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Simplified Predictions of Breakthrough Fronts for Constant-Pattern Adsorption and Ion Exchange

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SIMPLIFIED PREDICTIONS OF BREAKTHROUGH FRONTS FOR CONSTANT-PATTERN ADSORPTION AND ION EXCHANGE

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ABSTRACT

The loading cycle of many (perhaps most) commercial adsorption and ion exchange operations involves a favorable isotherm. Concentration fronts for favorable isotherms approach a constant pattern for long bed lengths, and most industrial adsorption and ion exchange operations use sufficiently deep beds that the constant-pattern conditions are approached. Once a constant pattern is established, the region around the front can be analyzed using conventional methods developed for continuous absorption/stripping operations, but the location of the feed and withdrawal points must be assumed to move down the bed at the same rate at which the front moves. Using this approach, the constant-pattern front can be calculated for any shape of constant-pattern isotherm. The dimensionless distance in the bed is expressed in terms of transfer units, and the shape of the front can be evaluated graphically even when the relations can not be integrated analytically. This procedure is illustrated for binary ion exchange isotherms. In the simplest cases, exchange of ions with like charge, the integration can be performed analytically. For other cases, numerical and graphical solutions are illustrated.

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INTRODUCTION

A large fraction of adsorption processes and binary ion exchange processes in deep beds involve systems with "favorable" isotherms (1). These are isotherms which have negative curvature, as illustrated in Figure 1. This means that the plot of loading on the solid vs concentration in the fluid is concave downward. In these cases, the shape of the isotherm results in "sharpening" forces that make the loading front sharper; that is, graphs of concentration vs position within the bed tend to become more nearly vertical. However, these "sharpening" forces are opposed by dispersive forces that tend to spread or flatten the concentration front. For very long beds, the opposing tendencies eventually balance each other, and a constant-shaped front is approached, a front that remains essentially unchanged as longer and longer beds are used. This results in a steady shape for the front known as "constant-pattern" conditions, and many industrial systems operate with such conditions.

In a constant-pattern system, scaleup to longer beds is relatively simple, especially if the shape of the concentration front is known. The pattern can be calculated for several of the more important isotherms (2-6). However, the solutions are not always expressed in terms of simple equations that are easily used by designers of adsorption processes. The purpose of this paper is to illustrate the principles behind these analyses; compare them with more familiar and simpler analyses that are used for steady state countercurrent processes, such as absorption or gas stripping; and illustrate the approach by showing fronts from one particular set of isotherms, the fronts produced by binary ion exchange.

While no new principles are involved in the following discussion, the explanation is expected to be useful for many readers. Development of the exact solutions mentioned earlier includes the principles involved in this analysis. However, the approach described in this paper and the suggestion for considering a generalized graphical approach for the complex experimentally determined isotherms were not found in the literature. The papers by Cooney and Lightfoot (3) and Cooney and Strusi (4) come closest to describing the approach in the same manner. There are often benefits in having graphical analyses available since, in many cases, the designer or investigator can gain additional insight from observing graphical steps in the solution, even if

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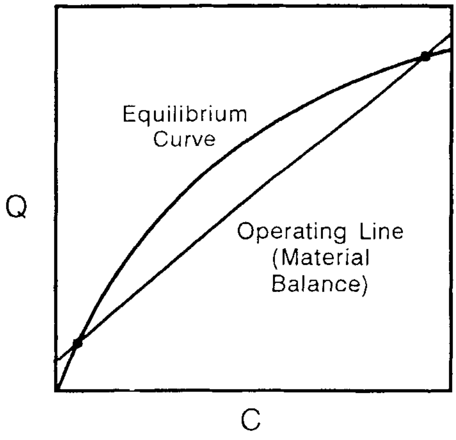

FIGURE 1. A "favorable" isotherm.

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numerical calculations are used for the more precise final calculations. This analysis is similar to an analysis of steady state countercurrent systems that is presented in the popular textbook by Treybal (7), but that analysis can be modified as presented here to describe the more common transient operation of fixed beds of adsorbents or ion exchange materials.

Comparisons of Constant-Pattern Fronts to Steady State Countercurrent Absorption

Consider a constant-pattern adsorption or ion exchange front moving down a bed, as illustrated in Figure 2. The superficial flow rate of fluid down the bed is V_s, and the velocity by which the front moves down the bed is V_f. The fluid velocity and the front velocity are easily related by considering an imaginary plane that crosses the bed and moves with the velocity of the front. This plane is denoted by the dashed line (a) in Figure 2. When the bed and the front are viewed from the moving plane, the bed appears to be at steady state, and the front appears to be fixed in the (moving) space. From the position of the moving plane, the bed appears to be a continuous countercurrent operation, with solid adsorbent moving upward with the same velocity

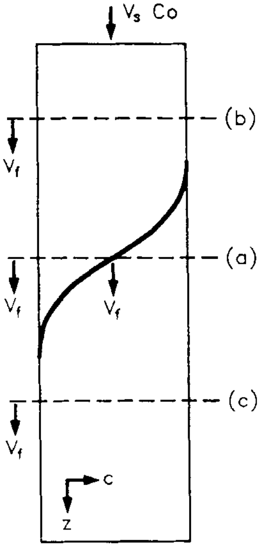

FIGURE 2. Movement of a constant-pattern front down an adsorption bed.

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by which the front is (actually) moving down the bed, and the fluid appears to be moving down the bed with a velocity equal to the actual superficial velocity minus the velocity of the front, V_s-V_f. Thus, when viewed from the position of the moving front, the bed appears much like a steady state countercurrent absorption/stripping or solvent extraction operation.

Next, consider another plane (b) far upstream and a plane far downstream (c); both planes are also moving down the bed with the same velocity as the front and are noted on Figure 2 by dashed lines. A material balance between the two dashed lines gives

$$(C_0 - C_{inf})(V_s - V_f) = (Q_{eq} - Q_0)V_f \qquad (1)$$

where C_0 is the concentration of the solute in the feed; C_{inf} is the concentration in the fluid that is in equilibrium with the bed far below the front (usually zero); Q_{eq} is the concentration of solid that is in equilibrium with the inlet fluid; and Q_0 is the initial concentration of solute in the bed (far downstream from the front). (Q_0 is often near zero.) C_0 and Q_0 should be known; and Q_{eq} and C_{inf} are obtained from two points on the equilibrium curve (the isotherm). Then the front velocity can be obtained by simply solving this linear material balance for V_f:

$$V_f = V_s(C_o - C_{inf})/(Q_{eq} - Q_o + C_o - C_{inf}) \ . \tag{2}$$

For the common case, where C_{inf} and Q_o are essentially zero, this simplifies to

$$V_f = V_s C_o/(Q_{eq} + C_o) \ . \tag{3}$$

To analyze the constant-pattern adsorption system like the conventional absorption systems, consider a material balance between the moving planes (a) and (b):

$$(C_o - C)(V_s - V_f) = (Q_{eq} - Q)V_f \ . \tag{4}$$

Here, C and Q denote concentrations of solute in the solid and fluid phases, respectively, at any position within the front. In terms of conventional countercurrent bed operations, this is called the operating line. It is linear; it goes through the point far upstream where C equals C_o and where Q equals Q_{eq}; and it has a slope:

$$\text{slope} = (V_s - V_f)/V_f \ . \tag{5}$$

This line is illustrated in Figure 1. However, the simplest way to plot the operating line is to note that when the plane (a) is moved far downstream, the concentrations are Q_o and C_{inf}; that is, the operating line intersects the equilibrium curve (isotherm) where C = C_{inf} and where C = C_o. (As noted before, C_{inf} will be zero when Q_o is zero, when the initial bed contains no solute.)

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Constant-Pattern Adsorption Fronts with Mass Transfer Resistance in the Fluid Film

Factors that "spread" the front are mixing (dispersion or nonuniform axial flow) and mass transfer resistance, which prevent the solid and fluid from reaching equilibrium. Consider first the effects of mass transfer resistance in the fluid phase. Using conventional analyses for absorption or stripping beds, the rate of mass transfer can be expressed as

$$V_s(dC/dz) = k_f a(C - C^*) \ . \tag{6}$$

Here, z is distance down the bed; k_f is the fluid film mass transfer coefficient; a is the area of adsorbent per unit volume of bed; and C^* is the concentration of solute in the liquid at the solid surface. For the case where all of the mass transfer resistance is in the fluid film, C^* is the fluid concentration that would be in equilibrium with the solute loading on the solid adsorbent, at that position in the bed. Following the traditional development of design equations for absorption/stripping equipment, this equation can be rearranged and integrated as follows:

$$z = [V_s/k_f a][dC/(C - C^*)] \tag{7}$$

$$= [HTU][NTU] \; ; \tag{8}$$

with C_1 and C_2 representing any concentrations on the front. This expression assumes that the velocities in the column are constant and do not have to be included inside the integral. That is a valid assumption for dilute systems or for systems in which the volume of the fluid does not change greatly with concentration of the solute. For gas-phase systems with high concentrations of the adsorbed solute, this relation would have to be changed slightly to express the gas flow rate and concentrations in terms of nonadsorbed gas, not the total flow rate of gas.

HTU refers to the term in the first set of brackets and is called the height of a transfer unit; NTU refers to the integral in the second set of brackets and is called the number of transfer units required between concentrations C_1 and C_2. Thus, the length of bed required to change the concentration of solute from one value to another value is determined by evaluating the integral (the NTU) from one concentration to the other concentration and multiplying the required NTU by the HTU, which consists of a group of terms that can be measured independently or measured as a group from absorption data at one bed height. To evaluate the integral, values of C^* must be determined from the operating line (material balance) and the equilibrium curve. C is located on the operating line, and C^* is located by looking horizontally (at the same Q) to the equilibrium curve.

To perform the integration graphically, $1/(C^*-C)$ is plotted as a function of C. The area under the curve between any two values of C is the change in the NTU that corresponds to the concentration change, between the limits of the integration. This is illustrated in Figures 3a and 3b, and the approach is exactly like that often used for absorption/stripping/extraction operations. To apply this approach to adsorption problems, it is best to think of dimensionless distances:

$$Z = z/[HTU] = [NTU] \; . \tag{9}$$

As indicated, the change in the NTU is equal to this ratio, but each value of NTU also corresponds to a change in concentration of solute in the fluid. A plot of C vs NTU is

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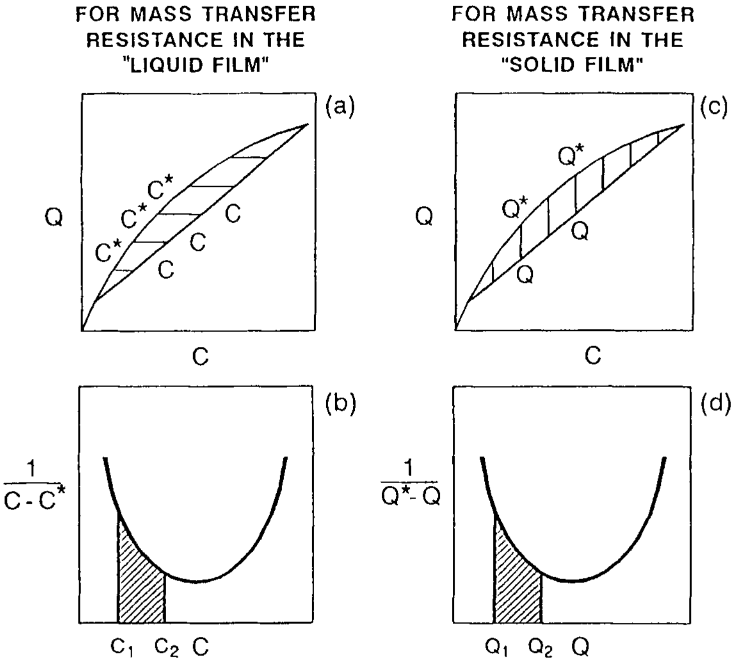
FOR MASS TRANSFER RESISTANCE IN THE "LIQUID FILM"

FOR MASS TRANSFER RESISTANCE IN THE "SOLID FILM"

FIGURE 3. Determination of NTU from a general favorable isotherm and the operating line. Curves (a) and (b) illustrate the case for mass transfer resistance in the fluid phase, and (c) and (d) are for cases where resistance is in the solid phase.

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equivalent to a plot of C vs dimensionless distance, Z. This is a plot of the loading front, but in units of dimensionless distance. To convert the results to real distances, it is only necessary to multiply the dimensionless distance, Z, by the HTU, that is, by V_s/k_fa.

For the general case, one need only look at the arbitrary adsorption given in Figures 1 and 3. If the isotherm follows no given equation, but is simply a curve fit to experimental data, one can still evaluate the plot of C vs NTU graphically by drawing numerous horizontal lines from the equilibrium curve, C^*, to the operating line, C, and using those two points to evaluate the integrand for the NTU as a function of C.

The purpose of this integration is not to determine where the front occurs, but to predict the shape of the front. The position of the front can be determined most effectively from the capacity of the adsorbent using equation (1) or from the rate at which the front moves, equation (2). If the slope of the front is symmetrical around the midpoint (where C/C_0 is 1/2), this will be the rate at which the midpoint moves down the bed. In other cases, this will be the point to the left of which the area above the curve and to the right of which the area below the curve are equal. In most cases, this is likely to be near the midpoint. The position of the front can not be obtained from the C-vs-NTU plot because the graph becomes inaccurate as the concentration in the solution approaches that in the feed; the integrand becomes infinity. However, the C-vs-NTU plot can be used to accurately predict the shape of the front around the midpoint and as far from the midpoint as one may wish to calculate.

In integrating to determine the NTU, it is necessary to start at some value of C not equal to C_0. Note from the operating line that at those conditions, the concentration in solution is in equilibrium with the solid and the integrand is infinity. Thus, the integration had to begin at least slightly removed from the end of the operating lines. The resulting absolute values of the NTU are then incorrect, but the differences in NTU from one value of C to another value are accurate. As noted earlier, the total length of the bed can not be calculated in this manner. An appropriate starting point is the midpoint in the breakthrough curve where the concentration is one-half the inlet concentration. The calculations described here are intended only to determine the shape of the front and thus to estimate how far in advance of the 50% breakthrough point the breakthrough concentration will reach a specified value.

By integrating for different distances from the midpoint, one can obtain values for the NTU as a function of concentration on the front. To obtain a view of the breakthrough curve, it is only necessary to plot C vs the value of NTU that corresponds to that value of C, as in Figure 3. If the value of the NTU at the midpoint is defined as zero, concentrations to the left of the midpoint will have negative NTU values and those to the right of the midpoint will have positive values. The integration for determining the NTU from $C = C_0/2$ can be performed graphically, as shown in Figure 3. If there is an expression for the isotherm, the integral (NTU) can be evaluated analytically or numerically. Note that NTU is a dimensionless distance; so this plot

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gives the shape of the front, but it does not give the actual width or spreading of the front. To obtain the width of the front, it is only necessary to convert the dimensionless distance to real distance by multiplying the NTU by the HTU, that is, by $V_f/k_f a$. If the value of NTU is assigned a value of zero at the 50% point, the distance values on the new plot will denote distance from the 50% point.

Breakthrough Fronts with Mass Transfer in the Solid Phase

This presentation focused first on adsorption systems with mass transfer resistance in the fluid film surrounding the adsorbent particles. Similar arguments can be used to develop relations for systems with mass transfer resistance in a "solid film." This is not an absolutely accurate concept, but it is a convenient way to approximate cases with mass transfer resistance in the solid. Although solid diffusion resistance is far more complicated than the simple fluid film concept, Glueckauf (8) demonstrated that for long beds and systems with linear isotherms, diffusion in a solid can be approximated reasonably accurately by an apparent solid film with a mass transfer coefficient of

$$k_d = 15D/r^2 ,$$

where D is the apparent diffusion coefficient in the solid and r is the radius of the particle. Others, including the author, have used this concept for nonlinear systems (9). However, one should be aware that the approximation is not always as accurate as it is for linear systems. The Glueckauf approximation will be more accurate when all of the solute in the adsorbent is free to diffuse, that is, for cases where surface or solid diffusion rates control the mass transfer. Then the solution for resistance in the particles follows the form approximated by Glueckauf. However, for pore diffusion when the solute adsorbed on the surfaces is unable to diffuse, the concentration fronts within the adsorbent will be different, and, in the limited case, the fronts will approximate "shrinking core" concentration profiles, which are much different from those assumed in the Glueckauf approximation.

For a solid film resistance, the NTU is defined as

$$Z = [V_s/k_d a][\int_{Q_1}^{Q_2} dQ/(Q^* - Q)] = [HTU][NTU] ,$$

where Q_f and Q_2 are concentrations of the solute on the adsorbent at two positions on

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the front. Note that the HTU and NTU are defined differently in this case, and one should not use the two sets of terms interchangeably. The integration to determine the NTU is made by taking vertical positions between the operating line and the equilibrium curve, as illustrated in Figures 3c and 3d. Otherwise, cases with solid film resistance can be handled in the same way that is used for systems controlled by fluid film resistance.

The breakthrough would normally be expressed as Q vs NTU. However, in this case, the concentration in the adsorbent is given instead of the concentration in the fluid. If it is preferable to plot the concentration in the fluid as a function of normalized position (and it usually is preferable), one can use the operation shown in Figure 3a to convert Q for each position to concentration. If the bed initially contains no solute, the normalized solid concentration, Q/Q_0, is equal to the normalized concentration in the fluid, C/C_0; so normalized plots of solid loading are the same as normalized plots of fluid concentration.

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Expressing Breakthrough Curves in Terms of Concentration vs Time

Although it was convenient to describe these relations in terms of concentration in the fluid as a function of position in the bed, most measurements give concentrations as a function of time at a given position in the bed, at the bed exit. Fortunately, such a conversion is simple for constant-pattern systems because the front moves down the bed with a constant velocity, V_f. To convert the front concentration profile from C vs distance, Z, to C vs time, it is only necessary to divide the distances by $-V_f$. Note that if the midpoint of the front is assigned the value of zero, distances in front of the front will be positive distances, and distances behind the midpoint will be negative distances. By dividing the length by $-V_f$, the positive distances are converted to negative times, time before the midpoint of the front reaches the exit, and negative distances are converted to positive times, time after the midpoint of the front passes the exit.

Ion Exchange Equilibrium

This approach can be used to predict concentration fronts in any constant-pattern system, and it will be illustrated for ion exchange processes. It is not uncommon to see investigators fitting ion exchange data to adsorption isotherms such as the Langmuir or

Fruendlich isotherms. Of course, if those isotherms accurately describe the equilibrium relations occurring within the front, the approaches just described will be reasonably accurate in predicting the ion exchange fronts. Furthermore, the exchanging ions retained within many strong base or strong acid ion exchange resins remain mobile, and the Glueckauf approximation may not be an unreasonable approximation for diffusion resistance in the solid phase. However, one should note that ion exchange processes involve the counter diffusion of charged species, and electrostatic forces prevent either ion from diffusing faster than the other. The observed or apparent diffusion coefficient that would be used in describing either fluid or solid "film" resistance would correspond to counter diffusion of the two ions and would not be the diffusion coefficient of either ion alone. Furthermore, counter diffusion may not be exactly the same as single-component diffusion considered by Glueckauf.

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For a little more generality, it is often better to look at ion exchange equilibria when applying the HTU-NTU approach to predicting concentration fronts. Binary ion exchange equilibria can be written as

$$(1/n_1)A^{+n_1} + (1/n_2)\underline{B} = (1/n_1)\underline{A} + (1/n_2)B^{+n_2} \ . \tag{10}$$

If one neglects variation in the activity coefficients in both the fluid (solution) and the solid, the equilibria can be written as

$$K_0 = [\underline{A}/A]^{1/n_1}[B/\underline{B}]^{1/n_2} \ , \tag{11}$$

or

$$K = [\underline{A}/A][B/\underline{B}]^{n_1/n_2} \ ; \tag{12}$$

where A and B are concentrations of ions A and B in the solution, and $\underline{A}$ and $\underline{B}$ are concentrations of A and B in the ion exchange resin. The valences of A and B are n_1 and n_2, respectively, and K is $K_0^{n_1}$. If activity coefficients do not change in either the solution or the resin during the exchange, K (and K_0) will remain approximately constant. Note that the total normality in the solution does not change during the ion exchange processes. However, values for the equilibrium constant, K, are likely to be different for different fronts if greatly different solution concentrations are used.

In equation (10), the ion A in solution is being exchanged for ion B in the resin. This has some similarity to adsorption of A onto an adsorbent. Solving the equilibrium relation for $\underline{A}$ gives the expression that is equivalent to an equilibrium isotherm:

$$\underline{A} = KA[\underline{B}/B]^{n_1/n_2} \ . \tag{13}$$

To make this expression similar to an adsorption isotherm, it is necessary to eliminate the concentrations of B in both the solution and the resin. For binary ion exchange, this is relatively simple since the total normality of both the solution and the resin remains constant throughout the process, throughout the concentration front:

$$B = [C_t - n_1A]/n_2 \; , \tag{14}$$

and

$$\underline{B} = [R_t - n_1\underline{A}]/n_2 \; . \tag{15}$$

Substituting these values for B and $\underline{B}$ gives

$$\underline{A} = KA\{[R_t - n_1\underline{A}]/[C_t - n_1A]\}^{n_1/n_2} \; . \tag{16}$$

This is equivalent to an isotherm when the equation is solved for $\underline{A}$, the concentration of A in the resin as a function of the concentration of A in solution. The general case for arbitrary values of n_1 and n_2 needs to be evaluated numerically; three examples are given in Figures 4-6. These are shown in dimensionless concentrations where

$$A' = A/C_t \; , \tag{17}$$

and

$$\underline{A}' = \underline{A}/R_t \; . \tag{18}$$

Then,

$$\underline{A}' = \{K[C_t/R_t]^{1-n_1/n_2}\}A'\{[1 - n_1\underline{A}']/[1 - n_1A]\}^{n_1/n_2} \; . \tag{19}$$

For the case where $n_1 = n_2$, this can be solved directly for $\underline{A}'$, and the integration to determine NTU as a function of A can be evaluated analytically; for the more general case, it will be necessary to do the evaluation numerically or graphically. The terms within the first {} can be grouped together into a term, K':

$$K' = K[C_t/R_t]^{1-n_1/n_2} \; .$$

Note that K' depends upon the ratio of C_t/R_t as well as the ion exchange equilibrium constant, K or K_0. Since R_t is a constant for any particular resin, the equilibrium curve, or isotherm, depends upon the solution concentration, C_t, as well as the ion exchange equilibrium constant, K. Since C_t is usually considerably smaller than R_t, K' usually increases with decreasing concentration when n_1 is greater than n_2, such as when a divalent ion is being exchanged for a monovalent ion. This is the widely recognized

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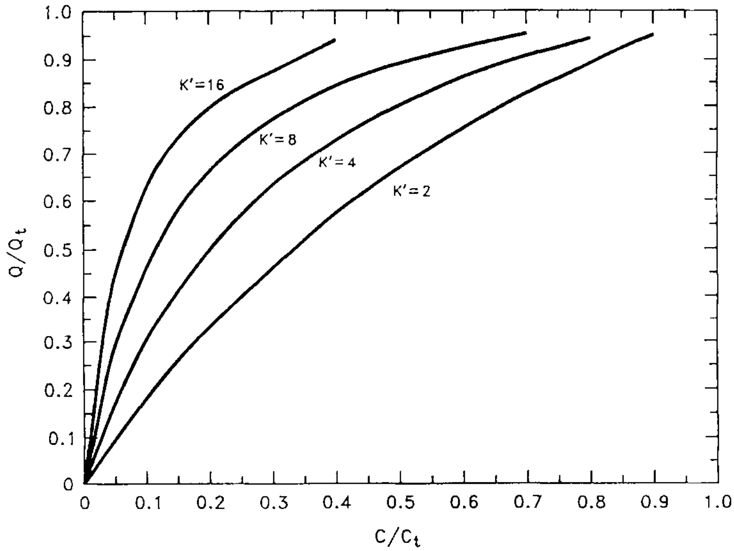

FIGURE 4. Ion exchange equilibria for exchange of ions with equal charges.

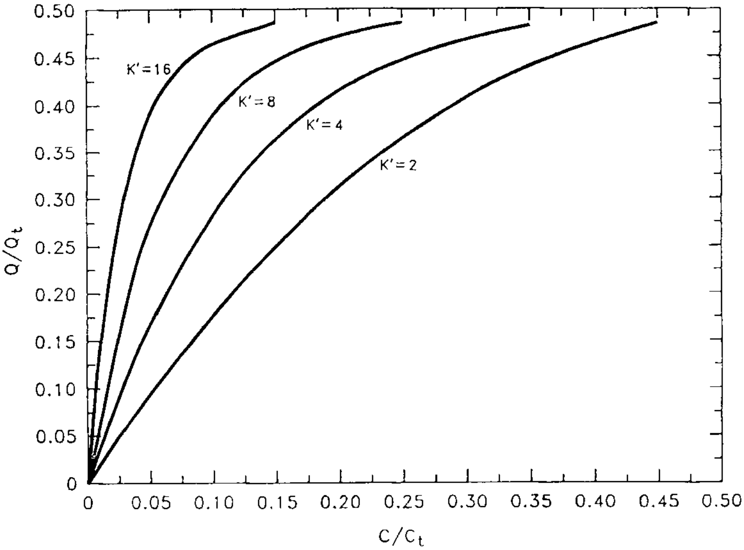

FIGURE 5. Ion exchange equilibria for exchange of a divalent ion for a monovalent ion.

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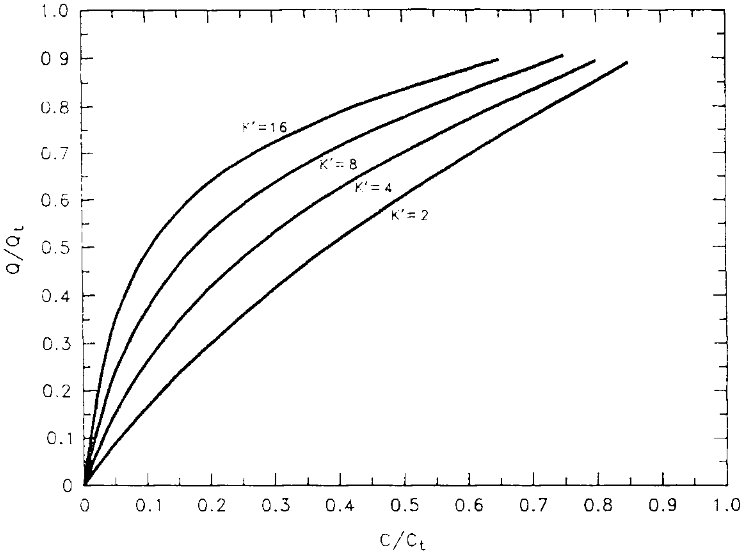

FIGURE 6. Ion exchange equilibria for exchange of a monovalent ion for a divalent ion.

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affinity of ion exchange resins for higher-valent ions from dilute solutions, and there is a converse lower affinity for the higher-valent ions from concentrated solutions.

Equilibrium relations for exchange of ions with equal valences are illustrated in Figure 4. Separate curves are presented for different values of K′. Note that the value of the exponent is zero; so K is the same as K′. The equilibrium curves are favorable as long as K (or K′) is greater than unity. Equilibrium curves are shown in Figures 5 and 6 for cases where the exchanging ions have equal charges, when a monovalent ion (in the fluid) is being exchanged for a divalent ion (in the ion exchange resin), and when a divalent ion is being exchanged for a monovalent ion. Separate curves are given on each figure for different values of K′, the ion exchange equilibrium constant. Equilibrium curves for other values of K′ can be estimated by interpolating between the curves presented.

The breakthrough curves calculated by the procedures just described are shown in Figures 7-9. In the cases shown, the resin was loaded with B and the feed solution contained only A. Thus, the operating line extends from the lower left corners in

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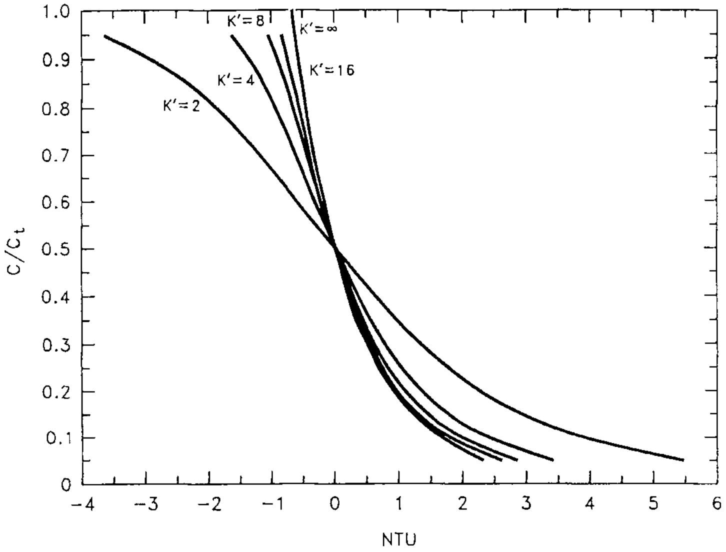

FIGURE 7. Normalized breakthrough fronts for exchange of ions with equal charge and mass transfer resistance in the fluid phase.

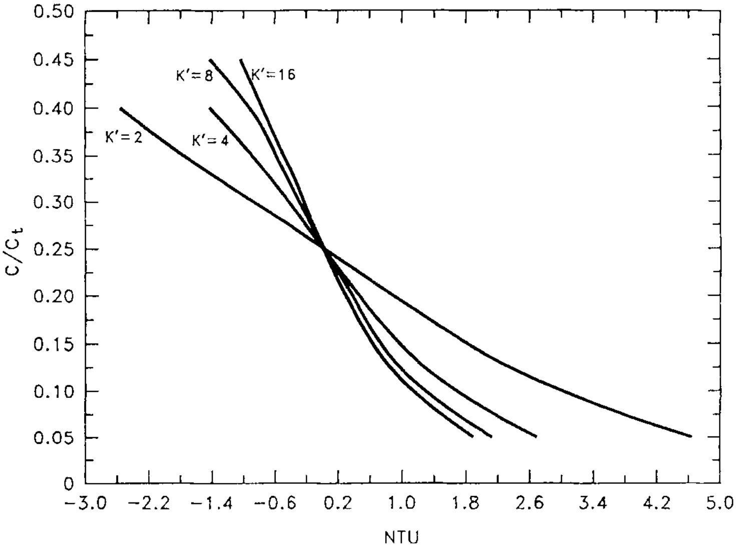

FIGURE 8. Normalized breakthrough fronts for exchange of a divalent ion for a monovalent ion and mass transfer resistance in the fluid phase.

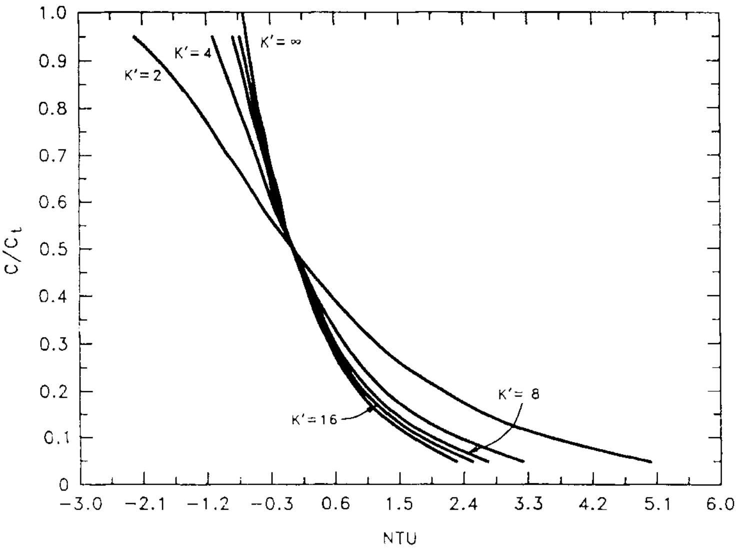

FIGURE 9. Normalized breakthrough fronts for exchange of a monovalent ion for a divalent ion and mass transfer resistance in the fluid phase.

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Figures 4-6 to the upper right corners. The integration to determine the breakthrough curves could be performed graphically, but the curves presented in Figures 7-9 were obtained using numerical integration since expressions for the equilibrium were available. (Analytical integration is possible for the case where the charges on the exchanging ions are equal.) The figure contains several curves that correspond to different values of the equilibrium constant, K′. Different figures are presented for exchange of monovalent ions for divalent ions and for the exchange of divalent ions for monovalent ions. These curves collectively describe a wide range of ion exchange fronts. Approximate breakthrough fronts can be estimated for other values of the ion exchange equilibrium constant by interpolating between the curves presented. Similar dimensionless breakthrough fronts based upon resistance in the solid film are presented in Figures 10-12.

These curves are expressed as a function of dimensionless distances, NTU. Thus, the width of the breakthrough curve is determined by the fluid film mass transfer

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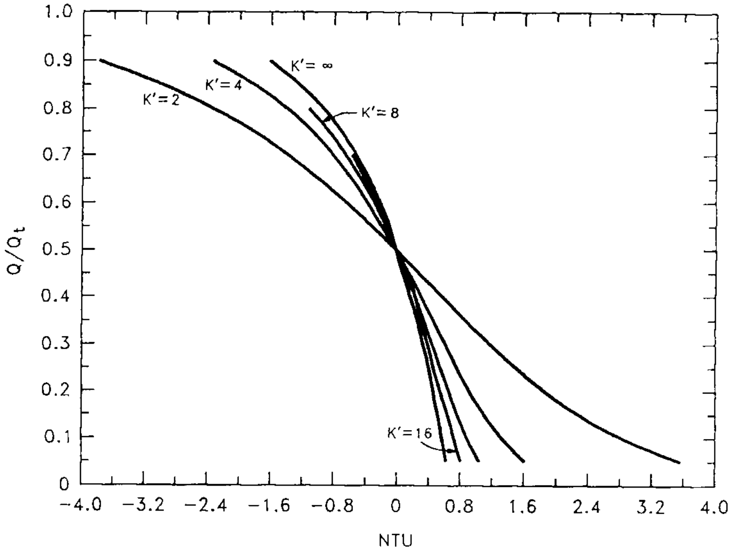

FIGURE 10. Normalized breakthrough fronts for exchange of ions with equal charges and mass transfer resistance in the solid phase.

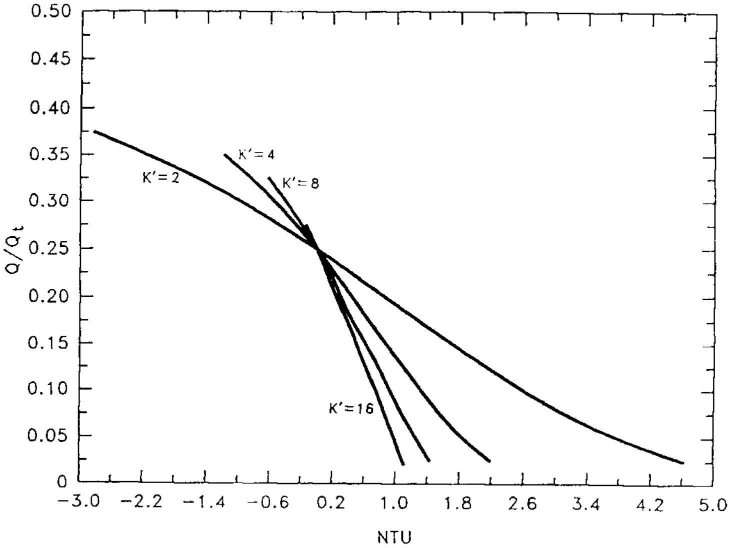

FIGURE 11. Normalized breakthrough fronts for exchange of a divalent ion for a monovalent ion and mass transfer resistance in the solid phase.

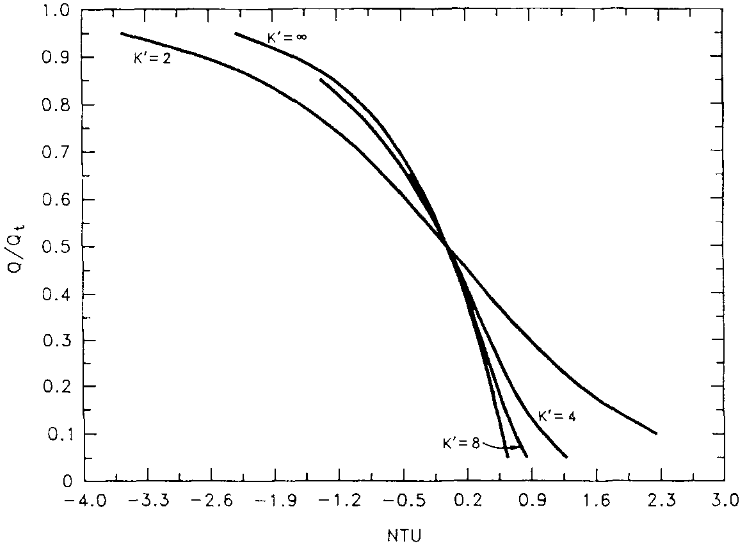

FIGURE 12. Normalized breakthrough fronts for exchange of a monovalent ion with a divalent ion and mass transfer resistance in the solid phase.

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coefficient and the fluid velocity (i.e., by the HTU) as well as for the curvature in the isotherm (as expressed in K'). For a given HTU, the front is broader (less steep) with lower values of K'. Furthermore, the curves for lower values of K' are more nearly like the symmetric curves produced by systems with linear isotherms.

Irreversible Isotherms - The Special Case When K' Approaches Infinity

As K' increases, the curves become less symmetric; in the limit with large values of K', the curves approach the solution for an irreversible isotherm. The irreversible isotherm is also shown in Figures 7-12. The irreversible isotherm as described by Cooper (10) is easily evaluated in the terms just described. In that case, C^* is always zero; thus, the NTU is easily integrated. For an irreversible isotherm,

$$\mathrm{NTU} = -\int dC/C = -\ln C + \text{constant} .$$

If one specifies that the NTU will be zero when C is 0.5 (the convention used in other examples in this paper), the constant becomes -ln(0.5), and the equation becomes

$$\mathrm{NTU} = -\ln(2C) .$$

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Solving the expression for C gives

$$C = 0.5\exp(-NTU) .$$

Note that this is not a symmetrical plot. The value of C declines exponentially with NTU (or position down the bed), but C would appear to be greater than unity for NTU less than -ln(2). This simply implies that the breakthrough front is very steep in this region, and for NTU less than -ln(2), C is unity. This breakthrough curve is also illustrated in Figures 7-9. Note that the breakthrough fronts approach close to the irreversible case, when K′ becomes 16 or greater.

Similarly, if the resistance is all in a solid "film," the NTU becomes

$$NTU = -\int dQ/(Q^{*}-Q) = -\int dQ/(1 - Q) = \ln(1 - Q) + \text{constant} .$$

For the irreversible isotherm, Q^{*} is 1 for all values of C. If the NTU is set equal to zero when Q is 0.5, the constant is -ln(0.5) and the equation becomes

$$NTU = \ln[2(1 - Q)] .$$

Expressed in terms of Q, this becomes

$$Q = 1 - 0.5\exp(NTU) .$$

This is also a nonsymmetric front. However, in this case, the curve becomes steep and C appears to become negative at values of NTU greater than +ln(2). In reality, C will be equal to zero for values of NTU greater than ln(2). This breakthrough front is shown in Figures 10-12. Note that the breakthrough curve approaches the irreversible case when K′ becomes 16 or greater.

In many cases, it is not possible to determine if the resistance to mass transfer is largely in the fluid film or in the solid phase from the shape of the breakthrough curve. In the case of the irreversible isotherm, this may be possible, but one should note that there are several reasons why this is usually very difficult. First, the view of the solid-phase resistance as a "film" is often greatly simplified. In many cases, such as where a significant fraction of the adsorbed solute is immobile, the Glueckauf approximation can become less accurate. Also, other "resistances" to mass transfer are usually present and contribute to spreading of the breakthrough front. Axial dispersion becomes important when both fluid- and solid-phase resistances are reduced sufficiently. Any or all of these effects can make it very difficult to determine the relative importance of the different resistances to mass transfer solely from the shape of breakthrough fronts, even for irreversible isotherms.

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Determination of Mass Transfer Coefficients from Breakthrough Data

Although the discussion given above assumed that the objective was to evaluate the shape and width of a breakthrough front from knowledge of the adsorption or ion exchange isotherm and the appropriate mass transfer coefficient, the same analysis can be used to determine the mass transfer coefficient from experimental constant-pattern fronts. This may be desirable in quantitatively evaluating different adsorbents or ion exchange resins. To determine the mass transfer coefficient, it is necessary to know the adsorption/ion exchange isotherm. The operating line is constructed from the specified initial condition of the bed and the final composition of the solution and the adsorbent/resin loading, as illustrated in Figure 1. The dimensionless breakthrough curve is then constructed, as illustrated in Figure 3. Note that the dimensionless breakthrough curve depends upon the isotherm and the operating line; it is dependent of the mass transfer resistance in the system only in the sense that one needs to know whether the NTU should be evaluated in terms of resistance in the fluid phase or in the solid phase. For many ion exchange processes, integration may not be necessary because the dimensionless fronts can be estimated by interpolating between the curves for different values of K′ presented in Figures 4-12.

To evaluate the mass transfer coefficient, one only needs to compare the data with the normalized breakthrough curve. For instance, the normalized breakthrough curve can be used to determine the NTU required for the concentration in the front to change from 0.2 times the inlet concentration to 0.8 times the inlet concentration. Then the time or distance for the same concentration change can be taken from the experimental curve. The ratio of these values will be the HTU:

$$\mathrm{HTU} = Z_m/Z_o ,$$

where Z_m is the measured distance, and Z_o is the dimensionless distance. Then the mass transfer coefficient is obtained by dividing the superficial fluid velocity by the HTU.

Once the change in NTU for a given change in concentration is determined, it can be used for determining the mass transfer coefficient at any number of fluid velocities, or flow rates. That is, the distance or time required for the change in concentration can be determined for each velocity used; these values can be used to determine the HTU for each velocity, and then the mass transfer coefficients can be determined. Similarly, a single normalized breakthrough curve could be used for a variety of particle diameters, as long as all of the particle material is the same and has the same isotherm.

CONCLUSIONS

Because they are unsteady state operations, fixed-bed adsorption and ion exchange are often evaluated superficially or incompletely. There are only a few exact solutions for common cases. Although many real systems can be approximated by one of the available solutions, even these are numerically difficult to evaluate and thus are often not used when they are needed. The graphical/numerical method suggested in this paper can be used for any constant-pattern adsorption of ion exchange systems. It is an extension of steady state analysis and design methods commonly used for absorption/stripping operations. The approach can be used either to predict the shape and width of adsorption or ion exchange fronts once mass transfer coefficients are known or to evaluate mass transfer coefficients from experimental measurements of breakthrough fronts. Normalized ion exchange equilibrium curves and breakthrough curves are presented which should be useful for approximating breakthrough fronts for a large number of binary ion exchange processes.

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