External Film and Particle Phase Control of Adsorber Breakthrough Behavior

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Many researchers including Helfferich (1962) have stated that the character of adsorbent bed breakthrough curves is dominated by external film diffusion at low solute concentrations and by particle diffusion at high solute concentrations. The numerical results of Liu and Weber (1981), which demonstrate the effects of the external film mass transfer coefficient (k_e) and of the intraparticle solute diffusivity (D_s) on breakthrough curves, confirm this. Yet it is not at all obvious why this is the case. Analyses in this paper elucidate what occurs in adsorbent beds at high and low solute concentrations, as well as why k_e controls at low concentrations and why D_s controls at high concentrations.

Development

The solute continuity equation for adsorption beds, neglecting axial dispersion (which is well justified for liquid-phase systems and represents only a minor compromise for gas-phase systems), is

$$\frac{\partial c}{\partial t} + v\frac{\partial c}{\partial z} + \frac{1-\epsilon}{\epsilon}\frac{\partial q}{\partial t} = 0 \qquad (1)$$

Assuming that favorable adsorption equilibria pertain, which is almost always the case in real systems, and that the bed is long enough to generate constant-pattern behavior (this requires only a modest bed length if the equilibrium isotherm is reasonably favorable), Eq. 1 reduces to the well-known relationship $X = Y$, where $X = c/c_o$ and $Y = q/q_o$ (Cooney, 1965).

Employing film-type rate laws of the form

$$\frac{\partial q}{\partial t} = \frac{15D_s}{R^2}(q_i - q) \qquad (2)$$

$$\frac{\partial q}{\partial t} = k_e a(c - c_i) \qquad (3)$$

and the fact that $a = 3/R$, we obtain the relationship

$$(5/Bi)(Y_i - Y) = X - X_i \qquad (4)$$

where the Biot number $Bi = k_e R/KD_s$, where $K = q_o/c_o$.

Now, assuming for the sake of illustration that the relevant equilibrium isotherm is of the Freundlich type ($q^* = A\,c^{1/n}$) and that the exponent has a typical value of $1/n = 0.15$, we have $Y_i = X_i^{0.15}$. Then, because $Y = X$ for constant pattern conditions, Eq. 4 can be written as

$$(5/Bi)(X_i^{0.15} - X) = X - X_i \qquad (5)$$

Solving this equation for the relationship between X_i and X as a function of Bi gives the behavior shown in Figure 1. Clearly, for low solute concentrations, $X_i \simeq 0$ over a significant X range, the size of which depends on the value of Bi.

An order-of-magnitude analysis of Eq. 5 shows that, for $X \rightarrow 0$, $X_i^{0.15} - X \simeq \delta$ for $Bi \rightarrow 0$ and $X - X_i = \delta$ for $Bi \rightarrow \infty$, where δ represents an arbitrary vanishingly small positive number. Therefore, it is clear that as $X \rightarrow 0$, $X_i \rightarrow 0$. The existence of the 0.15 power on X_i in the $Bi \rightarrow 0$ case means that X_i will be closer to zero over a wider range of low X values when $Bi \rightarrow 0$ than when $Bi \rightarrow \infty$, as Figure 1 indicates. However, such an order-of magnitude analysis, while indicating the *type* of limiting behavior to be expected, obviously does not convey the more quantitative information that Figure 1 contains.

Cooney (1965) has shown that, under constant pattern conditions, the rate law given as Eq. 3 can be written as

$$\frac{dY}{dz^*} = -\frac{k_e a}{\alpha K}(X - X_i) \qquad (6)$$

where $\alpha = \epsilon v/[\epsilon + (1-\epsilon)K]$ and z^*, a coordinate which moves with the solute front, is

$$z^* = z - \frac{\epsilon v t}{\epsilon + (1-\epsilon)K} \qquad (7)$$

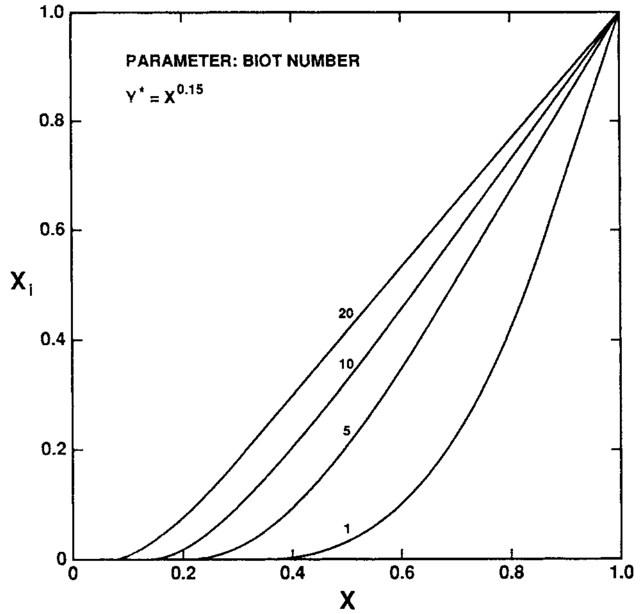

Figure 1. Relation between dimensionless interfacial and bulk fluid-phase concentrations for a typical Freundlich isotherm.

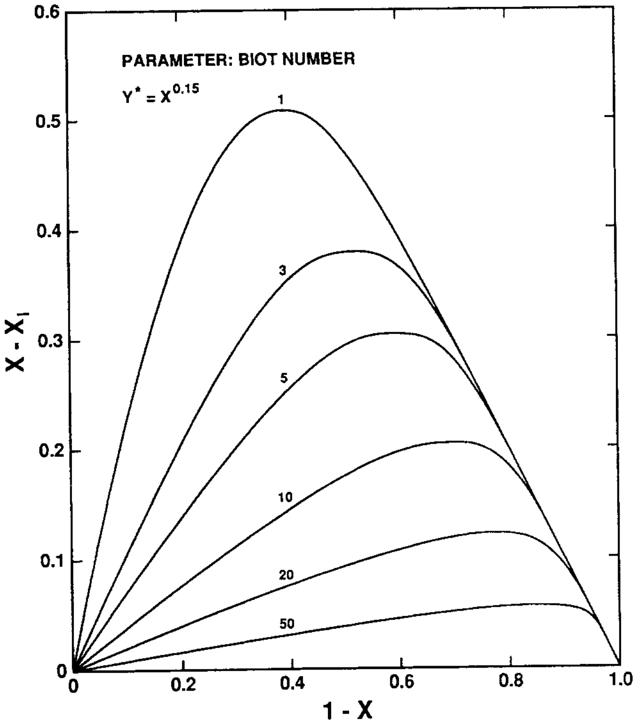

Figure 2. Dependence of the dimensionless fluid-phase concentration driving force on the dimensionless bulk fluid-phase concentration for a typical Freundlich isotherm.

Setting $dY/dz^* = dX/dz^*$ (because $Y = X$) and rearranging Eq. 6 yields

$$z^* = -\frac{\alpha K}{k_e a}\int \frac{dX}{X - X_i} \tag{8}$$

For the end of the bed ($z = L$) one can combine Eqs. 7 and 8 to obtain an expression for the breakthrough curve (X vs. t), which is

$$t = \left[\frac{\epsilon + (1 - \epsilon)K}{\epsilon v}\right]L + \frac{K}{k_e a}\int \frac{dX}{X - X_i} \tag{9}$$

As Figure 1 shows, $X_i \simeq 0$ for low X concentrations. Hence, from Eq. 9 it is clear that the breakthrough curve at low X values depends on k_e and *not* at all on D_s. Although the value of D_s does have an effect on the value of Bi, Figure 1 indicates that $X_i \simeq 0$ at low X *regardless* of the magnitude of Bi, unless Bi is fairly large.

Additional computations, shown in Figure 2, indicate that the initial slope of the relationship between $X - X_i$ and $1 - X$ is a strong function of the Biot number. [Note that for low X values, $X - X_i \simeq X$ (that is, $X_i \simeq 0$) as discussed previously.] The plot given as Figure 3 shows that the initial slopes (for small values of $1 - X$, that is, X values near 1) are essentially equal to m/Bi over a substantial Bi range, where m is a constant (equal to 4.25 in this case). Hence, $(X - X_i)/(1 - X) \simeq m/Bi$.

Indeed, letting $X = 1 - \beta$ and $X_i = 1 - \gamma$, where β and γ are small positive numbers, and allowing $X \rightarrow 1$ and $X_i \rightarrow 1$ gives, for Eq. 5,

$$(1 - \gamma)^{0.15} - (1 - \beta) = (\gamma - \beta)(Bi/5) \tag{10}$$

For small γ, $(1 - \gamma)^{0.15} \simeq 1 - 0.15\gamma$ and hence we obtain $\gamma/\beta = (1 + Bi/5)/(0.15 + Bi/5)$. Since $(X - X_i)/(1 - X) = (\gamma - \beta)/\beta = (\gamma/\beta) - 1$, then

$$\frac{X - X_i}{1 - X} = \frac{0.85}{0.15 + Bi/5} = \frac{4.25}{0.75 + Bi} \tag{11}$$

Clearly, as Bi becomes large ($1/Bi \rightarrow 0$ in Figure 3) it is clear that $(X - X_i)/(1 - X) \simeq 4.25/Bi$. One can also readily show that for Langmuir isotherms and $X, X_i \rightarrow 1, 1$ the relation in Figure 3 is similar in nature. Of course, the curvature of the relationship in Figure 3 depends on the degree of nonlinearity of the adsorption isotherm. A few sample computations readily indicate that, the more nonlinear the isotherm, the closer the relation stays to the "slope = 1" line in Figure 3 as $1/Bi$ gets larger [i.e., the relation conforms to $(X - X_i)/(1 - X) = m/Bi$ over a wider Biot number range as the isotherm becomes more convex].

Now, inserting $X - X_i = m(1 - X)/Bi$ into Eq. 9 shows that

$$t = \left[\frac{\epsilon + (1 - \epsilon)K}{\epsilon v}\right]L + \frac{R^2}{3mD_s}\int \frac{dX}{1 - X} \tag{12}$$

for high X values. Thus, the breakthrough curve behavior now depends on D_s only, and not at all on k_e. This is true for the range of Bi values over which Figure 3 indicates that $(X - X_i)/(1 - X) \simeq m/Bi$ and for X values over which the $X - X_i$ vs. $1 - X$ relationship, at the low end of the $1 - X$ range, remains essentially linear, as shown by Figure 2. Obviously, for isotherms which are not strongly convex and Bi values which are not "large," the relation $X - X_i = m(1 - X)/Bi$ does not quite

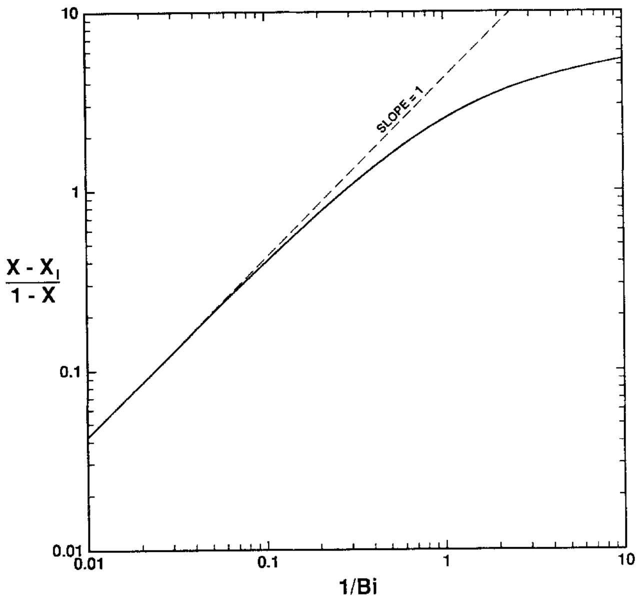

Figure 3. Initial slope of the $X - X_i$ vs. $1 - X$ relation in Figure 2 as a function of $1/Bi$.

hold, and the breakthrough behavior will depend partly on k_e as well as on D_s. However, its dependence on D_s will still generally be the dominant one at high X values.

Discussion

While the above equations mathematically show why X vs. t(at $z = L$) depends only on k_e at low X and only on D_s at high X, some discussion of the physical basis for such behavior seems warranted.

Clearly, because $X_i \simeq 0$ at low X, regardless of the value of D_s, the external film k_e parameter must control the mass transfer rate. D_s can, in general, affect the value of X_i. However, when $X \simeq 0$, $X_i \simeq 0$, and D_s has no effect on the fluid-phase driving force (and hence on the rate of solute transport) under these conditions. It should be pointed out that, even when $X_i \simeq 0$, Y_i can be quite substantial, due to the power law nature of their relationship. Hence, a significant concentration profile *does* exist in the particle phase, and indeed $(15D_s/R^2)(q_i - q) = k_e a(c - c_i)$ is always satisfied, as it must be.

At high X values, the results of Figure 2 indicate that the driving force $X - X_i$ in the fluid phase decreases linearly as $1 - X$ decreases, that is, as X approaches 1. This seems logical. Also, as one would expect, as k_e increases (Bi increases) the magnitude of the driving force $X - X_i$ decreases essentially proportionately (i.e., $X - X_i$ is very nearly proportional to $1/k_e$). This is also logical. However, although the nearly linear relationship between $X - X_i$ and $1/k_e$ (i.e., $1/Bi$) is certainly as one would expect, a physical reason as to why the relationship between $X - X_i$ and $1 - X$ should be truly linear at low $1/Bi$ values is not totally clear.

In conclusion, at low X, $X_i \simeq 0$ over a wide range of typical Bi values, regardless of D_s, and at high X, $X - X_i$ is very nearly proportional to KD_s/k_eR, which makes the constant in front of the integral in Eq. 9 almost exactly proportional to $1/D_s$ and independent of k_e. Hence, the external film process controls at low X, and the particle phase process controls at high X. The types of equations presented in this paper may be used to show that, regardless of the exact shape of the favorable isotherm, there is always a region at low X where $X_i \simeq 0$ and a region at high X where $(X - X_i) \simeq m(1 - X)/Bi$. In these regions, Eqs. 9 and 12 describe the breakthrough curve.

Notation

a = particle surface area per unit particle volume
A = parameter in Freundlich isotherm equation
Bi = Biot number, k_eR/KD_s
c = solute concentration in fluid phase
D_s = solute diffusivity in adsorbent particle
k_e = external film mass transfer coefficient
$K = q_o/c_o$
L = adsorbent bed length
m = constant
n = parameter in Freundlich isotherm equation
q = solute concentration in particle phase
R = particle radius
t = time
v = interstitial fluid velocity
X = dimensionless fluid phase solute concentration, c/c_o
Y = dimensionless particle phase solute concentration, q/q_o
z = axial distance

Greek letters

α = parameter equal to $\epsilon v/[\epsilon + (1 - \epsilon)K]$
β = differentially small positive number
γ = differentially small positive number
δ = differentially small positive number
ϵ = bed void fraction

Subscripts, superscripts

i = concentrations at the fluid/solid interface
o = concentrations corresponding to feed conditions
$*$ = equilibrium particle phase concentration (if on q or Y) or moving axial distance coordinate (if on z)

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