coefficient based on the net area of the discontinuous sources was larger

\[
\begin{align*}
q_0 & \quad = \text{saturated amount of adsorbed species per dry weight of adsorbent} \quad \text{[g/g]} \\
R & \quad = \text{particle radius} \quad \text{[cm]} \\
r & \quad = \text{radial position in a particle} \quad \text{[cm]} \\
r_\circ & \quad = \text{radial position of adsorption front} \quad \text{[cm]} \\
Sh & \quad = \frac{k_d}{\rho D_v} \\
V_L & \quad = \text{volume of liquid} \quad \text{[cm}^3\text{]} \\
W_S & \quad = \text{mass of adsorbent} \quad \text{[g]} \\
\alpha & \quad = \frac{V_L}{W_S K_a} \\
\varepsilon & \quad = \text{macropore fraction} \quad \text{[—]} \\
\xi & \quad = \frac{r_\circ}{R} \\
\rho_\circ & \quad = \text{particle density} \quad \text{[g/cm}^3\text{]} \\
\tau & \quad = \left( C_0 / \rho_\circ \Delta \right) \left( D_e l / R^2 \right) \\
\tau_\circ & \quad = D_e l / R^2
\end{align*}
\]

Literature Cited

6) Kawazoe, K.: Kagaku Kogaku, 29, 374, 404 (1965)
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