Exact Solution of a Model for Diffusion and Transient Adsorption in Particles and Longitudinal Dispersion in Packed Beds

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The importance of separating chemical components by fluid-solid operations has created a need for predicting the performance of adsorption equipment. A central problem in the design of fixed-bed adsorbers is the prediction of the concentration-time relationship, or breakthrough curve, of the effluent stream. Apart from the influence of axial dispersion, a mathematical model of adsorption from the flowing stream should take into account:

- Diffusion of the component from the main body of the flowing phase to the external surface of the adsorbent particle (external diffusion)
- Diffusion through the porous network of the particle (internal diffusion)
- The adsorption process itself

In the general case, all three steps can contribute to the overall rate of adsorption.

Mathematical solutions for the breakthrough curve have been presented for special cases where one of the three processes controls the rate. These results have supposed that the effect of longitudinal dispersion in the flowing phase in the bed is insignificant. It is also supposed that the equilibrium adsorption curve on the solid surface is linear. For example, for surface adsorption or external diffusion controlling the rate, Nusselt (1911), Anzelius (1926), and others (Furnas, 1932; Schumann, 1929) have presented equivalent mathematical developments. Thomas (1951), Rosen (1952) and Edeskuty and Amundson (1952) all solved the problem when only intraparticle diffusion is significant. Previous theoretical treatments which include more than one of the three rate-controlling resistances are limited to those of Rosen (1952, 1954) and Masamune and Smith (1964, 1965). Rosen considered the combined effects of intraparticle and external diffusion. Masamune and Smith developed a solution of the three-resistance case. However, they assumed in addition, negligible accumulation of the adsorbing component in the void space of bed and particles.

The effect of longitudinal dispersion is included in the papers by Lapidus and Amundson (1952) and Rasmuson and Neretnieks (1980). Lapidus and Amundson considered the effect of linear surface adsorption kinetics. Rasmuson and Neretnieks extended the solution of Rosen (1952) to include longitudinal dispersion.

This article presents a solution of the general three-resistance case, including longitudinal dispersion, in integral form.

THEORY

A bed of spherical particles (radius b) is at uniform temperature. Through the bed flows a fluid mixture consisting of an inert part and an adsorbable component whose concentration at the entrance is C_o. The major assumptions upon which the following equations are based are:

1. The particle diameter is small in comparison with the overall bed length and the bed is macroscopically uniform
2. The dispersion of fluid in a bed of particles is described by the "usual" one-dimensional differential equation for longitudinal dispersion, where the longitudinal dispersion coefficient is independent of the total bed length and the average solute concentration is defined by integration over the bed cross section
3. The adsorption equilibrium relationship is linear
4. The movement of solute within the particles can be described mathematically by a Fick's law diffusion equation where the effective intraparticle diffusion coefficient is constant and independent of concentration

With these restrictions the concentration $C(z, t)$ of the adsorbing component as a function of time and axial position in the bed can be obtained by solving the following system of equations: mass balance of the adsorbable component in the flowing phase:

$$\frac{\partial C}{\partial t} + V\frac{\partial C}{\partial z} - D_L\frac{\partial^2 C}{\partial z^2} = -\frac{1}{m}\left(\frac{\partial \bar{q}}{\partial t}\right) \tag{1}$$

mass balance of this component in the particle:

$$\epsilon_p\frac{\partial C_p}{\partial t} + \frac{\partial C_s}{\partial t} = \epsilon_p D_p\left(\frac{\partial^2 C_p}{\partial r^2} + \frac{2}{r}\frac{\partial C_p}{\partial r}\right) \tag{2}$$

rate of adsorption (assumed to be linear)

$$\frac{\partial C_s}{\partial t} = k_{\mathrm{ads}}(C_p - C_s/K_A) \tag{3}$$

The boundary conditions used are:

$$C(0, t) = C_o \tag{4}$$

$$C(\infty, t) = 0 \tag{5}$$

$$C(z, 0) = 0 \tag{6}$$

$$\frac{\partial C_p}{\partial r}(0, z, t) = 0 \tag{7}$$

$C_p(b, z, t) = C_p|_{r=b}$

$$\text{given by } \frac{\partial \bar{q}}{\partial t} = \frac{3k_f}{b}(C - C_p|_{r=b}) \tag{8}$$

$$C_p(r, z, 0) = C_s(r, z, 0) = 0 \tag{9}$$

The boundary condition (Eq. 8) is the link between the Eqs. 1 and 2. It states mathematically that the mass entering or leaving the particles must equal the flow of mass transported across a stagnant fluid film at the external surface.

The Laplace transform of C, $\bar{C}$, with the slightly different inlet condition:

$$C(0, t) = C_o \qquad 0 \leq t \leq t_o$$

$$C(0, t) = 0 \qquad t > t_o$$

has been derived by Kubin (1965), and was used to obtain up to the third central moment of the chromatographic curve $C(z, t)$. Using the properties of the Laplace-transform, the transform for the present inlet condition (Eq. 4) is simply obtained by dividing Kubin's result by $(1 - e^{-{}^{t}t_o^{s}})$ (or letting $t_o \rightarrow \infty$). In the present notation we obtain:

$\tilde{u}(z, s) = \bar{C}(z, s)/C_o$

$$= \frac{1}{s} \exp \left\{ \left(\frac{V}{2D_L} - \sqrt{\frac{V^2}{4D_L^2} + \frac{s}{D_L} + \frac{Y_T(s)}{mD_L}} \right) z \right\} \tag{10}$$

where

$$Y_T(s) = \frac{Y_D(s)}{R_F Y_D(s) + 1}$$

$$Y_D(s) = \gamma(w \cot w - 1)$$

$$\gamma = \frac{3D_p \epsilon_p}{b^2}$$

$$R_F = \frac{b}{3k_f}$$

$$w(s) = i[v(s)]^{\frac{1}{2}}$$

$$v(s) = \frac{sb^2}{D_p} \left[1 + \frac{k_{\text{ads}} K_A}{\epsilon_p (K_A s + k_{\text{ads}})} \right]$$

For further development we need $w(i\beta)$, β real:

$$v(i\beta) = \frac{i\beta b^2}{D_p} \left[1 + \frac{k_{\text{ads}} K_A}{\epsilon_p (K_A i\beta + k_{\text{ads}})} \right] = c + di \tag{11}$$

where

$$c = \frac{\beta^2 b^2}{D_p \epsilon_p} \frac{K_A^2 k_{\text{ads}}}{k_{\text{ads}}^2 + \beta^2 K_A^2} \tag{12}$$

$$d = \frac{\beta b^2}{D_p} \left[1 + \frac{K_A k_{\text{ads}}^2}{\epsilon_p} \frac{1}{k_{\text{ads}}^2 + \beta^2 K_A^2} \right] \tag{13}$$

Using de Moivre's theorem and trigonometric formulas we find that:

$$w(i\beta) = i(c + di)^{\frac{1}{2}} = \phi_1 + \phi_2 i \tag{14}$$

where

$$\phi_1 = (\mp) \sqrt{\frac{l - c}{2}} \tag{15}$$

$$\phi_2 = (\pm) \sqrt{\frac{l + c}{2}} \tag{16}$$

$$l = \sqrt{c^2 + d^2} \tag{17}$$

It should be noted that $-w$ gives the same final solution. To evaluate $Y_D(i\beta)$ we need:

$$\cot w = \frac{e^{iw} + e^{-iw}}{e^{iw} - e^{-iw}} i$$

We get:

$$\cot(\phi_1 + \phi_2 i) = \frac{\sin 2\phi_1}{\cosh 2\phi_2 - \cos 2\phi_1} - \frac{\sinh 2\phi_2}{\cosh 2\phi_2 - \cos 2\phi_1} i \tag{18}$$

We finally obtain an expression for $Y_D(i\beta)$ as:

$$Y_D(i\beta) = \gamma[H_{D_1}(\phi_1, \phi_2) + iH_{D_2}(\phi_1, \phi_2)] \tag{19}$$

with:

$$H_{D_1} = \frac{\phi_2 \sinh 2\phi_2 + \phi_1 \sin 2\phi_1}{\cosh 2\phi_2 - \cos 2\phi_1} - 1 \tag{20}$$

$$H_{D_2} = \frac{-\phi_1 \sinh 2\phi_2 + \phi_2 \sin 2\phi_1}{\cosh 2\phi_2 - \cos 2\phi_1} \tag{21}$$

The desired result $u(z, t)$ is given by the contour integral representing the inverse transform of $\bar{u}(z, s)$:

$$u(z, t) = C(z, t)/C_o$$

$$= \exp\left(\frac{V}{2D_L} z \right) \frac{1}{2\pi i} \int_{\alpha - i\infty}^{\alpha + i\infty} \frac{1}{s} \exp(st - zY_T'(s)) ds \tag{22}$$

where

$$Y_T'(s) = \sqrt{\frac{V^2}{4D_L^2} + \frac{s}{D_L} + \frac{Y_T(s)}{mD_L}} \tag{23}$$

The integration is to be performed along the straight line $\text{Re}(s) = \alpha$ parallel to the imaginary axis. The real number α is chosen so that $s = \alpha$ lies to the right of all singularities of the integrand but is otherwise arbitrary. This integral has been evaluated in Rasmuson and Neretnieks (1980).

Making the substitution $\beta = (k_{\text{ads}}/K_A)\ \lambda^2$ we finally obtain:

$$u(z, t) = C(z, t)/C_o = ½ + \frac{2}{\pi} \int_0^\infty \exp\left(\frac{VZ}{2D_L} - z \sqrt{\frac{\sqrt{x'(\lambda)^2 + y'(\lambda)^2} + x'(\lambda)}{2}} \right) \sin\left(\frac{k_{\text{ads}}}{K_A} \lambda^2 t - z \sqrt{\frac{\sqrt{x'(\lambda)^2 + y'(\lambda)^2} - x'(\lambda)}{2}} \right) \frac{d\lambda}{\lambda} \tag{24}$$

with

$$x'(\lambda) = \frac{V^2}{4D_L^2} + \frac{\gamma}{mD_L} H_1 \tag{25}$$

$$y'(\lambda) = \frac{k_{\text{ads}} \lambda^2}{K_A D_L} + \frac{\gamma}{mD_L} H_2 \tag{26}$$

H_1 and H_2 are complicated functions of λ:

$$H_1 = \frac{H_{D_1} + \nu(H_{D_1}^2 + H_{D_2}^2)}{(1 + \nu H_{D_1})^2 + (\nu H_{D_2})^2} \tag{27}$$

$$H_2 = \frac{H_{D_2}}{(1 + \nu H_{D_1})^2 + (\nu H_{D_2})^2} \tag{28}$$

H_{D_1} and H_{D_2} are defined as:

$$H_{D_1} = \frac{\phi_2 \sinh 2\phi_2 + \phi_1 \sin 2\phi_1}{\cosh 2\phi_2 - \cos 2\phi_1} - 1 \tag{29}$$

$$H_{D_2} = \frac{-\phi_1 \sinh 2\phi_2 + \phi_2 \sin 2\phi_1}{\cosh 2\phi_2 - \cos 2\phi_1} \tag{30}$$

where

$$\phi_1 = -\sqrt{\frac{l - c}{2}} \tag{31}$$

$$\phi_2 = +\sqrt{\frac{l + c}{2}} \tag{32}$$

$$l = \sqrt{c^2 + d^2} \tag{33}$$

$$c = \frac{b^2 k_{\text{ads}}}{D_p \epsilon_p} \frac{\lambda^4}{1 + \lambda^4} \tag{34}$$

$$d = \frac{b^2 k_{\text{ads}}}{D_p K_A} \left[1 + \frac{K_A}{\epsilon_p} \frac{1}{1 + \lambda^4} \right] \lambda^2 \tag{35}$$

The following dimensionless quantities are introduced:

$\delta = \frac{3D_p \epsilon_p}{b^2} \frac{z}{mV}$ bed length parameter

$\text{Pe} = \frac{zV}{D_L}$ Peclet number

$y = \frac{k_{\text{ads}}}{K_A} t$ contact time parameter

$R_1 = \frac{K}{m} = \frac{K_A + \epsilon_p}{m}$	distribution ratio, particles/void ratio of bed
$R_2 = \frac{K_A}{\epsilon_p}$	distribution ratio, solid/void of particles
$A = \frac{b^2 k_{\text{ads}}}{D_p \epsilon_p}$	internal diffusion resistance/adsorption rate resistance
$\nu = \gamma R_F$	external diffusion resistance/internal diffusion resistance

Equation 24 now becomes:

$$u(z, t) = ½ + \frac{2}{\pi} \int_0^\infty \exp\left(½ \text{ Pe} - \sqrt{\frac{\sqrt{(z^2x')^2 + (z^2y')^2} + z^2x'}{2}}\right) \sin\left(y\lambda^2 - \sqrt{\frac{\sqrt{(z^2x')^2 + (z^2y')^2} - z^2x'}{2}}\right) \frac{d\lambda}{\lambda} \tag{36}$$

with

$$z^2x' = \text{Pe}(¼ \text{ Pe} + \delta H_1) \tag{37}$$

$$z^2y' = \delta\text{Pe}\left[\frac{A\left(1 + \frac{1}{R_2}\right)}{3R_1}\lambda^2 + H_2\right] \tag{38}$$

and

$$c = A\frac{\lambda^4}{1 + \lambda^4} \tag{39}$$

$$d = A\left[\frac{1}{R_2} + \frac{1}{1 + \lambda^4}\right]\lambda^2 \tag{40}$$

SPECIAL CASES

It is interesting to note that the solutions of Rasmuson and Neretnieks (1980) and Masamune and Smith (1964) can be derived as limiting forms of Eq. 36.

I. Rasmuson and Neretnieks (1980)

Instantaneous chemical equilibrium $k_{\text{ads}} \to \infty$.

In obtaining the inverse transform of $\bar{u}(z, s)$ the substitution $\beta = (2D_p\epsilon_p/Kb^2)\lambda^2$ is now made. In this case $u(z, t)$ is given by Eq. 36 with:

$$z^2x' = \text{Pe}(¼ \text{ Pe} + \delta H_1)$$

$$z^2y' = \delta\text{Pe}(2/3\frac{\lambda^2}{R_1} + H_2)$$

$$y = \frac{2D_p\epsilon_p}{Kb^2}t$$

and

$$H_{D_1} = \lambda\left(\frac{\sinh 2\lambda + \sin 2\lambda}{\cosh 2\lambda - \cos 2\lambda}\right) - 1$$

$$H_{D_2} = \lambda\left(\frac{\sinh 2\lambda - \sin 2\lambda}{\cosh 2\lambda - \cos 2\lambda}\right)$$

II. Masamune and Smith (1964)

No longitudinal dispersion $\text{Pe} \to \infty$.

Negligible accumulation of adsorbing component in void spaces of bed and particles R_1, $R_2 \to \infty$.

For this case $u(z, t)$ is given by:

$$u(z, t) = ½ + \frac{2}{\pi}\int_0^\infty \exp(-\delta H_1)\sin(y\lambda^2 - \delta H_2)\frac{d\lambda}{\lambda}$$

and

$$\phi_1 = -\sqrt{A}\,\lambda\left[\frac{1}{2(\lambda^4 + 1)(\sqrt{\lambda^4 + 1} + \lambda^2)}\right]^{\frac{1}{2}}$$

$$\phi_2 = \sqrt{A}\,\lambda\left[\frac{1}{2(\lambda^4 + 1)(\sqrt{\lambda^4 + 1} - \lambda^2)}\right]^{\frac{1}{2}}$$

CONCLUDING REMARKS

A mathematical solution of a three-resistance adsorption model, including longitudinal dispersion, has been derived. The solution is a generalization of previous solutions by Rasmuson and Neretnieks (1980) and Masamune and Smith (1964, 1965).

The solution is given in form of an infinite integral. The integrand is the product of an exponential decaying function and a periodic sine function. The total function is thus a decaying sine wave in which both the period of oscillation and the degree of decay are functions of the system parameters. A method for integrating this sometimes highly oscillatory function is described in Rasmuson and Neretnieks (1980, 1981). In this method the integration is performed over each half-period of the sine-wave respectively. The convergence of the alternating series obtained is then accelerated by repeated averaging of the partial sums.

Quantitative treatment of rates of adsorption using this model requires values of the diffusion and adsorption rate constants that describe the three adsorption steps. Such constants can be evaluated from chromatographic measurements employing the statistical moments describing the chromatographic peak (Kubin, 1965; Kucera, 1965). This method was used, for example, by Schneider and Smith (1968) in evaluating experiments with adsorption of ethane, propane, and n-butane on silica gel. Other theoretical methods may also be used in the analysis of the pulse (Bashi and Gunn, 1977). From the constants determined from the pulse response and the mathematical solution presented above, it is then possible to predict breakthrough curves for the adsorption process.

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NOTATION

$A = \frac{b^2 k_{\text{ads}}}{D_p \epsilon_p}$
b = particle radius, m
C = concentration in fluid, mol/m³
C_p = concentration in fluid in intrapores, mol/m³
C_s = concentration in solid material, mol/m³
C_o = inlet concentration in fluid, mol/m³
c = see Eq. 34
D_L = longitudinal dispersion coefficient, m²/s
D_p = diffusivity in fluid in intrapores, m²/s
d = see Eq. 35
H_1 = see Eq. 27
H_2 = see Eq. 28
H_{D_1} = see Eq. 29
H_{D_2} = see Eq. 30
i = imaginary quantity
K = $K_A + \epsilon_p$, volume equilibrium constant, m³/m³
K_A = adsorption equilibrium constant, m³/m³

k_{ads} = adsorption rate constant, s^{-1}
k_f = mass transfer coefficient, m/s
l = $\sqrt{c^2 + d^2}$
m = $\frac{\epsilon}{1 - \epsilon}$
Pe = $\frac{zV}{D_L}$, Peclet number
$\bar{q}$ = volume averaged concentration in particles, mol/m^3
R_1 = $\frac{K}{m}$, distribution ratio
R_2 = $\frac{K_A}{\epsilon_p}$, distribution ratio
R_F = $\frac{b}{3k_f}$, film resistance, s
r = radial distance from center of spherical particle, m
s = Laplace transform variable, S^{-1}
t = time, s
u = C/C_o, dimensionless concentration in fluid
V = average linear pore velocity, m/s
x' = see Eq. 25, m^{-2}
y = $\frac{k_{ads}}{K_A} t$, contact time parameter
y' = see Eq. 26, m^{-2}
z = distance in flow direction, m

Greek Letters

γ = $\frac{3D_p\epsilon_p}{b^2}$, s^{-1}
δ = $\frac{\gamma z}{mV}$, bed length parameter
ϵ = void fraction of bed, m^3/m^3
ϵ_p = void fraction of particle, m^3/m^3
λ = variable of integration
ν = γR_F
ϕ_1 = see Eq. 31
ϕ_2 = see Eq. 32

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Measurement of Surface Self-Diffusion of Sulfur Dioxide on Porous Vycor Glass by Radioisotope Tracer Method

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When adsorbable gases flow or diffuse through microporous media, the flux is appreciably increased in the presence of the adsorbed phase. This additional flow, or surface flow, is important from the viewpoint of fundamental research or practical applications such as adsorption, catalytic reaction, gaseous separation and drying.

The models most commonly used to describe the surface flow mechanism are a hydrodynamic model (Babbit, 1950; Gilliland et al., 1958) and a hopping model (Hill, 1956; Higashi et al., 1963; Smith and Metzner, 1964; Weaver and Metzner, 1966; Gilliland et al., 1974; Ponzi et al., 1977). The authors have interpreted the surface flow from the standpoint of a random walk mechanism or a hopping mechanism rather than a viscous one and proposed a transport model (Okazaki et al., 1981; Tamon et al., 1981). The dependence of the surface flow coefficient on the amount adsorbed and the temperature for many experimental results can be correlated by this model.

The purpose of the present work is to obtain the surface self-diffusion coefficient and the surface flow coefficient of

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