Nonlinear Fixed-Bed Sorption When Mass Transfer and Sorption Are Controlling

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Separation processes based on adsorption followed by desorption are widely utilized. Sophisticated, yet solvable, models are required for the design of these processes. Considerable progress has been made over the past five decades in the modeling of fixed-bed adsorption and desorption of a single component from a dilute isothermal solution. The typical plots of effluent concentration vs. time have been obtained for a number of systems both for adsorption (i.e., the breakthrough curve) and desorption (i.e., elution curve). The "spreading" of these curves may be due to various mechanisms, including axial dispersion, film and pore diffusion resistances, and finite rates of adsorption and desorption.

Analytical solutions have been obtained for each of these mechanisms, operating alone or in combination, for systems marked by a linear equilibrium relationship between sorbate concentration in the fluid and adsorbate concentration on the solid. These solutions are reviewed by Ruthven (1983). However, for many adsorption and desorption processes, the isotherms are nonlinear, resulting in substantial changes in the breakthrough and elution curves (Garg et al., 1974; Arnold et al., 1986a). Analytical solutions are rarely possible for systems with a nonlinear isotherm or with nonlinear sorption kinetics. The only rigorous analytical solution for "Langmuir-type" sorption kinetics (as defined by Eq. 1) was presented by Thomas for fixed-bed adsorption, where sorption is rate-controlling (Thomas, 1944). Using this result, approximate analytical solutions have been obtained for the breakthrough curves when pore diffusion and film mass transfer are rate-limiting (Hiester et al., 1952).

With the exception of the Thomas solution, only numerical solutions have been obtained for adsorption or desorption processes with Langmuir-type sorption kinetics. For example, Zwiebel et al. (1972) computed breakthrough and elution curves where fluid film mass transfer is the rate-controlling step. Various other studies on pore diffusion or solid diffusion have also been reported for systems exhibiting nonlinear isotherms (Antonson and Dranoff, 1969; Carter and Hussain, 1972; Garg and Ruthven, 1973; Arve and Liapis, 1987).

In this report, a general model is presented for isothermal, single-component adsorption and desorption from a dilute solution in a fixed bed in which both the fluid film mass transfer step and the sorption step are rate-controlling. The sorption kinetics is described by a rate equation which is second order in the forward direction and first order in the reverse direction, and which reduces to the Langmuir isotherm at equilibrium: affinity adsorption (Chase, 1984; Arnold et al., 1986a); ion exchange (Hiester and Vermeulen, 1952); and various other adsorption systems are well represented by such an equation. Breakthrough and elution curves are computed utilizing the method of characteristics. The solutions are presented in terms of dimensionless parameters. These solutions apply rigorously to the case of simultaneous fluid film mass transfer resistance and sorption resistance. Under certain circumstances, this approach can be extrapolated to provide approximate solutions for the case where pore diffusion limitation is also significant.

Model Formulation

Isothermal sorption of a single dilute component in a fixed bed has been the subject of modelling efforts for almost 50 years. A fairly comprehensive set of model equations have evolved which describe: 1) the mass balance over the mobile phase; 2) mass transfer limitations between the mobile and adsorbent phase; and 3) the mass balance on the adsorbent particulate phase [See, for example, Eqs. 1 to 4 in Arnold et al. (1985).] Nonlinear sorption kinetics is frequently represented by the equation.

$$\frac{\partial q}{\partial t} = \mu_f c_i (Q - q) - \mu_r q \tag{1}$$

which reduces to the well-known Langmuir isotherm at equilib-

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rium. Certain simplifying assumptions can be made to make the problem more tractable. Specifically, it will be assumed in this development that both the sorption and fluid film mass transfer steps are rate-controlling, and all other potential sources of zone spreading can be ignored. It is also assumed that $s \approx \rho_p q$, since the solute concentration on the adsorbent is usually much higher than the solute concentration in pore liquid.

Utilizing these assumptions and the variable substitution suggested previously (Vermeulen et al., 1984), the modeling equations describing this system can be represented in dimensionless form. The mobile-phase continuity equation is described by the equation,

$$\frac{\partial X}{\partial Z} + \frac{\partial Y}{\partial T} = 0 \tag{2}$$

The mass balance over the spherical adsorbent particle and the sorption kinetics can be written as,

$$\frac{\partial Y}{\partial T} = \frac{3L(1-\epsilon)}{u_o R'} k_f (X - X_i) \tag{3}$$

$$\frac{\partial Y}{\partial T} = \frac{\mu_f X_i q_o L \rho_b}{u_o}\left(\frac{Q}{q_o} - Y\right) - \frac{\mu_r q_o \rho_b L Y}{c_o u_o} \tag{4}$$

where,

$$X = c/c_o$$

$$X_i = c_i/c_o$$

$$Y = q/q_o$$

$$Z = z/L$$

$$T = \frac{u_o t - \epsilon z}{\tau L}; \quad \tau = \rho_b q_o / c_o$$

Equation 2 has a form analogous to the two-dimensional incompressible flow continuity equation. This suggests use of a function, f, analogous to the stream function,

$$X = \partial f / \partial T \tag{5}$$

$$Y = -\partial f / \partial Z \tag{6}$$

After eliminating X_i from Eqs. 3 and 4 and then using the substitutions defined by Eqs. 5 and 6, we obtain,

$$\frac{\partial^2 f}{\partial Z \partial T} = N_f \left\{ -\frac{\partial f}{\partial T} + \frac{N_f \partial f/\partial T - N_R R \partial f/\partial Z}{N_R[1 + (1-R)\partial f/\partial Z] + N_f} \right\} \tag{7}$$

where

$$N_f = \frac{k_f a_p L}{u_o} \tag{8}$$

$$N_R = \frac{\rho_b \mu_f Q L}{u_o} \tag{9}$$

$$R = \frac{1}{1 + K_L c_o} \tag{10}$$

Equation 7 is a nonlinear hyperbolic partial differential equation of second order in its normalized form.

Initial and Boundary Conditions

Initial and boundary conditions depend on the mode of operation. For fixed-bed adsorption into an adsorbate-free column, the initial and boundary conditions would be,

$$Y = X = 0; \quad T = 0; \quad 0 < Z < 1$$

$$\& \; X = 1; \quad Z = 0; \quad T > 0$$

The corresponding conditions for the desorption problem would be,

$$X = 0; \quad Z = 0; \quad T > 0$$

and the concentration profile at time $t = 0$ must be specified. In this study, elution curves were computed based on the assumption that the entire column was initially saturated with adsorbate.

$$X = Y = 1; \quad T = 0; \quad 0 < Z < 1$$

Numerical Solution Method

Equation 7 is highly nonlinear hyperbolic partial differential equation. Numerical solutions for this equation with appropriate boundary conditions were computed using the method of characteristics (Courant, 1963). Unlike the finite difference method, the method of characteristics can be used to accurately solve problems like this one, in which discontinuities are present in the solution. In addition, this method requires less computation time than the finite difference method.

Results

The solution of Eq. 7 requires assignment of values to the three dimensionless parameter N_f, N_R and R, defined by Eqs. 8, 9 and 10. The parameter R characterizes the adsorption equilibrium. $R = 1$ corresponds to the linear equilibrium, and as R becomes smaller, the equilibrium becomes more and more favorable. In the limiting case of $R = 0$, the equilibrium is irreversible. R values of 0.1, 0.5, and 0.9, which represent highly favorable, moderately favorable and nearly linear equilibria, respectively, were considered in this study. N_f and N_R are dimensionless numbers of transfer units for fluid film mass transfer and sorption kinetics, respectively. The smaller the number of transfer units for a given mechanism, the higher is the resistance offered by that mechanism, as is evident from their definitions in Eqs. 8 and 9. N_f values of 10, 50, and 250, and N_R values of 20, 50, and 100 were selected to represent a broad range of potential operating conditions. Experimental data reported on affinity chromatography systems (Arnold and Blanch, 1986b; Chase, 1984) show that both the mass transfer and finite rate of sorption can be rate-controlling simultaneously, and the N_R and N_f values exhibited by these systems are typically in the same range as those chosen in this study. (Data for higher values of N_R and

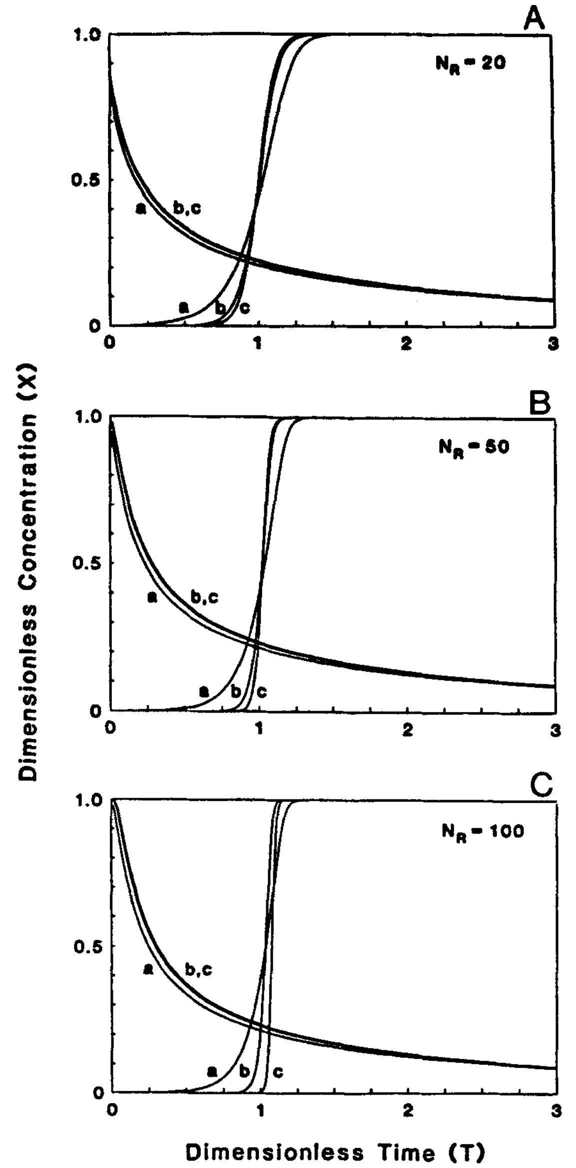

Figure 1. Elution and breakthrough curves for $R = 0.1$.
Curves a, b, and c represent results for N_f values of 10, 50, and 250, respectively.

N_f are not presented because breakthrough and elution curves are fairly insensitive to further increases in N_R and N_f—i.e., as N_R or N_f increases the resistance due to that step becomes insignificant.) Generalized breakthrough and elution curves were computed for the various combinations of R, N_f, and N_R, and the results are presented in Figures 1 to 3.

For fixed-bed adsorption and desorption, the effect of the parameter R on the breakthrough and elution curves is very significant. As can be seen in Figures 1 to 3, breakthrough curves become sharper as R becomes smaller. This effect is commonly known as "front sharpening." An opposite effect is observed for the elution curves. They become more dispersed as R becomes smaller. A similar effect was observed by Zwiebel et al. (1972). Under highly favorable equilibrium for a fixed value of N_f, the elution curves are found to be identical for $T > 1.5$ irrespective of their N_R values, Figure 1.

As N_R or N_f increases, the breakthrough and elution curves become sharper, Figures 1 to 3. This sharpening feature is more pronounced for higher values of R. An interesting result is observed for small N_R, when the equilibrium is highly favorable. Under these conditions, a discontinuity in the concentration, X, is observed in the elution curves at $T = 0$ for all values of N_f, Figure 1A. Conversely, at low values of N_f but high values of N_R, no discontinuities are observed in the elution curves, Figure 1C. No such discontinuity is observed in any of the breakthrough curves presented in Figures 1 to 3.

In general, it is observed that the sensitivity of the breakthrough and elution curves to changes in the parameter N_f and N_R is most pronounced as R increases, Figures 1 to 3. As N_f or N_R is increased while keeping the other parameters constant, an

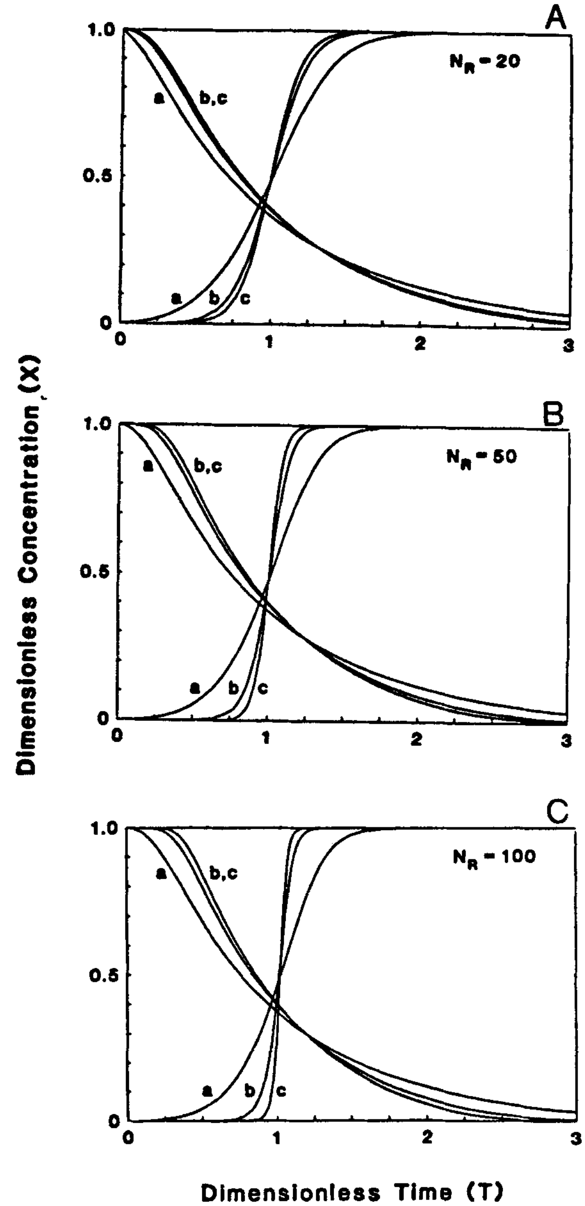

Figure 2. Elution and breakthrough curves for $R = 0.5$.
Curves a, b, and c represent results for N_f values of 10, 50, and 250, respectively.

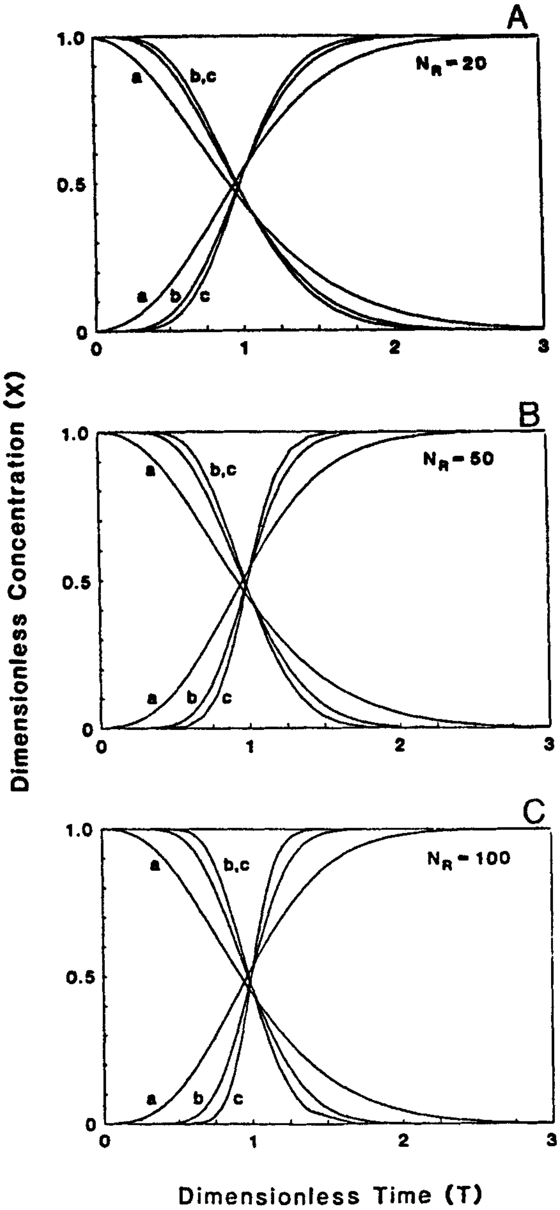

Figure 3. Elution and breakthrough curves for $R = 0.9$.
Curves a, b, and c represent results for N_f values of 10, 50, and 250, respectively.

asymptotic solution is reached for the breakthrough and elution curves. This asymptotic solution is approached at much lower values of N_f or N_R as equilibrium becomes more and more favorable.

Discussion

A general model is presented for isothermal adsorption and desorption of a single dilute component in a fixed bed, where both the fluid film mass transfer and the finite rates of sorption are rate-controlling. Langmuir-type sorption kinetics, as defined by Eq. 1, is assumed. Numerical solutions are computed for this system utilizing the method of characteristics. Generalized breakthrough and elution curves are presented in Figures 1 to 3 for a wide range of the dimensionless operating parameters, N_R, N_f, and R.

This is believed to be one of the first presentations of elution curves for fixed-bed desorption of a single component from a dilute isothermal solution when desorption, described by Langmuir-type kinetics, is a rate-controlling step. [See also the results of Arve and Liapis (1987).] Breakthrough curves for the case, where adsorption is rate-controlling, were obtained analytically by Thomas (1944). As expected, the breakthrough curves obtained in this study converge to the Thomas solution (Thomas, 1944) as film mass transfer resistance become negligible compared to sorption resistance (i.e., as N_f becomes much larger than N_R). The solution of Eq. 7 for $R = 1$ would be equivalent to the analytical solution obtained for linear sorption kinetics (Ruthven, 1983). This solution also shows that the breakthrough and elution curves approach being mirror images of each other as $R \rightarrow 1$, Figure 3, a result which has been previously reported (Ruthven, 1983).

Several interesting features of the solution are observed in Figures 1 to 3. The effects of N_R and N_f on spreading of breakthrough or elution curves are not similar, particularly at low values of R (i.e., highly favorable equilibrium). Under these conditions, a small value of N_R gives rise to a sharp discontinuity in the elution curves at $T = 0$, even at high values of N_f, Figure 1A. This corresponds to case when the equilibrium is highly favorable and the sorption resistance is high. Under these conditions, sufficient desorption does not take place to make $c = c_o$ by the time eluent reaches the bottom of the column (i.e., when $T = 0$). A discontinuity occurs as the effluent concentration drops to a value which is less than c_o. Conversely, no discontinuity is observed for small values of N_f when N_R is large, Figure 1C, which is consistent with the previous results of Zwiebal et al. (1972) who examined the case where fluid film mass transfer is the only rate-controlling step. The distinctive effects of N_f and N_R on the breakthrough and elution curves indicate that their combination into a single, dimensionless number of transfer units to obtain breakthrough and elution curves may obscure the characteristic features of the solution.

This study has been restricted to consideration of chromatography based on frontal methods. Other important modes of operation, such as pulse feed or cyclic operation, could be also analyzed by solving Eq. 7 with appropriate initial and boundary conditions. Another important class of operations, in which feed or eluent characteristics are not constant (e.g., elution with a gradient of ph or salt concentration), could also be analyzed using the approach outlined in this study. However, in this case, it would be desirable to work with dimensional form of Eqs. 2 to 4, since Q, μ_f, μ_r, c_o and q_o also become functions of θ and dimensionless Eqs. 2 to 4 are, therefore, no longer valid.

In many practical situations, such as affinity chromatography, the rate-controlling mechanisms will be pore diffusion and sorption kinetics, and film mass transfer is usually insignificant. The approach outlined in this report can be modified to accommodate this situation or the situation where all three resistances are simultaneously significant, if an overall mass transfer coefficient K_{OL} can be defined. For systems with linear sorption kinetics, pore diffusion and fluid film mass transfer contributions can be combined to define an overall mass transfer coefficient (Bogue, 1960)

$$\frac{1}{K_{OL}a_p} = \frac{R'^2}{15\,(1-\epsilon)}\left(\frac{1}{D_i} + \frac{5}{k_f R'}\right) \tag{11}$$

For the system outlined in this report, an approximate solution can be obtained through definition of a similar overall mass transfer coefficient. This approach provides good representation for elution curves over the entire range of R (Ruthven, 1983). For breakthrough curves this approximation is adequate for a moderately favorable isotherm, but is inadequate when isotherm is highly favorable (i.e., $R < 0.5$) (Ruthven, 1983).

In summary, the analysis presented in this study will describe the performance of a wide variety of isothermal, single component, fixed-bed adsorption and desorption processes. Most adsorption/desorption systems can be approximated well by the Langmuir-type sorption kinetics chosen for this study. This analysis is suitable particularly for systems with nonporous adsorbents. It is possible to extend the applicability of this approach to obtain breakthrough and elution curves for most cases where pore diffusion is also rate-limiting; this approach would probably not be appropriate for obtaining breakthrough curves under highly favorable equilibria when pore diffusion resistance is significant.

Notation

a_p = particle surface area per unit volume, cm^{-1}
c = bulk liquid concentration, M
c_i = solute concentration in pore liquid or adjacent to particle surface, M
c_o = feed concentration (adsorption), solute concentration in saturated column (desorption, M)
D_i = effective diffusivity of solute in particle $\text{cm}^2 \cdot \text{s}^{-1}$
f = analogus to stream funcion
K_L = Langmuir constant, $[\mu_f/\mu_r]$, M^{-1}
K_{OL} = overall mass transfer coefficient, $\text{cm} \cdot \text{s}^{-1}$
k_f = fluid film mass transfer coefficient, $\text{cm} \cdot \text{s}^{-1}$
L = length of the column, cm
N_f = dimensionless number of transfer units for fluid film mass transfer
N_R = dimensionless number of transfer units for sorption kinetics
Q = maximum available sites on adsorbent, $\text{mol} \cdot \text{kg}^{-1} \cdot$ particle
q = adsorbate concentration per unit mass of adsorbent, $\text{mol} \cdot \text{kg}^{-1} \cdot$ particle
q_o = adsorbate concentration in equilibrium with c_o, $\text{mol} \cdot \text{kg}^{-1} \cdot$ particle
R = dimensionless separation factor
R' = adsorbent particle radius, cm
s = average concentration in particle, including pore liquid
T = dimensionless time
t = time elapsed since introduction of feed, s
u_o = superficial mobile-phase velocity, $\text{cm} \cdot \text{s}^{-1}$
X = dimensionless solute concentration
X_i = dimensionless solute concentration corresponding to c_i
Y = dimensionless adsorbate concentration
Z = dimensionless column length
z = distance along column, cm

Greek letters

β = fraction of mobile phase in the particle
ϵ = column void fraction
μ_f = forward binding rate constant, $\text{M}^{-1} \cdot \text{s}^{-1}$
μ_r = reverse binding rate constant, s^{-1}
ρ_b = particle bulk density $[(1 - \epsilon)\rho_p]$, $\text{g} \cdot \text{cm}^{-3} \cdot$ bed volume
ρ_p = particle density, $\text{g} \cdot \text{cm}^{-3} \cdot$ particle
τ = distribution parameter, $(\rho_b q_o / c_o)$
θ = contact time, $(t - \epsilon z / u_o)$

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