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Constant-Pattern Adsorption Fronts with Mass Transfer Resistances in Both Solid and Fluid Films

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ABSTRACT

The shape and width of constant-pattern adsorption fronts can be predicted by relatively simple graphical/numerical methods analogous to methods used for analyzing concentration profiles in countercurrent extraction or adsorption systems when there is significant mass transfer resistance in both the fluid and solid film. This paper presents an extension of procedures described by the author for predicting constant-pattern fronts with film resistance in only one phase. The procedure is illustrated for systems with Langmuir isotherms, and the results are shown in a series of dimensionless figures that cover a wide range of equilibrium conditions and mass transfer coefficients.

INTRODUCTION

In an earlier study (1) the author illustrated that well-known graphic or numerical procedures for analyzing countercurrent extraction or absorption processes can be modified to describe the shape of constant-pattern adsorption or ion-exchange processes in fixed beds. The procedure is analogous to the development of exact solutions (2), but the exact solutions are often complex, difficult to use, and available for only selected isotherms (3–6). Major advantages of the numerical/graphical solutions are simplicity and the ability to describe constant-pattern breakthrough

fronts for any shape of equilibrium isotherm. The procedure gives only the width and shape of fully established breakthrough fronts; the position of the front is more readily established by conventional means from the capacity of the adsorbent or ion-exchange material, the concentration of solute in the fluid, and the flow rate.

This procedure is also limited to cases where the mass transfer in both phases can be described in terms of mass transfer coefficients, often called "film coefficients." Mass transfer in the fluid phase is usually best described using film coefficients, but they are not always satisfactory for describing mass transfer in the solid adsorbent. However, an effective approximation can be obtained when the adsorbent is free to diffuse within the solid particles, such as in most ion-exchange systems and adsorption systems with surface diffusion or solid diffusion within the particles. A good approximation is unlikely when the adsorbed molecules are attached rigidly to the solid pore surfaces and only a small fraction of molecules in the pore fluid that is not attached to the solid surfaces is free to diffuse.

BACKGROUND

In an earlier study an analysis was presented for cases with mass transfer resistance in only one phase. Ion-exchange equilibrium (isotherm) was illustrated in which analytical solutions were not available. The results were presented in a series of dimensionless graphs that described constant-pattern fronts for a wide range of ion-exchange conditions (isotherms, mass transfer coefficients, and flow rates).

The analogy between constant-pattern adsorption fronts and countercurrent extraction or absorption becomes apparent when the front is viewed from a reference moving down the bed at the same rate as the front. The fluid then appears to be moving down the bed with a velocity of $V - V_f$, where V is the fluid velocity and V_f is the velocity of the front, and the solid appears to be moving upward at a velocity of V_f. The operating line for such a countercurrent operation (for dilute systems where the fluid velocity does not change) is shown to be a straight line connecting the point on the isotherm that represents the initial condition of the bed (the origin if the bed initially contains no solute) and the point on the isotherm that represents the final condition after the front has passed (the point on the isotherm corresponding to the concentration of solute in the feed). The operating line is developed from a material balance between an arbitrary cross section of the column and a cross section far (an infinite distance) upstream or downstream in an infinitely long column. This is analogous to material balances (operating lines) in countercurrent absorption or liquid–liquid extraction columns, but there are two impor-

tant differences. The first difference is that the concentration profile (front) in the column must be viewed from a moving reference so that the adsorbent particles appear to be moving up the column at the same rate the front moves down the column. The second difference is that the column is assumed to be infinitely long, meaning that the operating line and the equilibrium curve intersect at infinite distances in either direction from the concentration front. This is illustrated in Fig. 1.

The number of transfer units (NTU) in such a column is assumed to be infinite, but important information comes from determining the NTU in finite portions of the column, those portions that are within the moving front. The NTU can be calculated for any portion of the region between the two intersections of the operating line with the equilibrium isotherm. A series of positions on the operating line (C for the concentration in the fluid and Q for the concentration in the solid) and on the equilibrium isotherm are used to find C^*, the concentration in the fluid that would be in equilibrium with the solid loading, or Q^*, the concentration in the solid that would be in equilibrium with the concentration in the bulk fluid. These values are used to integrate graphically, numerically, or analytically and determine the NTU based upon resistance in either the fluid (f) or solid (s) phases.

$$\mathrm{NTU_f} = \int_{C_1}^{C_2} dC/(C - C^*) \tag{1}$$

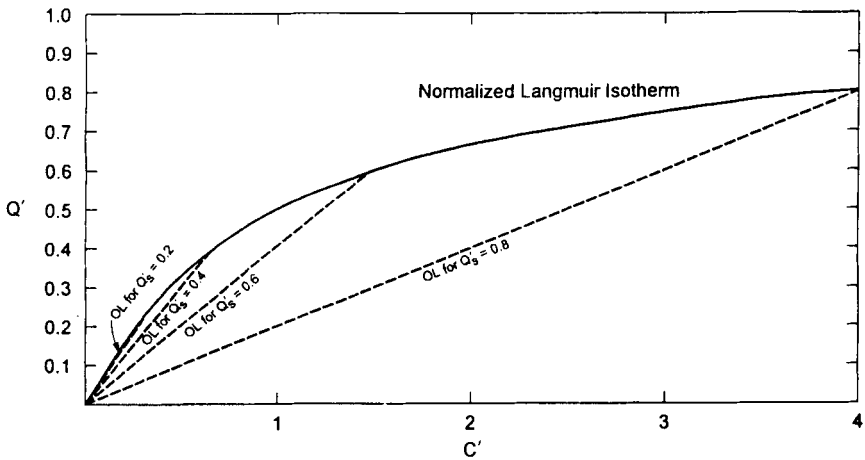

FIG. 1 Illustration of an equilibrium isotherm, an operating line, and calculation of the bulk and interfacial concentrations with mass transfer resistance in both phases.

and

$$\mathrm{NTU_s} = \int_{Q_1}^{Q_2} dQ/(Q^* - Q) \tag{2}$$

The integration is made from C_1 to C_2 (or from Q_1 to Q_2). The calculations are similar to those used for countercurrent systems and are described in standard textbooks on separations (7, 8). The NTU can be calculated from the position in the front where the concentration has any arbitrary value. It is convenient for the starting value to be the point where the concentration is halfway between the inlet concentration and the concentration far downstream where the fluid is in equilibrium with the inlet adsorbent (the initial solids in the bed); this is often called the 50% breakthrough point in the front. The following example is the most common case in which the initial adsorbent is free of solute. Then the final concentration in the fluid far downstream is zero.

A plot of C (or Q) vs NTU is a dimensionless plot of the breakthrough front. If the calculations start from the 50% breakthrough point on the front, the NTU will be zero at that point, and the NTU at different concentrations will correspond to the changes in the NTU between the 50% breakthrough point and the new concentration. Note that the calculation cannot begin at either end point where the operating line crosses the equilibrium isotherm because the value of the integrals for NTU would be indeterminant. Hence, it is more convenient to begin the integration at the concentration where C is one-half the inlet concentration rather than where C is at one end of the column. Remember that the concentrations in the bulk fluid and bulk solid phases are both given by the operating line; therefore, the position in the front is where the concentration is one-half the distance from the inlet fluid concentration, and the final fluid concentration is also the position where the concentration in the solid is midway between the initial concentration and the final concentration.

The integral can be evaluated as far as desired in any direction from that 50% breakthrough point to establish the shape of as much of the breakthrough front as desired. The dimensionless breakthrough curve (C vs NTU) applies to all mass transfer coefficients and can be converted to a dimensional front by multiplying the NTU values by the height of a transfer unit, HTU, or $(V - V_f)/k_f a$, for resistance in the fluid phase. The column length that corresponds to any change in concentration is the product of the HTU and the NTU that corresponds to the change in concentration:

$$Z_1 - Z_2 = [\mathrm{HTU}][\mathrm{NTU}] = \left(\frac{V - V_f}{k_f a}\right)[\mathrm{NTU}] \tag{3}$$

The mass transfer coefficient in the fluid phase is k_f, and the external surface area of adsorbent particles per unit volume of column is a.

RESISTANCE IN BOTH FLUID AND SOLID FILMS

When there is resistance in both phases, breakthrough curves can be calculated using the same principles, but one must account for resistances in both phases to obtain the concentrations at the solid–fluid interface. The way to approach the problem has already been outlined in related methods for absorption of extraction systems. Neglecting accumulation of solute in the fluid or solid films, the rates of solute transport through the two films can be equated (8):

$$k_f(C - C_i) = k_s(Q_i - Q) \tag{4}$$

$$k_f/k_s = (Q_i - Q)/(C_i - C) \tag{5}$$

where C_i and Q_i refer to concentrations at the solid–fluid interface and k_f and k_s are mass transfer coefficients in the fluid and solid "films," respectively. This equation describes a "tie" line joining positions at the interface to conditions in the bulk fluid and solid (see Fig. 1). The slope of the line is $-k_f/k_s$; thus, the dimensionless distance (NTU) can be calculated based upon the resistance in either film. Based upon the fluid film, the dimensionless distance is

$$\mathrm{NTU}_f = \int_{C_1}^{C_2} dC/(C - C_I) \tag{6}$$

and based upon the solid film,

$$\mathrm{NTU}_s = \int_{Q_1}^{Q_2} dQ/(Q_I - Q) \tag{7}$$

The integral can be evaluated from the 50% breakthrough point by integrating in both directions from that point. The location of the concentrations at the interface is illustrated in Fig. 1. The integral can be evaluated by selecting several points on the operating line and evaluating C and C_i (or Q and Q_i). The integration can be done analytically, numerically, or even graphically if there is no algebraic expression for the equilibrium curve. Figure 1 shows a series of lines with a slope of $-k_f/k_s$, and different values of $(C - C_i)$ or $(Q - Q_i)$ for different values of C. The result of the integration is a breakthrough curve based upon the dimensionless distance: C (or Q) is plotted against NTU. This can be converted into the more familiar dimensioned breakthrough curve by multiplying all of the dimensionless distances (NTU) by $V/k_f a$ (or $V/k_f a$); that is, multiply the NTU by the HTU.

This approach has broad applications and can be applied to any constant-pattern breakthrough curve when the mass transfer resistance can be described in term of mass transfer coefficients (film resistances). As noted earlier, constant-pattern fronts are common in commercial adsorption and ion-exchange operations, and the most common situation where the analysis cannot be applied is when mass transfer in the solid phase is by "pore diffusion," diffusion of unadsorbed molecules in the pores.

ILLUSTRATION OF THE APPROACH USING THE LANGMUIR ISOTHERM

As noted, the integration can be done, at least graphically, for even the most complex equilibrium curves. To illustrate the approach, the Langmuir isotherm will be used. Analytical expressions are available for breakthrough curves with resistance in only one phase, but this paper will show the results for resistances in two films. The calculations will be performed numerically and presented in generalized dimensionless forms so they can be applied most generally.

The Langmuir isotherm is usually written

$$Q = Q_m kC/(1 + kC) \tag{8}$$

where Q is the loading in the solid, Q_m is the maximum loading in the solid which occurs as C approaches infinity, k is a Langmuir constant that corresponds to the distribution coefficient (slope of the isotherm) at very low concentrations, and C is the concentration in the fluid. This expression can be written in terms of dimensionless variables:

$$Q' = Q/Q_m = C'/(1 + C) \tag{9}$$

where C' is the product kC, and Q' is the fraction of the solid adsorption capacity occupied by solute. The normalized Langmuir isotherm is shown in Fig. 2.

The operating line connects the two points on the operating line that correspond to the initial loading of the bed and the equilibrium loading after the front has passed, that is, the loading when the bed is in equilibrium with the feed. If the feed concentration is C_0', the loading of the bed after the bed is saturated will be Q_s'. The saturated solid concentration will be less than the maximum capacity of the adsorbent; therefore, Q_s' will be less than unity. Similarly, the concentration in the fluid exiting the column will be in equilibrium with the initial loading in the original bed:

$$C_0' = Q_0'/(1 - Q_0') \tag{10}$$

The subscript 0 refers to conditions in the initial bed. For the numerical

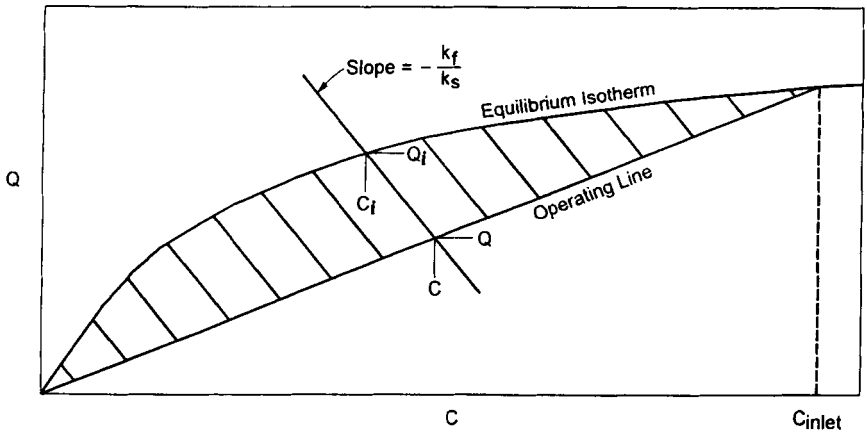

FIG. 2 The normalized Langmuir isotherm and operating lines for cases where the concentration in the fluid feed loads the adsorbent to 20, 40, 60, and 80% of the maximum adsorbent capacity.

illustration of the two film resistances with a Langmuir isotherm, the initial loading in the bed will be assumed to be zero; hence, Q'_0 and C'_0 will be zero, and the operating line will go through the origin of the isotherm.

RESULTS

The results based upon resistance in the fluid phase are shown in Figs. 3 through 10. Each curve represents a different value of Q'_s ranging from 0.2 to 0.8. The operating lines for each case are shown in Fig. 2. Figures 3 through 6 correspond to cases where the reference phase is the fluid phase, and the integration is described in Eq. (6). Figures 7 through 10 correspond to cases where the reference phase is the solid phase, and the integration is described by Eq. (7). There are several curves on each figure, and each curve corresponds to a different value of the ratios of the film coefficients, k_f/k_s. These plots hold for all (absolute) values of k_f and k_s. The absolute value of the coefficients is included in the HTU, the factor that converts the NTU shown in the figures to actual column distances. Four figures are given for transfer units based upon the fluid-phase resistance, and four figures are given for transfer units based upon resistance within the solid phase. The four figures in each set correspond to different inlet concentrations in the fluid, but the inlet concentrations are expressed as the fraction of the adsorbent adsorption capacity that is

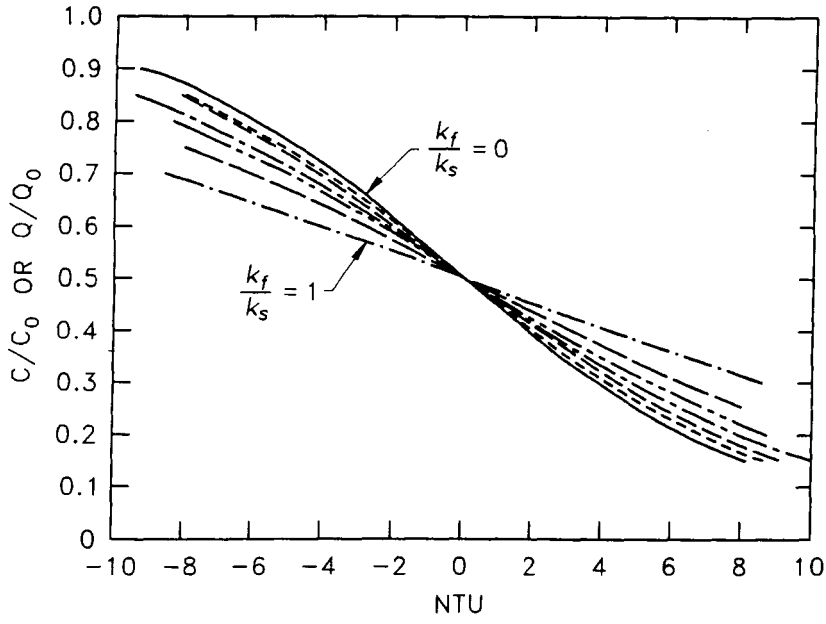

FIG. 3 Normalized breakthrough curves based upon concentrations in the fluid phase and a fluid feed concentration that loads the adsorbent to 20% of its maximum capacity (individual curves correspond to k_f/k_s = 0.0, 0.05, 0.1, 0.2, 0.3, 0.5, and 1.0).

occupied by the adsorbed molecules when in equilibrium with the feed (values of Q' of 0.2, 0.4, 0.6, and 0.8). This is illustrated in Fig. 2, where the normalized Langmuir isotherm is shown along with four operating lines that each correspond to a different feed concentration used in the calculated results. The normalized fluid concentrations, C', can be determined from Eq. (10) or from the interactions of the operating lines with the equilibrium curve given in Fig. 2.

Each figure contains several curves, and each curve corresponds to different ratios of the mass transfer coefficients for the fluid film to the mass transfer coefficient for the solid film. The different values of the ratio are given in the figure captions. Since many of the curves lie relatively close together, the figures would have been cluttered if each curve had been labeled. Instead of labeling every curve, only the highest and the lowest values of the ratio are shown. The values for the ratio for the other curves can be obtained by counting from the curve with the highest or lowest value for the ratio k_f/k_s.

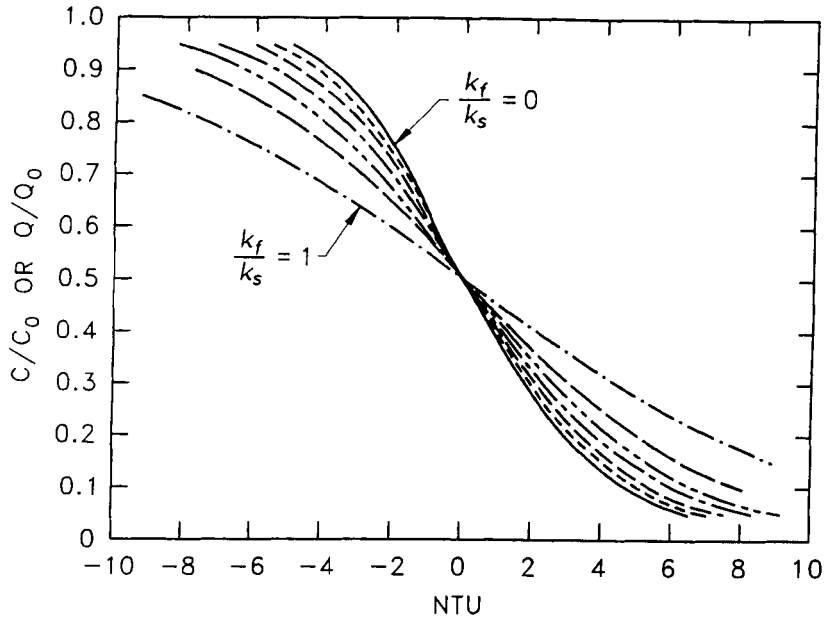

FIG. 4 Normalized breakthrough curves based upon concentrations in the fluid phase and a fluid feed concentration that loads the adsorbent to 40% of its maximum capacity (individual curves correspond to k_f/k_s = 0.0, 0.05, 0.1, 0.2, 0.3, 0.5, and 1.0).

When the transfer units are based upon the fluid phase, a value of k_f/k_s equal to zero corresponds to the case where all of the resistance is in the fluid film. That ratio gives the sharpest curves shown in those figures. Any additional mass transfer resistance in the solid phase makes the breakthrough curves more diffuse. Note also that as the value of Q' increases, the portion of the isotherm used has more curvature, and the breakthrough curves become sharper. When the transfer units are based upon the resistance in the solid film, the ratio k_f/k_s is infinite when there is no resistance in the fluid film. This corresponds to the sharpest breakthrough curves shown based upon the solid phase resistance, and addition of mass transfer resistance in the fluid phase causes the breakthrough curve to become more diffuse.

These are normalized breakthrough curves with the distances on the horizontal axes expressed in dimensionless units, NTU. The actual axis expressed in units such as meters depends upon the HTU and thus upon the actual values of the mass transfer coefficients in the reference phase

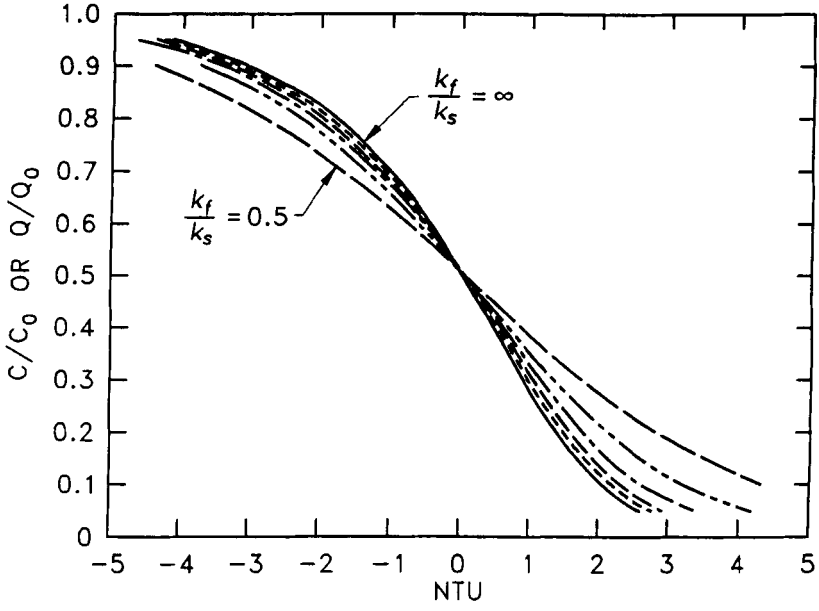

FIG. 5 Normalized breakthrough curves based upon concentrations in the fluid phase and a fluid feed concentration that loads the adsorbent to 60% of its maximum capacity (individual curves correspond to k_f/k_s = 0.0, 0.05, 0.1, 0.2, 0.3, 0.5, and 1.0).

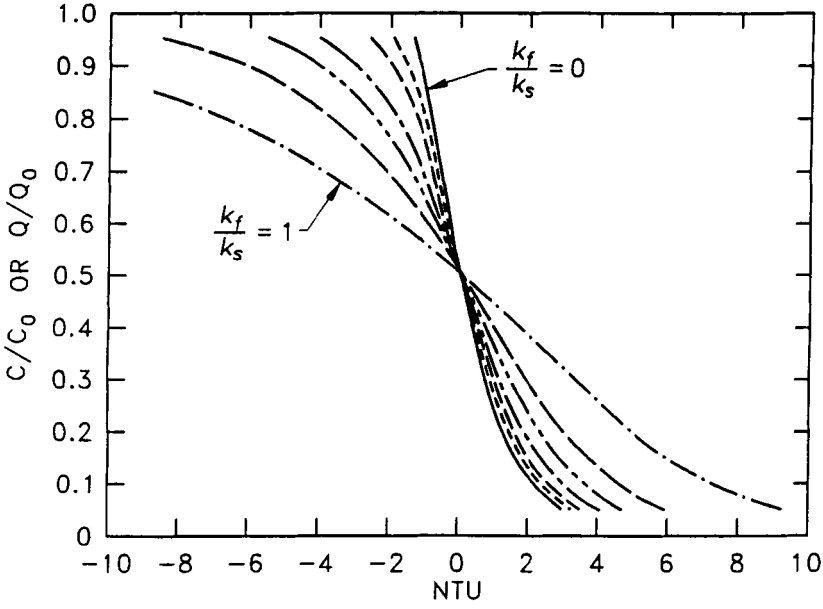

FIG. 6 Normalized breakthrough curves based upon concentrations in the fluid phase and a fluid feed concentration that loads the adsorbent to 80% of its maximum capacity (individual curves correspond to k_f/k_s = 0.0, 0.05, 0.1, 0.2, 0.3, 0.5, and 1.0).

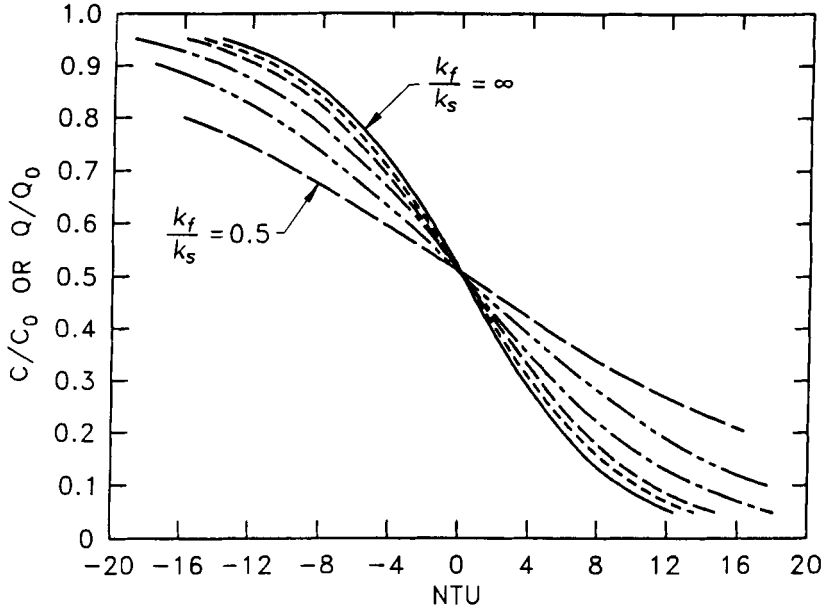

FIG. 7 Normalized breakthrough curves based upon concentrations in the solid phase and a fluid feed concentration that loads the adsorbent to 20% of its maximum capacity (individual curves correspond to k_f/k_s = 0.5, 1.0, 2.0, 5.0, 10.0, and infinity).

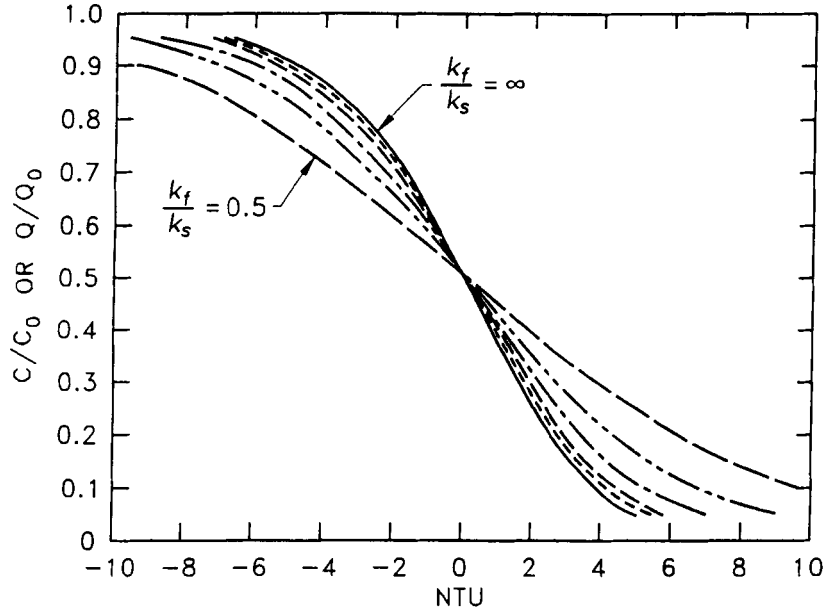

FIG. 8 Normalized breakthrough curves based upon concentrations in the solid phase and a fluid feed concentration that loads the adsorbent to 40% of its maximum capacity (individual curves correspond to k_f/k_s = 0.5, 1.0, 2.0, 5.0, 10.0, and infinity).

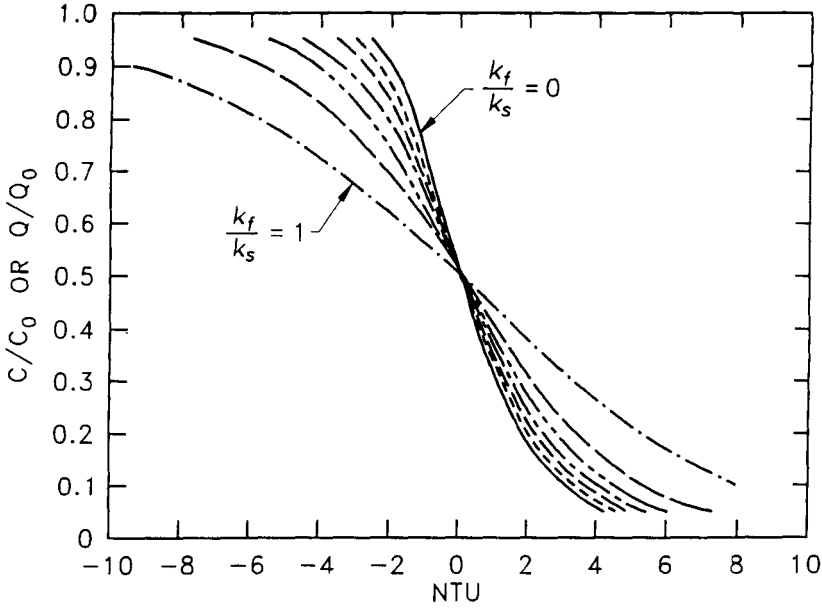

FIG. 9 Normalized breakthrough curves based upon concentrations in the solid phase and a fluid feed concentration that loads the adsorbent to 60% of its maximum capacity (individual curves correspond to k_f/k_s = 0.5, 1.0, 2.0, 5.0, 10.0, and infinity).

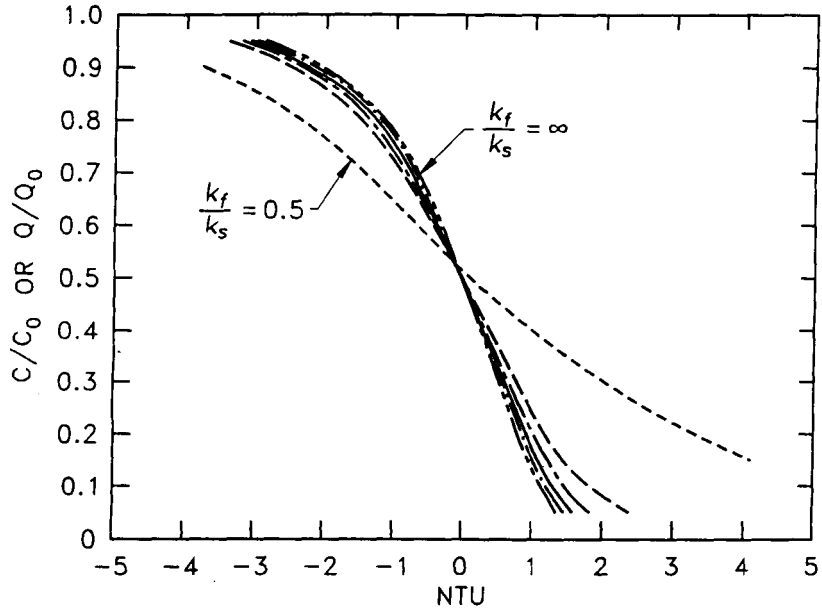

FIG. 10 Normalized breakthrough curves based upon concentrations in the solid phase and a fluid feed concentration that loads the adsorbent to 80% of its maximum capacity (individual curves correspond to k_f/k_s = 0.1, 0.5, 1.0, 2.0, 5.0, 10.0, and infinity).

and the fluid velocity. The breakthrough curves can be sharp or diffuse depending upon the HTU, but if the distance (or time) scale is expanded sufficiently, the shape of the front will look like these normalized curves.

No values of Q'_s below 0.2 were studied because the isotherm approaches the simple linear case for lower values of Q'_s. Although an isotherm with any negative curvature (favorable isotherm) will eventually approach a constant pattern, increased time and distance may be required to establish the constant pattern. The NTU can be calculated from the position in the front where the concentration has any arbitrary value.

USE OF THE RESULTS

The results are presented in Figs. 3–10, and those working on systems with Langmuir isotherms can use these figures directly unless their conditions (Q'_s or k_f/k_s) are beyond the range of conditions covered by the figures. Those working on systems with other isotherms can generate similar figures, including isotherms that are only available as graphs of experimental data.

The dimensionless breakthrough curves presented here can be used in any of several ways. The appropriate figure can be selected that corresponds to the fractional loading, Q'_s, of the adsorbent at saturation with the feed fluid. Of course, it may be necessary to interpolate between curves on two figures.

If the mass transfer coefficients are known, the HTU can be calculated and used to convert the dimensionless distances (NTU) to the actual distances and predict the breakthrough curves. It is more common to observe concentrations in fluid leaving a column with a given length than to observe the concentrations within the column at a given time. If the breakthrough front is to be predicted for a given position as a function of time, the real distances can be divided by $-V_f$, the velocity of the front, to convert the distances to time.

If only the ratio of the mass transfer coefficients were known, measurements of breakthrough curves could be used to evaluate the value of the HTU, and thus the absolute value of the mass transfer coefficients, by comparing the actual distances (or breakthrough times) with the NTU required to reach two specific concentrations on the breakthrough curve. The distance (or time) between two concentrations on the breakthrough curve divided by the NTU between those two concentrations is the HTU. The mass transfer coefficient can be obtained by dividing the velocity $(V - V_f)$ by the HTU.

The analysis is more complex if the ratio k_f/k_s is not known, which is likely to be the case. It is more likely that one resistance, such as fluid film resistance, will be known. The fluid film resistance can be estimated

from correlations developed from data on similarly shaped packing material in other adsorption beds or even chemical reactors. The solid film resistance can then be estimated. Note that the curves in these figures represent different values for the ratio of the mass transfer coefficients in the fluid and solid phases. [If the fluid film coefficient is known (or estimated) from correlations, the dimensionless distance given in terms of the NTU can be based upon the mass transfer coefficient for the fluid film and can be converted into dimensioned units.]

$$Z = Z_{50\%} + [\text{HTU}][\text{NTU}] = Z_{50\%} + \left(\frac{V - V_f}{k_f a}\right)[\text{NTU}] \qquad (11)$$

where $Z_{50\%}$ is the position in the column where the breakthrough concentration is 50% of the final or maximum concentration. The predicted curves for different ratios of the mass transfer coefficients can then be compared directly with the experimental data. As the ratio of the solid film coefficient to the fluid film coefficient increases, the predicted front becomes broader and less "sharp." One can interpolate between the curves to find the best value of the ratio to match the data and, thus, the best estimate for the mass transfer coefficient in the solid "film." Of course, the experimental time should be multiplied by $(V - V_f)/k_f a V_f$ to convert the experimental breakthrough curve to the dimensionless form for comparison with the calculated curves and the estimation of the effective solid film resistance.

The comparison of predicted and experimental fronts should be relatively simple, provided the shapes of the experimental curves are essentially the same as those of the predicted curves. However, if the experimental curve does not lie between two curves in Figs. 3 through 10 and seems to cross two or more curves, estimates of the solid-film mass transfer coefficient may be difficult. Such a problem can arise if the two-film model is not correct. One should remember that the assumption of a solid film is particularly questionable for some situations. The assumption that mass transfer in the solid can be treated as "film" comes from Glueckauf's observation that the long-term solution for mass transfer into solids with linear isotherms can be approximated by an effective film resistance (9). The equations are similar for systems with nonlinear isotherms only when all of the solute in the solid is free to diffuse with the same diffusion coefficient. This occurs when diffusion within the solid is dominated by surface diffusion or diffusion through the solid, and essentially all of the solute is on the surfaces or in the solid. The equations are significantly different for pore diffusion when diffusion occurs only in the pores and most of the solute is on the surfaces or in the solid and is relatively immobile.

Note also that the contributions from dispersion were neglected. In systems with linear isotherms, the effects of fluid dispersion can be combined with the two-film resistances to give easily estimated overall resistance to mass transfer. However, in systems with nonlinear isotherms, these combinations are not so straightforward, and this is another potential reason why the predicted shape of the curves may be different from those observed experimentally.

CONCLUSIONS

A relatively simple approach to the prediction of constant-pattern adsorption fronts can be used with significant resistances in both the fluid and solid phases, provided these resistances can be expressed in terms of film coefficients, and the results are presented in graphs that cover a wide range of conditions for systems with Langmuir isotherms. Similar graphs can be developed for other common isotherms, or graphs can be developed for essentially and empirically measured isotherms. The procedures are relatively simple extensions of design procedures used for countercurrent absorption and/or extraction systems. However, when using the procedure, one should remember that when mass transfer resistance in the solid cannot be described as a film resistance or when fluid dispersion is important, the procedure is inappropriate and can give significantly incorrect results.

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