R&D NOTES

Comparison of Simple Adsorber Breakthrough Curve Method with Exact Solution

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Cooney (1990) recently described a simple method for calculating adsorber bed concentration profiles and breakthrough curves. The method is based on a model that assumes constant pattern behavior (favorable isotherms and sufficient bed length) and linear driving force (LDF) rate laws for both the fluid and solid phases of the form:

$$\frac{\partial Y}{\partial t}=\frac{15D_s}{R^2}\,(Y_i-Y) \tag{1}$$

$$\frac{\partial Y}{\partial t}=\frac{k_fS_o}{K}\,(X-X_i) \tag{2}$$

Equating Eqs. 1 and 2, noting that $Y=X$ for constant pattern behavior (Cooney, 1990), and assuming a Freundlich isotherm applies ($Y_i^*=X_i^m$, where $m=1/n$), gave:

$$\beta(X_i^m-X)=(X-X_i) \tag{3}$$

where $\beta=15D_sK/R^2k_fS_o=5/Bi$ (since $S_o=3/R$). Equation 3 can be rearranged to:

$$X=(\beta X_i^m+X_i)/(\beta+1) \tag{4}$$

from which one can generate a set of X, X_i values which can be easily fit to an nth-order polynomial using standard software. The $X_i=f(X)$ polynomial expression which results is then inserted into:

$$t=\left[\frac{\epsilon+(1-\epsilon)K}{\epsilon v}\right]L+\frac{K}{k_fS_o}\int_{X_0}^{X}\frac{dX}{X-X_i} \tag{5}$$

which is then integrated by any convenient numerical scheme to get X vs. t at $z=L$, that is, the adsorber breakthrough curve.

The virtue of this simple method is that it is not restricted to any *specific* favorable isotherm (such as Freundlich or Langmuir) and can be solved for *any* values of the important parameters (such as $1/n$ and the Biot number). Previous solutions for constant pattern systems which have been generated by the numerical solution of the relevant equations (using various rate laws) all present their results for discrete values of $1/n$, Bi, and so on, and hence are *not* easily usable for parameter values that do not match those for which the solutions are given.

Examples include the solutions given by Hand et al. (1984), by Fleck et al. (1973), by Hall et al. (1966), and by Vermeulen (1953). Therefore, the simple method of Cooney has advantages. It *does* require that one go through the computations for one's particular case, but the computations are straightforward and require relatively little time. Of course, if one's parameter values match those of a previously tabulated solution, such tabulated solutions would be faster; however, such a match would generally be unusual.

It might be mentioned in passing that for the case of a Freundlich isotherm where $m=1/n=0.5$ and for the case of a Langmuir isotherm, Eq. 4 may be rearranged to a quadratic form, enabling one to express $X-X_i=f(X)$ analytically. In these cases, a polynomial relationship for $X-X_i$ need not be generated. In neither case, however, does an analytical solution to Eq. 5 exist, and therefore, numerical integration of Eq. 5 is still required.

Another point worth mention is that, during the numerical integration of Eq. 5, when one has a given X value and requires the corresponding X_i value, this X_i value could be obtained by a root-finding procedure applied to Eq. 4. This approach would avoid the polynomial fitting step. However, computationally, this approach is much more time-consuming and involves some uncertainty that the correct X_i root will be found.

The study by Hand et al. (1984) presents essentially *exact* numerical solutions to a constant pattern model which assumes Freundlich isotherms, an LDF rate law (Eq. 2) for the fluid phase, and a homogeneous solid-phase diffusion model (HSDM) rate law for the adsorbent phase:

$$\frac{\partial Q}{\partial t}=\frac{D_s}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial Q}{\partial r}\right] \tag{6}$$

Since Eq. 6 is generally regarded to be more realistic than the LDF solid-phase rate law (Eq. 1) used by Cooney and other previous investigators, the existence of the exact solutions of Hand et al. (1984) afforded us the opportunity of comparing the predictions of Cooney's simple LDF model to the predictions of an exact HSDM model, at least for Freundlich isotherms. Those comparisons have been done for several representative cases, and they show excellent agreement between the two models.

The only important parameter groups in Cooney's model which affect the breakthrough curve are the Biot number, k_fR/KD_s, in Eq. 4 and the group K/k_fS_o in Eq. 5. The group $[\epsilon+(1-\epsilon)K](L/\epsilon v)$ in Eq. 5 affects only the *position* of the midpoint of the breakthrough curve in time, but not its degree of spread or its curved shape.

From Eq. 5, one can see that the group in front of the integral (K/k_fS_o, or $KR/3k_f$) affects the degree of *spreading out* of the S-shaped breakthrough curve, but not its basic shape. The value of the Biot number does affect the *shape* of the breakthrough curve because, as Eq. 4 shows, Bi affects the nature of the X_i vs. X relationship, and hence affects the nature of the integrand in Eq. 5 (which determines the shape of the breakthrough curve). Hence, the Biot number is the key parameter in defining the shape of the breakthrough curve; its value must be varied widely if one wishes to explore the comparison between Cooney's model and that of Hand et al.

As a point of interest, Hand et al. have stated that, in their view, reasonably complete dominance of the liquid film resistance exists for $Bi<0.5$ and reasonably complete dominance of the intraparticle resistance exists at $Bi>30$. These are, of course, somewhat approximate criteria. Our comparisons, given below, explore the range of $0.5<Bi<25$, or essentially the range from liquid film control to particle control.

Base-Case Comparison

The model of Cooney and of Hand et al. were evaluated for the following "base-case" parameters:

$$\epsilon=0.35$$

$$v=0.80 \text{ cm/s}$$

$$R=0.05 \text{ cm}$$

$$L=500 \text{ cm}$$

$$1/n=0.20$$

$$K=714.3$$

$$D_s=3.5\times10^{-8} \text{ cm}^2\text{/s}$$

$$k_f=0.005 \text{ cm/s}$$

The value $\epsilon=0.35$ is typical. $v=0.8$ cm/s corresponds to a hydraulic loading of 4 gpm/ft^2 (2.7 L/s/m^2) which is common in industrial practice (Cooney, 1988) and $R=0.05$ cm is also in the midrange of industrial adsorbent particle sizes (Cooney, 1988). $D_s=3.5\times10^{-8}$ cm^2/s is a typical value, as given for phenol by Crittenden and Weber (1978). The k_f value was computed from the Williamson et al. (1963) correlation, which Crittenden and Weber (1978) found provided the best match of several correlations to their data, using water at 20°C as the fluid and a liquid-phase solute diffusivity of 1×10^{-5} cm^2/s (a typical value). The L value of 500 cm (16.4 ft) is typical, but in any case has no effect on the comparison being made. Its value merely determines the "midpoint" of the breakthrough curve in time, not its shape.

A Freundlich exponent of 0.20 is representative, and a K of 714.3 (chosen to make Bi be a discrete integer, equal to one of those for which Hand et al. have provided a solution) is also typical (since $K=Q_f/C_f$, its value can be varied over a wide range by merely using different inlet concentrations C_f. C_f values in the range of 100-200 mg/L usually give K values in the range of 500-1,000 for many common solute/sorbent systems).

Based on these parameter values, $Bi=10.0$ and $\beta=5/Bi=0.50$. The exact HSDM solution of Hand et al. was evaluated just as they have outlined ($Bi=10$, $1/n=0.20$ is one of 55 cases whose solutions they give; overall they present nine solutions each for different Bi and $1/n=0.05, 0.10, 0.20, 0.30, 0.40$, plus 6 solutions for different Bi and $1/n=0.50$ and 4 solutions for different Bi and $1/n=0.60$). The model of Cooney was also evaluated just as he has described (Cooney, 1990). In general, about 10-12 X_i, X points were generated from Eq. 4, which were fit by a 4th order polynomial. Since the X_i vs. X relation varies sharply at low X_i, X values [see Figure 1 of Cooney (1990)], extra "weight" was given to the polynomial fit at low X_i, X in order to obtain an accurate fit for all values. Typically, points at $X_i=0$, 0.01, 0.02, 0.04, 0.08, 0.12, 0.20, 0.40, 0.60, 0.80, and 1.0 were used for the fit.

The polynomial $X_i=a+bX+cX^2+dX^3+eX^4$ obtained generally had a very small "a" value, which was set to zero in order to make $X_i=0$ at $X=0$. To then make $X_i=1$ when $X=1$, the value of d (an arbitrary choice) was adjusted slightly. The choice of which other constant to adjust after setting $a=0$ made no significant difference.

$X-X_i=(1-b)X-cX^2-dX^3-eX^4$ was then inserted into Eq. 5, which was then integrated numerically by a simple 4th-order Runge-Kutta scheme to give the breakthrough curve. The correct X_o value was determined easily by trial-and-error, as discussed by Cooney (1990).

For this case, X_o was 0.590. Figure 1 contains the curves obtained from the two models (Cooney and Hand et al.) for this $Bi=10$, $1/n=0.20$ situation. One can see that the results are very similar.

Comparison for Other Cases

We also evaluated the two models for the following changes to the "base case" conditions:

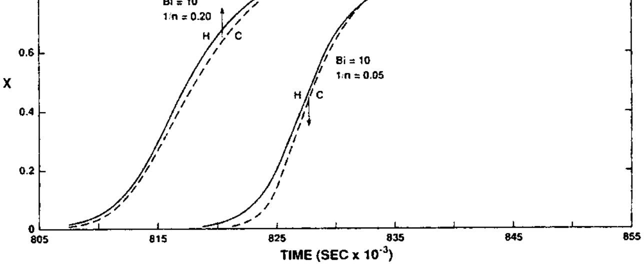

Figure 1. Comparison of Hand (H) and Cooney (C) models for $Bi=10$, $1/n=0.20$ and $Bi=10$, $1/n=0.05$.

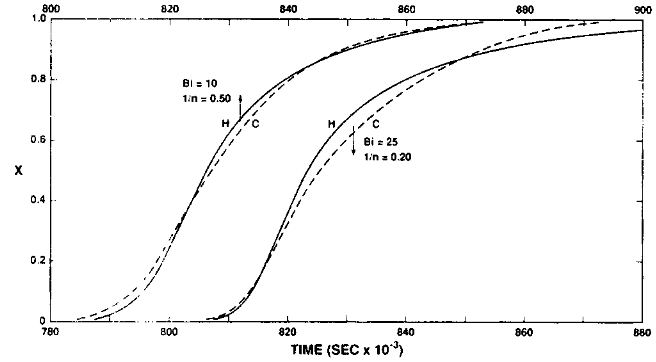

Figure 2. Comparison of Hand (H) and Cooney (C) models for $Bi = 10$, $1/n = 0.50$ and $Bi = 25$, $1/n = 0.20$.

(a) $1/n = 0.05$ and 0.50 instead of 0.20 (the X_o values were 0.607 and 0.570, respectively).

(b) $D_s = 1.4 \times 10^{-8}$ cm^2/s instead of 3.5×10^{-8} cm^2/s (this gives $Bi = 25.0$ and $X_o = 0.587$).

(c) $R = 0.02$, $k_f = 0.009$, $Bi = 4.0$, instead of $R = 0.05$, $k_f = 0.005$, $Bi = 10.0$. One cannot simply change R without changing k_f. If v is unchanged, the correlation of Williamson et al. (1963) states that k_f is proportional to R to the minus 0.66 power. Hence, if we change R from 0.05 to 0.02, k_f rises from 0.005 to 0.009. We then need $K = 1{,}285.714$ to obtain our desired Bi value of 4 (one for which Hand et al. give a solution). X_o was 0.548 for this case.

(d) An extreme case where $R = 0.01$, k_f is assumed to remain at 0.005 due to a decrease in v (this would occur if the column diameter increases), and $K = 2{,}857.14$. This gives a Biot number of 0.5 (one for which Hand et al. present a solution). The value of X_o was 0.393.

Figures 1 through 4 show the results obtained. Again, agreement between the two models is quite good. Note that, in Figures 1 and 2, two pairs of curves are to be read using the lower time scales and two pairs are to be read using the upper time scales. This permits the information for these four cases to be presented on two plots, with enough separation so that the four curves in each figure do not all overlap.

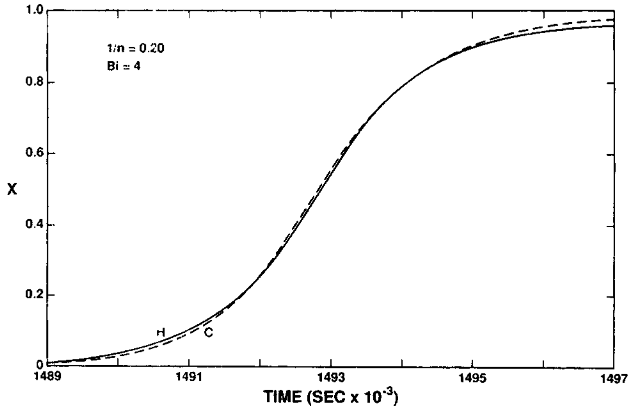

Figure 3. Comparison of Hand (H) and Cooney (C) models for $Bi = 4$ and $1/n = 0.20$.

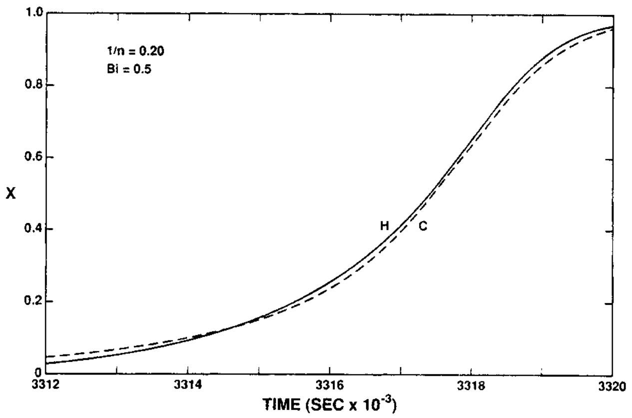

Figure 4. Comparison of Hand (H) and Cooney (C) models for $Bi = 0.5$ and $1/n = 0.20$.

A careful scrutiny of all of the computed results indicates several things. First, changing $1/n$ from 0.05 to 0.20 to 0.50 (all at $Bi = 10$) leads to a progressive broadening of the breakthrough curves predicted by both models, as one would expect (as the isotherm becomes less sharp, the breakthrough curve tends to broaden). However, the differences between the results for $1/n = 0.05$ and $1/n = 0.20$ are fairly small (the $1/n = 0.20$ isotherm is already so convex that a further increase in its convexity has little additional effect). Secondly, the curves for $Bi = 4$ are the most nearly symmetrical of all of the curves, indicating that the degree of "tailing" due to internal diffusion control and the degree of "leakage" due to external film control are similar in magnitude. As Bi increases from 4 to 10 to 25 (at $1/n = 0.20$), progressively more "tailing" occurs due to the greater importance of the internal diffusion resistance. As Bi decreases from 4 to 0.5, the degree of "leakage" (early breakthrough) increases, reflecting the greater importance of the external film resistance. Note that the X_o values for all cases where asymmetry due to tailing occurs are greater than 0.5 (the greater the tailing, the higher the X_o value) and that the X_o value for the last case, where substantial asymmetry due to leakage occurs, is less than 0.5. The value of X_o is 0.5 for a perfectly symmetrical breakthrough curve and becomes either higher or lower than 0.5 as the combination of the Bi value and the nature of the adsorption isotherm combine to produce asymmetry. All of these types of behaviors are well known.

With respect to the *relative* predictions of the two models, it appears that the match is quite good for low Bi (where external film diffusion is important), but not as good at high Bi (where the internal diffusion resistance is important), particularly for the "trailing" part of the curves, where the effects of the internal resistance occur. This is as expected, since both models use the same rate law to characterize external diffusion and their difference lies in the rate laws used to characterize internal diffusion. The model of Hand et al. uses the more accurate of the two internal diffusion rate laws, and hence its solutions for high Bi are probably more representative of reality than those of the Cooney model. However, it must be recalled that one often does not care about the trailing part of the breakthrough curve, since the adsorber usually will be taken off-line when X reaches some fairly low value (for example, 0.05). Hence, it is the predictions at low X which are important. The two models clearly agree very well at low X values, and so in terms of the predicted times at which a bed would most likely be removed from service, the two models are nearly equivalent. Again, this is not unexpected. The early part of the breakthrough curve is determined by external film diffusion, and both models use the same external diffusion rate law.

The comparisons made here suggest that the model of Cooney (1990), which has the advantage of being readily solvable for *any* type of favorable isotherm and *noninteger* values of *Bi* and the isotherm parameters, is as accurate as the more realistic HSDM solution. We have, of course, proved this here only for Freundlich isotherms, but there is no reason to expect the Cooney model to be any less accurate for other types of favorable isotherms.

Notation

a = constant in polynomial
b = constant in polynomial
Bi = Biot number, $k_f R/KD_s$, dimensionless
c = constant in polynomial
C = concentration of solute in fluid-phase, mass per fluid-phase volume
C_f = concentration of solute in the fluid-phase feed stream, mass per fluid-phase volume
d = constant in polynomial
D_s = diffusivity of solute in adsorbent phase (homogeneous diffusion model), length^2/time
e = constant in polynomial
k_f = external fluid-film mass-transfer coefficient, length/time
K = constant equal to Q_f/C_f, fluid-phase volume per solid-phase volume
L = bed length, length
m = constant equal to $1/n$
n = constant in Freundlich isotherm equation
Q = average concentration of solute in the adsorbent phase, mass per solid-phase volume
Q_f = value of Q in equilibrium with fluid-phase feed concentration, mass per solid-phase volume
Q^* = value of Q in equilibrium with any fluid-phase concentration C, mass of solute per solid-phase volume
r = radial distance coordinate for adsorbent particle, length
R = radius of adsorbent particles (assumed to be uniform and spherical), length
S_o = particle surface area per particle volume, length^2/length^3
t = time, time
v = interstitial fluid-phase velocity, length/time
X = dimensionless concentration of solute in the fluid phase, equal to C/C_f
X_i = interfacial value of X at solid-fluid boundary, dimensionless
X_o = value of X corresponding to the center of gravity of the front, dimensionless
Y = dimensionless average concentration of solute in the adsorbent phase, equal to Q/Q_f
Y_i = interfacial value of Y at solid-fluid boundary, dimensionless
Y^* = value of Y in equilibrium with X, dimensionless

Greek letters

β = parameter equal to $5/Bi$, dimensionless
ϵ = void fraction in bed (volume of voids per volume of bed), length^3/length^3

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