Determining External Film Mass Transfer Coefficients for Adsorption Columns

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Radcliffe et al. (1982), while presenting a method for determining the external film mass transfer coefficient k_e by the analysis of initial breakthrough concentrations, stated that external film mass transfer dominates mass transfer behavior during the early portion of breakthrough curves obtained from fixed-bed adsorbers. It is important, however, to define the conditions under which their assumptions and their method are valid, as will be discussed in this note.

Development

The solute continuity equation for a fixed-bed adsorber, with provision for axial dispersion, is

$$\left(\frac{\partial c}{\partial t}\right)_z + v\left(\frac{\partial c}{\partial z}\right)_t + \frac{(1-\epsilon)}{\epsilon}\left(\frac{\partial q}{\partial t}\right)_z = D_a\left(\frac{\partial^2 c}{\partial z^2}\right)_t \tag{1}$$

for "dilute" systems (i.e., systems for which v is essentially constant). Assuming that only external film mass transfer is of importance during the early part of the breakthrough curve, Radcliffe et al. employed the rate law

$$\frac{\partial q}{\partial t} = k_e a(c - c_i) \tag{2}$$

where c_i is the interfacial fluid-phase solute concentration. They stated that "initially the fluid-phase concentration at the particle surface is zero." Hence, setting $c_i = 0$, substituting Eq. 2 into Eq. 1, and letting $(\partial c/\partial t)_z$ be zero based on the physical argument that it is small (this assumption is valid if the solute distribution ratio, q_o/c_o, is large), we get

$$v\frac{dc}{dz} + \frac{(1-\epsilon)}{\epsilon}k_e ac = D_a\frac{d^2c}{dz^2} \tag{3}$$

Solving for c as a function of z, with the boundary condition that $c = c_o$ at $z = 0$, yields

$$\frac{c}{c_o} = \exp\left\{\frac{v}{2D_a} - \left(\frac{v^2}{4D_a^2} + \frac{(1-\epsilon)k_e a}{\epsilon D_a}\right)^{1/2}\right\}z \tag{4}$$

Evaluating this at the end of the bed ($z = L$) and defining $Pe = vL/D_a$ gives

$$\frac{c}{c_o} = \exp\left\{\frac{Pe}{2} - \left(\frac{Pe^2}{4} + \frac{(1-\epsilon)k_e a L^2}{\epsilon D_a}\right)^{1/2}\right\} \tag{5}$$

Plotting experimental values of c/c_o vs. time, and extrapolating back to $\theta = t/\bar{t} = 1$ (where $\bar{t}$, equal to L/v, is the time required for the first parcel of the solute-rich feed stream to traverse the length of the bed) allows one to determine k_e from Eq. 5, if D_a, v, a, L, and ϵ are known. Of course, the flow rate in the bed must be large enough and/or the bed short enough to generate a nonzero value of c/c_o in order for this method to work.

The analogous solution for $D_a = 0$ (which is often the case, especially when the fluid phase is a liquid) is:

$$\frac{c}{c_o} = \exp\left\{-\frac{(1-\epsilon)k_e a L}{\epsilon v}\right\} \tag{6}$$

Again, a plot of c/c_o vs. θ, extrapolated back to $\theta = 1$, allows one to determine k_e, if ϵ, a, L, and v are known. (Frequently, "a" is unknown and hence is lumped together with k_e, and the combined quantity $k_e a$ is determined. This procedure is acceptable because the product $k_e a$, and not either one alone, is what really matters in determining the fixed-bed behavior).

The question arises as to whether the assumption that $c_i = 0$ at $\theta = 1$ is indeed correct, thereby validating this method. Consideration of the simple limiting case where the solid phase has *no* adsorption capacity whatsoever is sufficient to prove that $c_i > 0$ can easily exist near $\theta = 1$. When fluid containing solute first contacts the solid phase, diffusion starts to occur across the fluid boundary layer. After a relatively short time (on the order of 10 s), the interfacial concentration c_i wil be nonzero. Extrapolation of c/c_o data to obtain k_e values is typically done with data obtained during the first few *minutes* after breakthrough, and during all but the first few seconds of this time, c_i clearly is nonzero. Relaxing the assumption that the solid phase has no adsorption capacity and assuming instead that the solid phase has a small adsorption capacity, one would expect c_i to be smaller, but still far from zero. Only when the

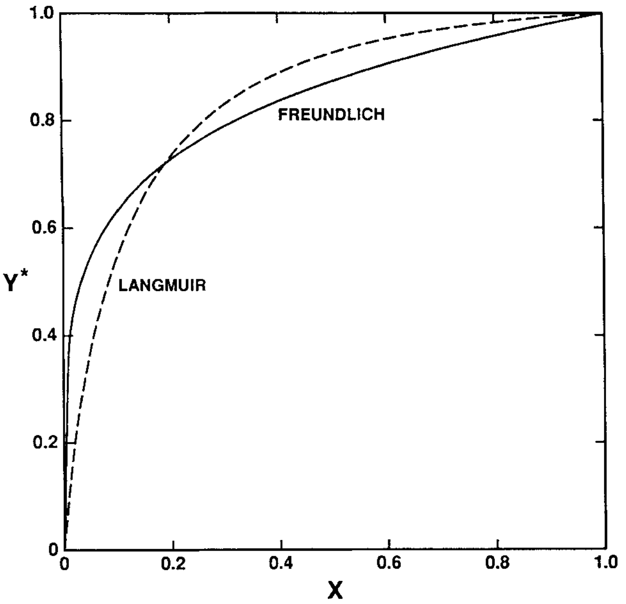

Figure 1. Typical Freundlich and Langmuir adsorption isotherms.

solid-phase adsorption capacity is allowed to be significant and when D_s is of reasonable size compared to k_e, will c_i approach zero.

We have tried to assess the conditions which will produce $c_i \cong 0$ by the following: First, we recognize that generally

$$\frac{\partial q}{\partial t} = k_e a (c - c_i) = \frac{15 D_s}{R^2} (q_i - q) \tag{7}$$

where we have used a linear-driving-force rate law for characterizing the solid-phase mass transfer process. This "solid-film" rate law is only approximately correct, but is sufficiently valid for present purposes. This leads to (using $a = 3/R$)

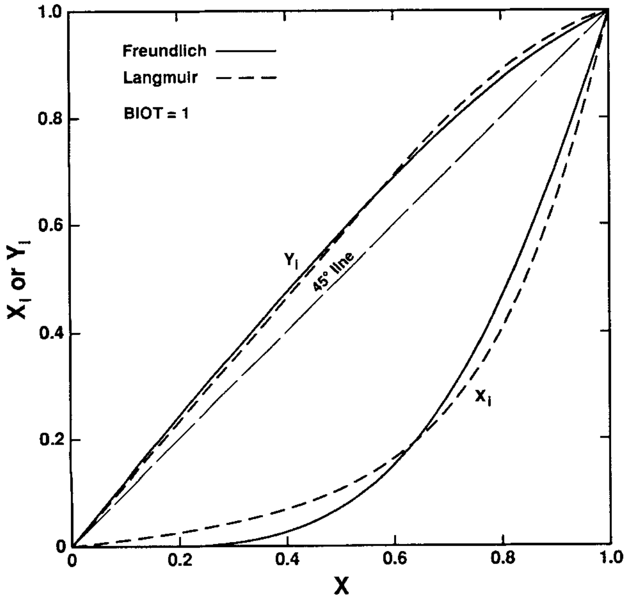

Figure 2. Interfacial concentrations vs. bulk fluid-phase concentration for a Freundlich isotherm (1/n = 0.20) and a Langmuir isotherm for Bi = 1.

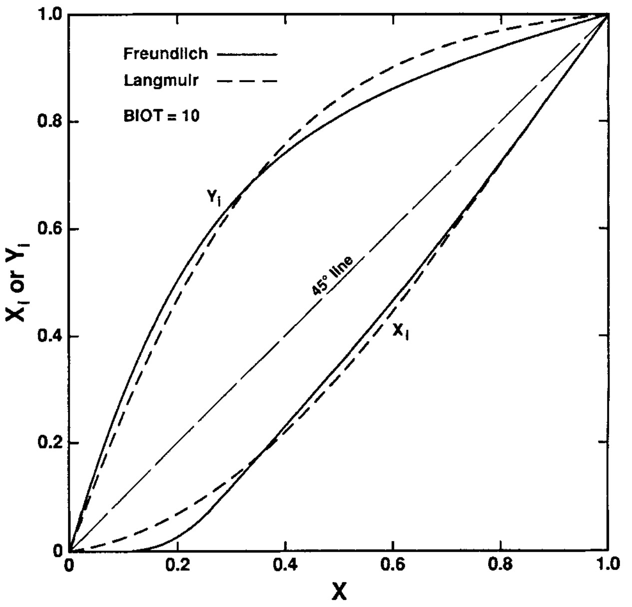

Figure 3. Interfacial concentrations vs. bulk fluid-phase concentration for a Freundlich isotherm (1/n = 0.20) and a Langmuir isotherm for Bi = 10.

$$(Bi/5)(X - X_i) = (Y_i - Y) \tag{8}$$

where $X = c/c_o$ and $Y = q/q_o$. Bi is the Biot number and is equal to $k_e R/K D_s$, where $K = q_o/c_o$.

Now let us assume that the adsorption isotherm for the system is favorable, which is usually the case, and that the fixed bed is long enough to produce a constant-pattern front. In such a case, $X = Y$, as shown by Cooney (1965) and many others. Then, $(Bi/5)(X - X_i) = (Y_i - X)$ and if Y_i is expressed as a function of X_i, using an equilibrium isotherm equation, we can obtain a relationship between X and X_i.

We shall consider two common favorable isotherms. First, for a Freundlich isotherm, $Y_i = X_i^m$, where $m = 1/n$ (the Freundlich isotherm is usually written as $q^* = A\,c^{1/n}$, where A and n are constants). Hence, we get

$$X = \left(\frac{5}{Bi} X_i^m + X_i\right) \Bigg/ \left(\frac{5}{Bi} + 1\right) \tag{9}$$

For a Langmuir isotherm, $q^* = BQc/(1 + Bc)$, we have $Y_i = (1 + Bc_o)X_i/(1 + Bc_o X_i)$, and hence

$$X = \frac{\dfrac{Bi}{5} X_i + \dfrac{(1 + Bc_o)X_i}{1 + Bc_o X_i}}{\dfrac{Bi}{5} + 1} \tag{10}$$

As example cases, we take a Freundlich isotherm of the form $Y_i = X_i^{0.20}$. The exponent 0.20 is a typical value. For a Langmuir isotherm, we take the case where $c_o = 0.005$ mol/L and $B = 2{,}000$ L/mol. Figure 1 shows these two isotherms, and it is apparent that they are roughly similar in character, although the Freundlich isotherm is, of course, much steeper at low X values.

For Biot numbers of 1 and 10 (typical values), we have calculated the X vs. X_i relationships from Eq. 9 for the Freundlich isotherm ($m = 0.20$). These are presented in Figures 2 and 3. Computations for other reasonable exponent values gave quite similar results. Also shown are the Y_i values which coexist with the various X and X_i values. It is clear that for the higher Biot number ($Bi = 10$), the range of X values over which X_i is essentially zero is quite limited, being restricted to X values of roughly 0.10 or less. For $Bi = 1$, the range over which X_i is essentially zero is larger, covering X values of roughly 0.24 or less.

Figures 2 and 3 show similar information for the Langmuir isotherm, for $Bi = 1$ and $Bi = 10$. One can see that the range of X values for which X_i is essentially zero is nonexistent. For higher Biot numbers, the X_i curve would be even closer to the 45-degree line, and the value of X_i for any given X would be even higher. In general, for Langmuir isotherms, the region over which $X_i = 0$ is more limited than that for Freundlich isotherms.

Additional computations show that the less curved the Freundlich or Langmuir isotherm (that is, the closer the isotherm is to linearity), the smaller is the range over which $X_i \cong 0$ for any Biot number. Indeed, for isotherms significantly less curved than those shown in Figure 1, X_i is never close to zero for any reasonable Biot number.

The 45 degree lines in these figures are given for reference purposes, because the vertical distance between the line for Y_i and the 45-degree line represents the solid-phase driving force $(Y_i - Y)$, and the vertical distance between the 45-degree line and the X_i line represents the fluid-phase driving force $(X - X_i)$. These driving forces vary with the type of isotherm involved and with the value of the Biot number. The driving force values must of course satisfy Eq. 8. It is noteworthy that, for the Freundlich isotherm, the values of Y_i can be substantial even when the X_i values are nearly zero. This, of course, is due to the power-law nature of the Freundlich isotherm and its steepness near $X_i = 0$ (its slope $\rightarrow \infty$ as $X_i \rightarrow 0$).

Therefore, we have seen that, if a Langmuir isotherm governs the system behavior and the Biot number is on the order of 10 or higher, X_i will not be very close to zero for any reasonably finite X value. Yet, both a $X_i \cong 0$ value at $\theta = 1$ and a reasonably finite X value at $\theta = 1$ are required for the method of Radcliffe et al. (1982) to work. For systems governed by Freundlich equilibria, the situation is somewhat more hopeful. If the Biot number is small enough, the value of X_i corresponding to the initial breakthrough value of X may be close enough to zero to validate the Radcliffe et al. method. In most real cases, however, it is doubtful whether the $X_i = 0$ criterion will be met. One must perform calculations similar to those shown in Figures 2 and 3 to check whether $X_i \cong 0$ for the observed value of X at $\theta = 1$.

Our conclusion is that, in many cases, the assumption that $c_i = 0$ will not be valid at $\theta = 1$, and therefore the Radcliffe et al. method of obtaining k_e will not be usable. Let us now consider what alternative is available.

Starting from Eq. 7, let us consider the simple case of a system possessing a linear equilibrium adsorption isotherm, $q^* = Kc$. Then, one can write $c_i = q_i/K$ and $c^* = q/K$. Since $(c - c^*) = (c - c_i) + (c_i - c^*) = (c - c_i) + (q_i - q)/K$, we find from Eq. 7 that

$$\frac{\partial q}{\partial t} = \frac{(c - c^*)}{\left[\frac{R^2}{15 D_s K} + \frac{1}{k_e a}\right]} \tag{11}$$

or

$$\frac{\partial q}{\partial t} = K_e a (c - c^*) \tag{12}$$

where

$$\frac{1}{K_e a} = \frac{1}{k_e a} + \frac{R^2}{15 D_s K} \tag{13}$$

If we let $1/K_e a = R_T$ (the total mass transfer resistance), $Re = 1/k_e a$ (the fluid-phase mass transfer resistance), and $R_s = R^2/15 D_s K$ (the solid-phase mass transfer resistance), then $R_T = R_e + R_s$.

Now, for a favorable adsorption isotherm rather than a linear one, the above equations can be considered to apply *approximately* if K is taken to be q_o/c_o (that is, now K is equal to the slope of the line connecting q, $c = 0$, 0 and q, $c = q_o$, c_o on the favorable isotherm).

Then, using Eq. 12 in place of Eq. 2 and recognizing that c^* *does* equal zero near $\theta = 1$ (the *average* solid-phase concentration q will be essentially zero at $\theta = 1$, even if a finite q_i exists; hence, c^* must also be essentially zero) obviously leads to the same solutions as before (Eqs. 5 and 6) except that now instead of k_e we have the overall coefficient K_e. Whereas before (when k_e was used) there was the question as to whether $c_i = 0$ at $\theta = 1$, now the question is whether $c^* = 0$ at $\theta = 1$, and we know this fact is true. Hence, plotting c/c_o vs. θ and extrapolating back to $\theta = 1$ gives one a value for $(1 - \epsilon) K_e a L/\epsilon v$ (for the $D_a = 0$ case), and hence for $R_T = 1/K_e a$, if ϵ, v, and L are known (which they usually are). Then, as Cooney et al. (1978) have shown, by varying F (the volumetric flow rate), plotting R_T vs. $F^{-0.5}$ and extrapolating back to $F^{-0.5} = 0$ (that is, effectively to $F = \infty$, for which $R_e = 0$), one can obtain a value for R_s only. Then, going back to any desired finite F, one may obtain R_e from $R_e = R_T - R_s$. Hence, one therefore can determine R_s and R_e for any desired F value.

Figure 4 shows a plot presented earlier by Cooney et al. (1978), in which R_s and R_e at $F = 200$ mL/min were determined in the manner described for three different hemoperfusion columns. The three columns were the Sandev unit (300 g of 2-4-mm-diameter activated carbon granules coated with a 5-μm-thick layer of a highly porous acrylic hydrogel polymer), the Gambro unit (300 g of a 1-mm-diameter, 2-mm-long cylindrical, activated carbon extrudate coated with a 3-5-μm-thick, highly-porous, cellulose polymer coating), and the Becton-Dickinson unit (94 g of 0.30-0.84-mm-diameter, uncoated, activated carbon granules. The fluid was a physiological saline solution containing 1 g/L of sodium salicylate (the adsorbable solute). Cooney et al. (1978) give details on the experiments conducted as well as further information on the columns themselves.

Table 1 presents the R_T, R_e, and R_s values obtained. As one can see, R_s increases as the granule size increases, as one would expect, knowing that $R_s = R^2/(15 D_s K)$. Indeed, taking the geometric mean diameters of the Sandev and B & D granules, and

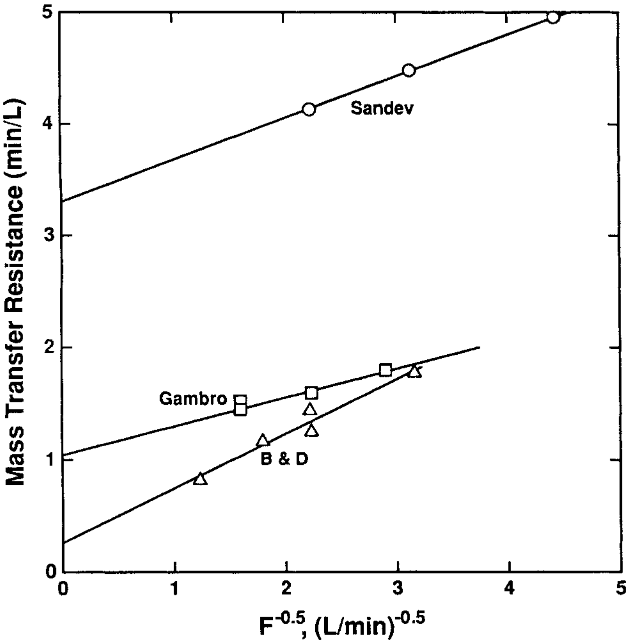

Figure 4. Overall mass transfer resistances as a function of inverse square root of fluid flow rate for three hemoperfusion columns.

Table 1. Hemoperfusion Column Mass Transfer Resistances*

Column Type	Total (R_T)	Solid (R_s)	Fluid (R_e)
	Resistance at 200 mL/min Flow Rate		
Sandev	4.18	3.31	0.87
Gambro	1.62	1.06	0.56
B & D	1.32	0.26	1.06

*in min/L

the equivalent spherical diameter of the cylindrical Gambro particles, one does find that R_s is essentially proportional to the diameter (or radius) squared. This assumes, of course, that K and D_s are similar for the three activated carbons. Also, the mass transfer resistances of the very thin, highly porous polymer coatings on the Sandev and Gambro carbons are assumed not to affect the R_s values significantly.

The data shown in Figure 4 and in Table 1 were analyzed again to determine whether the assumption of a finite X_i value was met in each run. Since "a" = $3/R$, then R_s/R_e can be shown to be equal to $Bi/5$. Thus, from Table 1, our Biot numbers for the Sandev, Gambro, and B & D units were 19.02, 9.46, and 1.23. Since Kane (1980) has shown that for sodium salicylate adsorption on the Gambro activated carbon and on similar activated carbons the Freundlich exponent is about 0.20, computations similar to those shown in Figures 2 and 3 for $m = 0.20$ and for $Bi = 19.02$, 9.46, and 1.23 indicate that the breakthrough X values would have to be greater than about 0.04, 0.10, and 0.24, respectively, for X_i to be nonzero.

Our experimental data show that these critical X values were exceeded in the Sandev and Gambro runs, but not in the B & D runs. Hence, our earlier analysis, which was based on the assumption that X_i was nonzero (and hence assumed that the solid-phase mass transfer resistance existed), was incorrect for the B & D column runs. This only proves the need for, and the value of, the type of X vs. X_i computations discussed earlier, in which the X ranges over which $X_i = 0$ and $X_i > 0$ were determined. Thus, the reanalysis done here shows that the data in Figure 4 for the B & D unit should extrapolate exactly to the origin, since an R_s value could not have existed. Since the computed R_s value for the B & D unit was small, one could easily argue that, within the limits of experimental error, an R_s of zero is quite reasonable. As Cooney et al. (1979) have pointed out, the B & D unit has significant nonuniform flow characteristics, which makes its behavior somewhat different from that of ordinary packed adsorber columns. This fact could easily explain the failure of the B & D data to extrapolate to zero in Figure 4.

In summary, the examples considered here have shown that the assumption of a zero interfacial fluid-phase concentration at $\theta = 1$ is met only when the adsorption isotherm shape and Biot number fall within certain limits. When the interfacial fluid-phase concentration is not zero, the "external mass transfer coefficient" analysis procedure yields instead a value for the overall mass transfer coefficient. One needs to be aware of whether $X_i = 0$ or $X_i > 0$ for each particular situation to correctly interpret the results of the initial breakthrough curve analysis.

Notation

a = external particle surface area, m^2/m^3 solid
c = solute concentration in fluid phase, kg solute/m^3 fluid phase
D_a = axial dispersion coefficient, m^2/s
D_s = diffusivity of solute in solid phase, m^2/s
F = volumetric flow rate, m^3 fluid/s
K = slope of linear adsorption isotherm, m^3 fluid/m^3 solid
k_e = individual fluid-phase mass transfer coefficient, m/s
K_e = overall fluid-phase mass transfer coefficient, m/s
L = adsorbent bed length, m
Pe = Peclet Number, Lv/D_a, dimensionless
q = solute concentration in solid phase, kg solute/m^3 solid
R = adsorbent particle radius, m
R_e = external film mass transfer resistance, s/m^3
R_s = solid phase mass transfer resistance, s/m^3
R_T = overall mass transfer resistance, $R_e + R_s$, s/m^3
t = time, s
$\bar{t}$ = residence time in bed, L/v, s
v = interstitial fluid velocity, m/s
X = dimensionless fluid-phase concentration, c/c_o
Y = dimensionless solid-phase solute concentration, q/q_o
z = axial distance, m

Greek letters

ϵ = packed bed porosity, m^3 voids/m^3 bed = m^3 fluid/m^3 bed
θ = dimensionless time, $t/\bar{t} = tv/L$

subscripts/superscripts

i = interfacial concentration (solid/fluid boundary)
o = value corresponding to feed conditions or equilibrium with the feed
$*$ = equilibrium value

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