β_a = void fraction of porous solid
ϵ = void fraction of packed bed
η = reduced second moment
θ_y = see table 1
κ = capacity factor for tracer
$/u_0$ = zeroth moment
$/u'_1$ = first absolute moment, s
$/u_2$ = second central moment, s^2
$/u_3$ = third central moment, s^3
ξ = see Eq. 27
ρ = total resistance term, s
σ = standard deviation
τ = diffusional time constant, s
ϕ = fraction of plugged pores
ζ = tortuosity factor

Indices

0 = of the particle
1 = of the unobstructed region
2 = of the plugged regions
emp = empirical value
mod = model
min = minimal value
fr = of the fresh particles
opt = optimal value

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An Analysis of Bacterial Growth in Fluidized-Bed Adsorption Column

An analysis is presented to describe the dynamics of fluidized bed adsorption columns. A microbial film model (recently proposed by the authors) is used to characterize the bacterial activity and its interaction with adsorption and solids mixing. Solids mixing and mixing in the liquid phase are included in the analysis, as is the effect of microbial film growth on the settling velocity of the adsorbent particles. The interplay of film growth, bed stratification and solids mixing is discussed in detail.

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SCOPE

It is known that bacterial films may develop on the surface of activated carbon particles in adsorption columns treating biodegradable wastewaters. The films have some beneficial effects, including direct uptake of organic matter from the waste stream and "bioregeneration" of the carbon. Because of these effects, fluidized-bed columns in which bacterial growth is encouraged have been proposed as combined bacteria/carbon treatment units. However, there are also deleterious effects such as the extra mass-transfer resistance that the film presents to adsorption.

This paper gives a mathematical model that can be used to include all these effects in the design of adsorption columns, and to evaluate various schemes for fluidized-bed, bacteria/carbon treatment units. This is the first published model to incorporate uncontrolled active bacterial growth. The resulting thick films not only cause bioregeneration but also alter the settling velocity of the carbon particles. This leads to a varying bed height, a

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difficulty eliminated from the model by a variable transformation. It can also affect the solids mixing in the bed. Some insight into the problem of solids mixing with variable settling velocities (a problem with applications to other liquid-fluidized reactors) is gained by considering the limiting cases of complete random mixing and no random mixing.

Mixing of the liquid phase is included in the model by an axial dispersion term. An original iterative method is given for the numerical solution of the resulting second-order, non-linear, partial differential equation.

CONCLUSIONS AND SIGNIFICANCE

A bacterial film growing uncontrolled will eventually reach a steadystate thickness at which new cell growth is balanced by decay processes (cell maintenance requirements, wash-off, endogenous metabolism). Whether or not a film develops in an absorption column depends on the value of the dimensionless film decay parameter. A procedure for evaluating this parameter for a particular wastewater is available (Andrews and Tien, 1981).

In the absence of any tendency for random mixing a liquid-fluidized bed will be perfectly stratified according to the particles' settling velocities. Given a "reaction" like film growth that reduces the settling velocity and whose rate depends strongly on the concentration of a reactant in the liquid, such a bed tends to a state in which all particles have identical settling velocities. This state, called here a disordered stratified bed, is difficult to model mathematically, but a second-order Runge-Kutta routine gives an intuitively reasonable approximation.

The interplay of film growth and solids mixing in a real bed of monosized carbon particles is complex, but should produce a stable condition in which the tendency to stratify is balanced by random mixing. The breakthrough curve cannot be predicted unless the mixing tendency can be quantified. However, the curves for two cases, complete liquid mixing and even initial coverage of the carbon with film, can be considered as solved. In both of these cases the average substrate concentration to which a particle is exposed is effectively independent of the solids mixing condition.

The breakthrough curves predicted by the model for beds of monosize particles are qualitatively different from published experimental curves for beds of 8 × 35 mesh carbon. This suggests that the particle size range is an important factor in the performance of fluidized bed bacteria/carbon treatment units. With a large size range the bed remains stratified on the basis of particle size and never becomes disordered. This scheme is analogous to an upflow packed bed and gives generally superior breakthrough characteristics. However, in a bed of monosize particles, thick films simultaneously cause bioregeneration and stratification. This suggests an alternative scheme in which heavily-coated particles are removed from the top of the bed, washed to remove the film, and put back in the bed where their adsorptive capacity is re-used.

INTRODUCTION

It has been known since the early seventies that biological treatment and adsorption on activated carbon work well together for the removal of soluble organic matter from wastewater. There are three main reasons for this. Adsorption and biodegradation tend to be complementary in the type of molecule they remove from solution (Andrews, 1979). Adsorption can protect biological treatment by removing toxic organics from solution. Finally, bacterial growth can "bio-regenerate" spent carbon (Sigurdson and Richardson, 1978).

Several treatment systems have been proposed to take advantage of this co-operation. They include various combinations of separate adsorption columns and biological treatment units (Ford and Buerklin, 1972), the addition of powdered activated carbon to activated sludge tanks (Flynn and Standick, 1976) and in-situ bioregeneration of adsorption columns (Rodman and Shunney, 1971). The spontaneous appearance of bacteria in conventional, packed-bed adsorption columns was once seen as a nuisance because it lead to anaerobic operation and bed clogging. Now that improved operating procedures have overcome these problems, it is generally seen as a positive factor that increases the apparent capacity of the carbon (Magsood and Benedek, 1977).

Weber, et al. (1972) argued that, instead of just adding a biological element to existing adsorption systems or vice-versa, better results could be achieved with a new "biophysiochemical" treatment unit designed to take full advantage of the adsorption/biodegradation co-operation. They also showed that a fluidized bed of granular carbon coated with a bacterial film is a promising layout for this unit. A fluidized bed will not clog because it can expand to accommodate the volume of a growing film.

A mathematical model of this unit would be useful for evaluating its design and performance. Several attempts have been made to produce a model but none has been completely satisfactory. Andrews and Tien (1974) assumed complete mixing of both the liquid and solid phases as well as uniform coverage of all particles with film; an unlikely situation. Furthermore, the inclusion of particulate organics in the model necessitated an over-simplification of the rate equations that invalidated the model at large film thickness. An attempt by Peel and Benedek (1977) overcame some of these problems but it treated the film thickness as a constant, externally defined parameter. This is inadequate. In practice a carbon bed starts with a low concentration of bacteria and zero adsorbate. During operation these two variables increase together, but at different rates in different parts of the bed (depending on the local substrate concentration). This was appreciated by Ying and Weber (1978). But their model was based on the idea that the bacteria in the column would be kept below a certain level by washing and air scouring of the bed. This assumed maximum level is so low that several major bacteria/carbon interactions are left out of the model. They include bed expansion, bioregeneration, and the extra mass transfer resistance for adsorption created by the bacterial film.

In a previous paper (Andrews and Tien, 1981) the authors presented a rate model for simultaneous adsorption and film growth that has several advantages over previous work. It is applicable to actively growing films of any thickness, it predicts bioregeneration as a natural consequence of film growth, and it gives reasonable agreement with data from experiments on a synthetic wastewater. The objective of the present work is to apply this rate model to a fluidized bed of granular carbon, carry out sample calculations and draw conclusions about how carbon adsorption and bacterial growth can best be combined.

The use of the resulting computer program in the design of adsorption columns would represent a considerable advance on present design methods which largely ignore the substantial effects that bacterial growth can exert on the removal of organic matter. Experience has shown the importance of questions like: "Will bacterial activity become significant?"; "If so, how long will it take?"; "Should it be allowed or controlled". The answers can not be given here because they depend on the characteristics of the particular wastewater. Our intent is to offer the designer a complete procedure for finding the answers for any organic wastewater whose constituents are soluble, adsorbable and biodegradable. This procedure involves first testing the rate model and evaluating the model parameters using the experimental techniques developed in the previous paper (Andrews and Tien, 1981). These parameters can then be used in the computer program presented here in order to assess the relative merits of various possible operating conditions.

It is not possible at present to compare the computer predictions with experimental data because there is as yet no wastewater/

carbon combination for which all the biological and adsorptive parameter values and an experimentally determined breakthrough curve are available. (Forcing a fit with experimental data by judicious selection of parameter values would be a meaningless exercise. The complexity of the program is such that it is capable of predicting breakthrough curves of almost any shape). It is hoped that the availability of the above procedure will encourage designers to provide the required information for several real wastewaters, something that we cannot do in our laboratory.

There are two additional reasons why the work reported here will be useful. First, the program can describe transient conditions (i.e. conditions of active microbial growth) in various types of fluidized-bed bioreactors. These include fermentors and the beds of coal or sand now being used for secondary wastewater treatment and denitrification (Jeris and Owen, 1977; Greenshield and Smith, 1974). Previously, only steady-state models for these processes were available (La Motta and Mulcahy, 1978).

Second the problem considered here belongs to the general class of liquid-fluidized bed reactors in which the reaction (bacterial film growth in this case) alters the settling velocity of the solid particles. The solid phase in liquid-fluidized beds tends to stratify according to the particles' settling velocity. Also, reactions usually proceed fastest at the base of the bed where the reactant concentration is highest. Clearly, a reaction that increased the particle settling velocity would tend to reinforce the stratification, whereas a reaction that decreased it would tend to equalize settling velocities through the bed, and so reduce the stratification and encourage solids mixing. So the reaction-induced changes in settling velocity can affect the solids mixing. They also affect the bed height (Andrews and Tien, 1979). This paper demonstrates an original approach to these complications that may be of interest in related reactor problems, including coal liquefaction and fluidized-bed crystallization.

THEORY

Using the axial dispersion model to describe liquid mixing, the concentration of organic substrate in the bed is given by the solution of:

$$\frac{\partial}{\partial z}\left(\epsilon D_d \frac{\partial s}{\partial z}\right) - u\frac{\partial s}{\partial z} - \frac{1-\epsilon}{1+x}\overline{N}_{Tc} = \epsilon\frac{\partial s}{\partial t} \tag{1}$$

The difficulties involved in solving this equation are as follows. It is a partial differential equation and is non-linear because of the complex variation of the uptake rate $\overline{N}_{Tc}$ with s. The boundary conditions are not simple because, since the bed continually expands to accommodate the volume of the growing bacterial film, the top of the bed is a moving boundary. The bed porosity, ϵ, is in general a function both of z, due to bed stratification, and t, due to bed expansion (terms involving $\partial\epsilon/\partial t$ that, strictly speaking, should appear in Eq. 1 are found to be negligible). These changes in porosity may affect the value of the axial dispersion coefficient D_d. Finally, the substrate uptake rate at a particular point in the bed, $\overline{N}_{Tc}$, depends not only on the substrate concentration, s, but also on the amount of bacterial film and the concentration of adsorbate in the solid phase at that point. The distribution of film and adsorbate through the bed depends critically on the solids mixing condition.

These difficulties are now considered separately, and the ways they are resolved in the final numerical solution are described.

Porosity

The bed porosity is related to the particle settling velocity by a correlation of the form given by Richardson and Zaki (1954).

$$\frac{\epsilon}{\epsilon_c} = \left(\frac{u_{sc}}{u_s}\right)^{1/n} \tag{2}$$

The parameter n is assumed to be independent of bacterial film volume.

The particle settling velocity is altered by both the adsorbate concentration and the bacterial film thickness. Little is known about the former effect, and it is assumed to be negligible compared with the latter. Film growth affects both the particle diameter and its average density. If the particle drag coefficient is taken as proportional to Re^{-e}, the net result is

$$\frac{u_s}{u_{sc}} = \frac{(1+Bx)^{1/(2-e)}}{(1+x)^{1/3}} \tag{3}$$

Note that the quantities ϵ_c and u_{sc}, which relate to beds of clean (i.e., no bacterial film) particles are treated as constants. This involves the implicit assumption that the clean particles are monosized.

Equation 3 is plotted in Figure 1 for $e = 0.73$ which is correct for carbon particles in the $5 \sim 50$ mesh size range. Since $B \approx 0.1$ for activated carbon it is clear that the overall effect of film growth is a reduction in settling velocity, and thus (from Eq. 2) an increase in bed porosity.

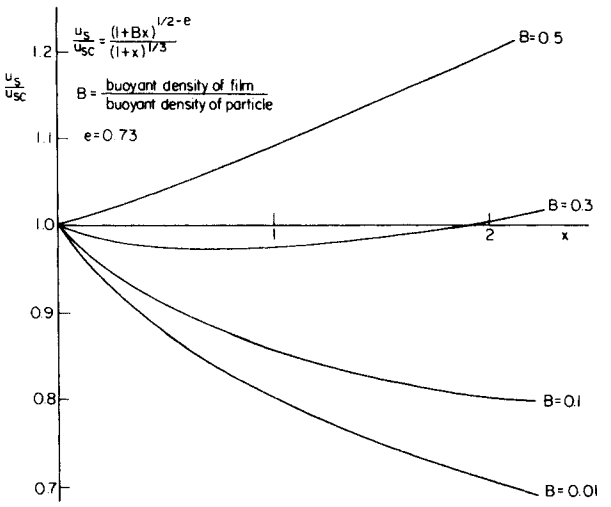

Figure 1. Effect of film volume on settling velocity.

Boundary Conditions

Since the bed height increases with time as the film grows, the distance from the base of the bed, z, is inconvenient as the independent variable. It is replaced by y, the fraction of the clean carbon volume that is below a point in the bed. This eliminates the moving boundary because the top of the bed must be at $y = 1$. This transformation is (Andrews and Tien, 1979).

$$\frac{dz}{dy} = vF(x) \tag{4}$$

Equation 1 is now written entirely in dimensionless variables.

$$\frac{\partial}{\partial y}\left(\frac{1}{P_e}\frac{\partial c}{\partial y}\right) - \frac{\partial c}{\partial y} - RN_{Tc} = Rk_1\epsilon F(x)\frac{\partial c}{\partial \tau} \tag{5}$$

The boundary conditions are those given by Dankwerts (1953)

$$-\frac{1}{P_e}\frac{\partial c}{\partial y} = 1 - c \quad \text{at} \quad y = 0$$

$$\frac{\partial c}{\partial y} = 0 \quad \text{at} \quad y = 1$$

$$c = 0 \quad \text{at} \quad \tau = 0.$$

The Axial Dispersion Coefficient

The variable transformation in the previous section lumps two quantities that may vary through the bed, the porosity and the axial dispersion coefficient, into a single parameter, a modified Peclet number, Pe. (Note that this variation depends on the solids mixing condition; it is obviously zero for a completely mixed bed.) The best estimate for this parameter is found from the correlation of Chung and Wen (1968); modified to account for the presence of the film.

$$Pe = \frac{33.7v[(1 + 3.59 \times 10^{-5}\,\mathrm{Ga}(1 + Bx))^{1/2} - 1][0.2 + 0.011(1 + x)^{0.16}\mathrm{Re}_c^{0.48}](1 + x)^{1/3}}{\mathrm{Re}_c d_c \epsilon (1 - \epsilon)} \tag{6}$$

The conceptual basis for the uptake rate model is illustrated in Figure 2. After a small time of exposure to substrate, the film thickness and the average adsorbate concentration in the particle (q) will both be small [Figure 2(a)]. The substrate concentration at the film/liquid interface (c_s) will be close to that in the liquid (c), so the linear driving force expression adopted for the adsorption kinetics predicts a positive rate of adsorption. However, as time passes, adsorption continues while film growth continually reduces c_s. Eventually q becomes greater than q^* (the adsorbate concentration in equilibrium with c_s) so the adsorption rate becomes negative and bioregeneration starts [Figure 2(b)].

The major assumptions adopted are that the mass transfer resistance in the liquid film around the particle is negligible, adsorption is completely reversible, the film properties (density, substrate diffusivity, etc.) do not vary with film depth, and that the film can be treated as if it were growing on a flat plate. The latter assumption is justified because the active depth of a bacterial film [L in Figure 2(b)] is $100 \sim 200\ \mu$, much less than the radius of a typical adsorbent particle. A first-order expression is used to describe substrate uptake kinetics in the film, a valid approximation for relatively dilute wastewaters. With these assumptions Andrews and Tien (1981) derived the following dimensionless equations for the rates of adsorption and total substrate uptake.

$$N_A = \frac{c - c_s \cosh k_1 x}{\sinh k_1 x} = Ka\left(\frac{c_s}{b + c_s} - q\right) \tag{7}$$

$$N_T = \frac{c \cosh k_1 x - c_s}{\sinh k_1 x} \tag{8}$$

(Note that the symbols $q, a, c, c_s, b, N_A, N_T, \rho$) used in the previous paper to represent dimensional variables here represent the corresponding dimensionless quantities).

Solving the second equality in Eq. 7 gives an equation for c_s, the substrate concentration at the film/carbon interface. The quadratic form of this equation, a consequence of the Langmuir form adopted from the adsorption isotherm, causes the non-linearity in the uptake term in Eq. 5. Because this non-linearity is inconvenient, the solution for c_s is best written in a pseudo-linear form.

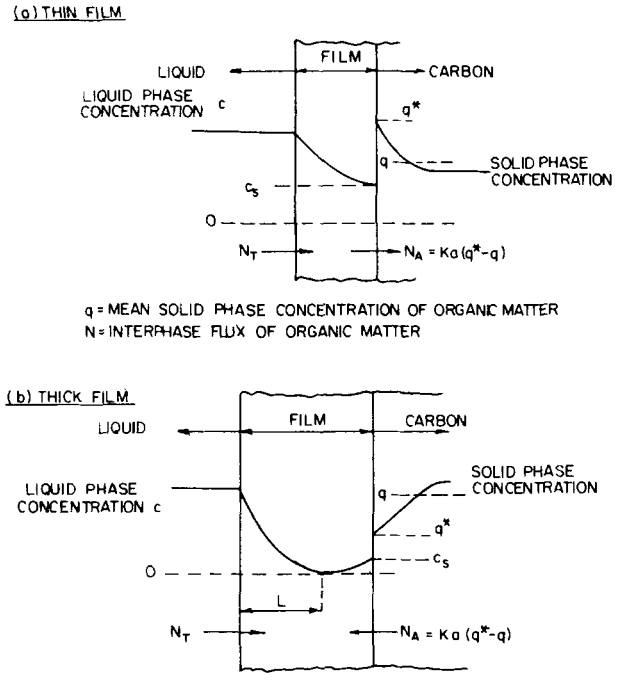

Figure 2. Growth of a bacterial film on an adsorbent surface.

$$c_s = M(c\,\mathrm{sech} k_1 x + qA - \gamma)$$

$$M = \frac{(b + A + \beta)(1 - 2P)^{1/2} - (b + A - \beta)}{2(\beta - \gamma)} \tag{9}$$

The form of Eq. 9 is decided by considering the limiting cases of the isotherm. The linear approximation for low concentrations gives $\gamma = 0$, $M = b/(A + b)$. The constant limiting case for high concentrations gives $\gamma = A$, $M = 1$. In the general case $A > \gamma > 0$ and M depends on c. In order for the linearization to be successful, γ must be chosen so that M varies as little as possible with c. It can be shown that $\partial M/\partial c = 0$ when:

$$\gamma = \frac{\beta}{P}[1 - P - (1 - 2P)^{1/2}] \approx \frac{\beta P}{2}\left(1 + P + \frac{5P^2}{4}\right) \tag{10}$$

The second, approximate equation for γ must be used in the computer calculation as $P \to 0$ to prevent excessive accumulation of rounding errors.

Film Volume and Adsorbate Concentration

The dimensionless forms of the equations for film growth and change in adsorbate concentration are (Andrews and Tien, 1981)

$$\frac{dk_1 x}{d\tau} = \frac{N_T - N_A - Sk_1 x}{\rho} \tag{11}$$

$$\frac{dq}{d\tau} = \frac{N_A}{a} \tag{12}$$

$$x = x_0 \quad q = 0 \quad \text{at } \tau = 0.$$

The final term in Eq. 11 is a lumped term that approximates the effects of cell wash-off, cell maintenance requirements, endogenous metabolism, and other processes that cause the film to decay as it grows thicker. Note that in the absence of mass-transfer resistance in the bacterial film, the substrate uptake rate onto the film (per unit volume of clean particles) would be $k_v xs$. Therefore, the quantity $(N_T - N_A)/k_1 xc$ is an effectiveness factor and must be less than one. It follows that the right hand side of Eq. 11 is negative, and the film declines, whenever $c < S$. So the value of the parameter S for a particular wastewater will determine whether or not a bacterial film develops in an adsorption column.

The uptake rates N_T and N_A depend not only on the film volume, x, and the adsorbate concentration, q, but also on the substrate concentration, c (Eqs. 7–9). So, Eqs. 11 and 12 show that the values of x and q for a particle at any time will depend on two things; the number of cells on the particle at time zero, and the history of substrate concentrations to which it has been exposed since then. The latter depends on the history of the particles position in the bed and thus on the solids mixing condition. Since both the number of bacteria on a carbon particle at time zero and the velocity vector of a particle in a fluidized bed are random variables, this implies that each particle can in general have a unique set of values of x and q. There would be one set of Eqs. 11 and 12 for each particle.

A solution for this case is clearly impossible, not just because of computational complexity but also because the theory of solids mixing in liquid fluidized beds is not sufficiently advanced to provide the required information about particle position. So, the solution is given only for the two extreme cases of solids mixing. The important simplifying feature of both of these cases is that particles that start with the same value of x_0 are all exposed to the same history of substrate concentrations.

Solids Mixing and Stratification

Whatever the solids mixing condition, the particles at time zero will not be evenly covered with film, and film growth will always be faster on particles at the base of the bed than on those at the top.

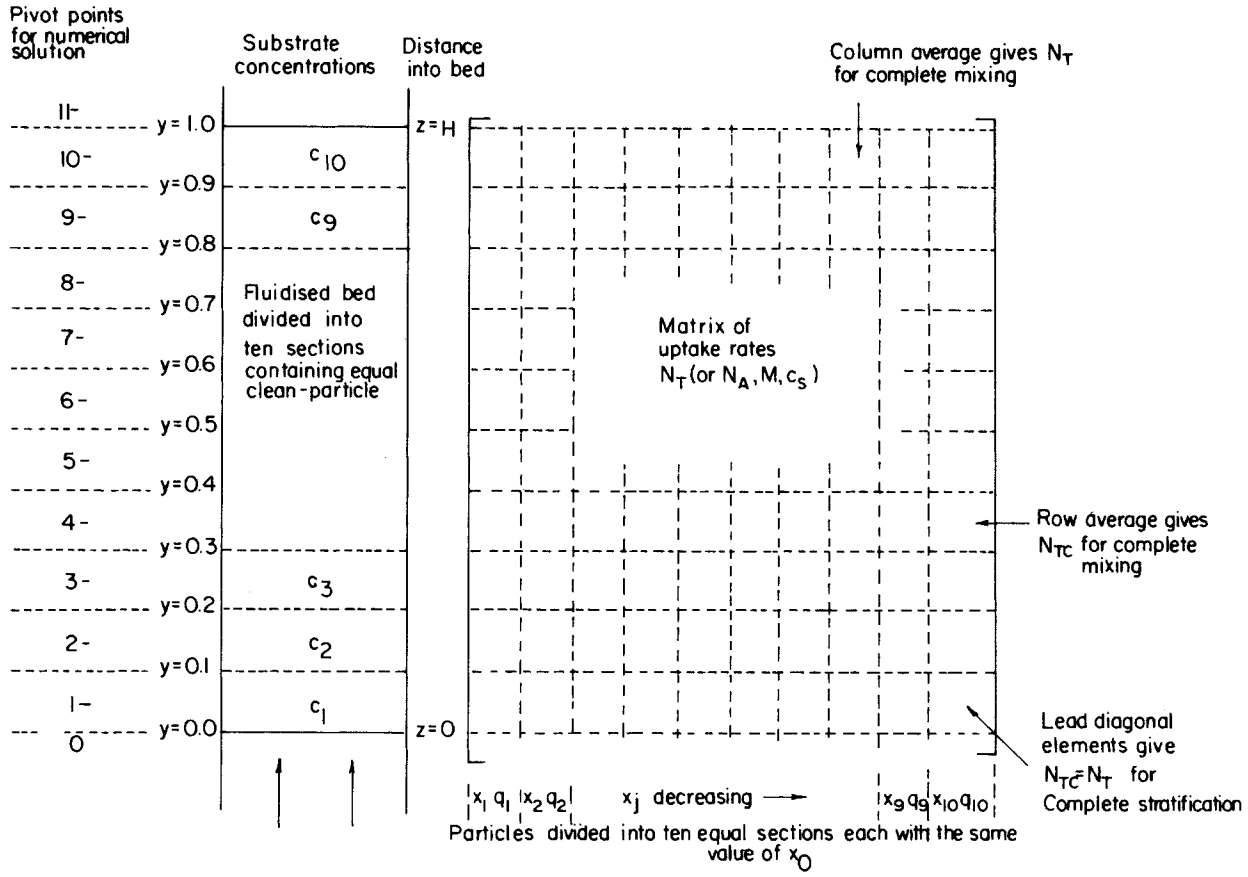

Figure 3. Calculation of uptake rates.

So film volume must be represented not by a single value, x, but by a distribution function $g(x)$ with a finite variance. For computational purposes $g(x)$ is given by a ten-valued discrete distribution; that is the particles are divided into ten equal groups all the particles in any group having the same value of x (and q).

The bed may also be divided vertically into ten compartments at equal increments of the variable y. Each compartment therefore contains an equal number of particles. It is assumed, again for computational purposes, that the substrate concentration is constant throughout each compartment. This means that any quantity that is a function of c, x and q (N_T, N_A, c_s, M, γ) can be represented as a 10 × 10 matrix (figure 2).

Consider first the condition of complete solids mixing. In a completely mixed bed all particles spend equal amounts of time in all parts of the bed. So, N_T and N_A in Eqs. 11 and 12 (which are in fact averages over a time increment $d\tau$) must be given by an average over a column of the relevant matrix. Note that there is one pair of values for N_T, N_A and one pair of Eqs. 11 and 12 for each group of particles. But $dx/d\tau$ and $dq/d\tau$ will be identical for all the particles in a group, so x and q will continue to be the same for all the particles in the group after any time increment.

Another characteristic of a completely mixed bed is that each compartment must contain a complete sample of the distribution $g(x)$ at any instant. It follows that N_{Tc} in Eq. 5 (the substrate uptake rate averaged over all the particles exposed to substrate concentration c) is given by an average over a row of the N_T matrix.

It is generally believed that, in the absence of any tendency for random solids mixing, a liquid-fluidized could be analyzed like an upflow packed bed. For a bed of non-monosized particles of unchanging settling velocity this is perfectly true. Such a bed would stratify according to particle settling velocity shortly after the flow was started (Scarlett and Blogg, 1967) and the particles would thereafter remain in the same relative positions. However, we are considering here a bed of monosize particles whose settling velocity drops as the bacterial film develops. Because film growth is fastest at the base of the bed where the substrate concentration is highest, the packed-bed assumption would predict low settling velocities at the base of the bed and high settling velocities at the top. Such inverse stratification would not be maintained in practice.

The true opposite extreme from complete solids mixing is a condition of complete stratification, in which no particle is ever above another that has a higher settling velocity. This situation is easily represented in the matrix of Figure 3 if the groups of particles are arranged in order of increasing settling velocity (Figure 1 shows that this is usually, but not necessarily, the order of decreasing x). Given complete stratification the top bed compartment would then be filled by the first group, and so on down the bed. So only the lead diagonal elements of the matrices of N_T, N_A, etc. are relevant to the problem.

TABLE 1. BASE PARAMETER SET

Fortran Variable	Algebraic Equivalent	Value
AP	a	1000
B	B	0.1
BP	b	1
K	K	0.001
$K1$	k_1	1
HC/DC	$\frac{H_c}{d_c} = \frac{v}{d_c(1-\epsilon_c)}$	6120
GA	Ga	356
N	n	3.5
R	R	8.61
S	S	0.1
RE	Re_c	1.3
YV	$1/\rho$	0.0005
EPC	ϵ_c	0.65
KVT Increment	$\Delta\tau$	200
	$g(x_0)$	(1.9, 1.7, 1.5, 1.3, 1.1, 0.9, 0.7, 0.5, 0.3, 0.1) × 10^{-3}

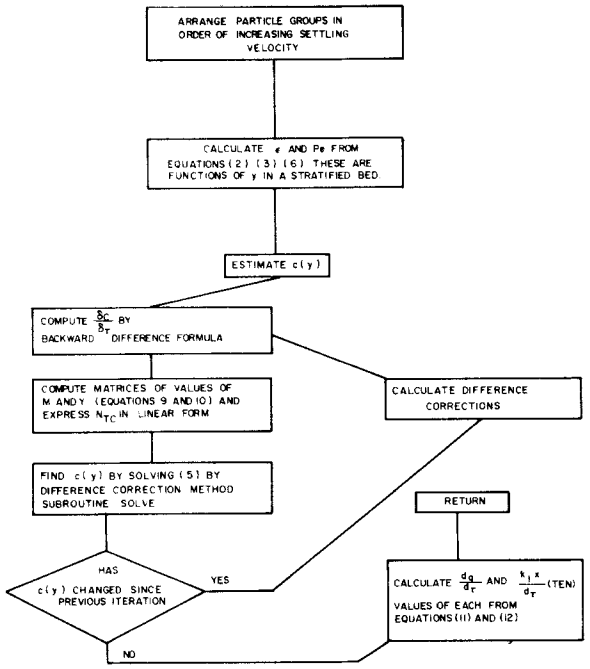

Figure 4. Subroutine FCT.

Several points should be noted here. First, the N_{Tc} of Eq. 5 is now equal to the N_T of Eq. 11. Second, as in the complete mixing case there is one pair of Eqs. 11 and 12 for each group of particles, a total of 20 equations. Third, again as in the completely mixed case, all the particles in a group will have identical values of $dq/d\tau$ and $dx/d\tau$, so x and q will remain the same throughout the group. Fourth, the complete stratification condition is self-destructive. Particles lightly covered with film are at the base of the bed where the film growth rate is high, while heavily covered particles are at the top where the growth rate is low. So the variance of the distribution $g(x)$ will tend to zero and the particle ordering imposed by stratification will disappear. A completely stratified bed in which all particles have the same settling velocity is a contradiction in terms (it requires that all the particles be at exactly the same height in the bed). What actually happens is that any particle that achieves an incremental gain in film volume immediately moves up the bed to a region of lower film growth rate. The bed is disordered but regulates itself to keep the same film volume on all particles.

NUMERICAL SOLUTION

Complete details of the Fortran program used to solve Eqs. 2–12 for the two solids mixing conditions is given by Andrews (1979).

In choosing an algorithm to solve Eqs. 11 and 12 (ten of each) a major consideration was to achieve a reasonable mathematical representation of the disordered stratified bed discussed above. Most algorithms would require that the order of the particle groups in the bed remain the same throughout the integration interval $\Delta\tau$. This does not correspond with the reality of continuous rearrangement of particles in response to small differences in film volume. A second-order Runge-Kutta routine was adopted because it gives the following, intuitively reasonable approximation to this reality: (1) The growth rates of x and q are calculated based on the completely stratified order of the particle groups at time τ. (2) x and q at $\tau + \Delta\tau$ are calculated assuming these rates are maintained throughout $\Delta\tau$. (3) Since this gives a bed not properly stratified at $\tau + \Delta\tau$ the particle groups are rearranged in order of decreasing settling velocity up the bed (thus changing the substrate concentration to which each group is exposed). (4) The growth rates of x and q at $\tau + \Delta\tau$ are calculated with this new arrangement. (5) The actual growth rates during $\Delta\tau$ are taken as the average of (1) and (4) and new values of x and q at $\tau + \Delta\tau$ are computed. (6) The particle groups are again rearranged to give complete stratification at $\tau + \Delta\tau$.

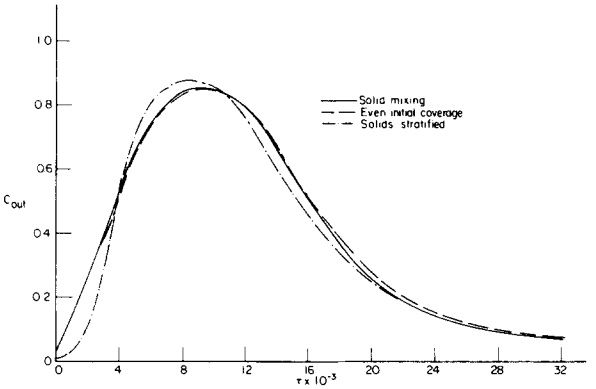

Figure 5. Effect of solids mixing on the breakthrough curve.

In order to calculate the growth rates of x and q (the right hand sides of Eqs. 11 and 12) the substrate concentration profile through the bed ($c(y)$) must be known. This involves solving Eq. 5, a procedure carried out by sub-routine *FCT* (Figure 4). The procedure is iterative, based on estimating $c(y)$ and using this estimate to compute the coefficients M and γ in the linearized form of the uptake rate (N_{Tc}) and the values of the accumulation term [the right hand side of Eq. 5]. Using an estimate for the accumulation term is justified because, after the short start-up transient, it is small compared with the other terms. This reduces Eq. 5 to an ordinary linear differential equation solvable by the difference correction method (Fox, 1957). This procedure converged in less than ten iterations for all conditions studied.

The pivot points used in the difference-correction solution are shown in Figure 3. It is more usual when dealing with differential boundary conditions to establish pseudo pivot points outside the bed. This was not possible in this case because there is no rational way of extrapolating the values of ϵ and Pe to points outside the bed. This limits the ability of the program to accurately predict very sharp concentration profiles. For example, the plug-flow, adsorption-only solution with $q = 0$ and $b = 1$ will maintain three figure accuracy only if $RKa < 15$. For taller beds or larger rate constants the y increment must be reduced from its present value of 0.1.

The accuracy of the numerical method developed in this work was tested by applying the method to specific problems with known and exact solutions. In all cases the agreement between the numerical solution and the exact solution was good. Details of the comparison were given in Andrews' dissertation (1979).

RESULTS AND DISCUSSION

The parameter values used for the sample calculations are shown in Table 1. They are based on a bed of monosized, 35 mesh particles

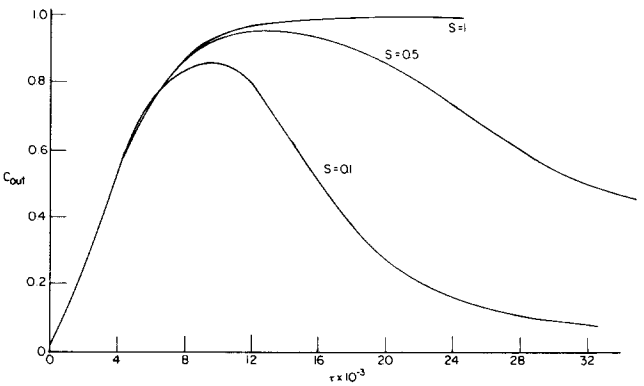

Figure 6. Effect of the film decay parameter.

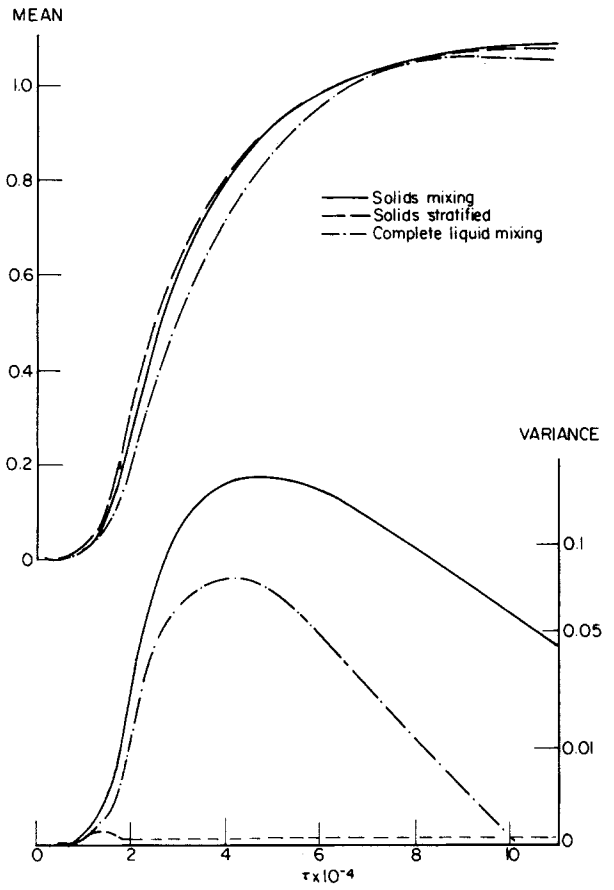

Figure 7. Effect of mixing on $g(x)$.

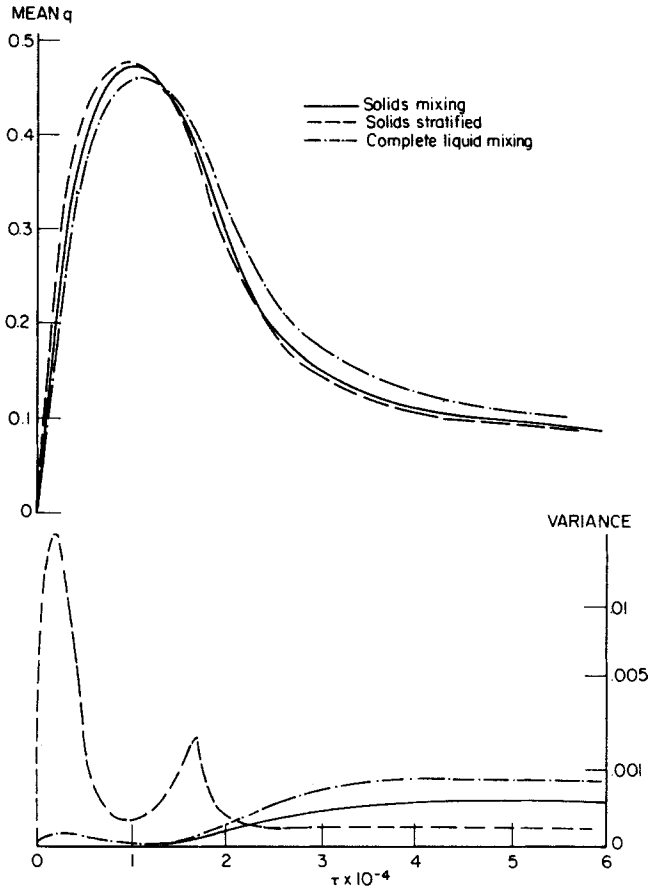

Figure 8. Effect of mixing on the adsorbate concentration.

with a superficial velocity of 15.6 cm/min giving a clean-bed porosity of 65% and a clean-bed height of 3.05 m. The initial film volume, x_0, is assumed to have a uniform distribution between 0 and 0.002. The average (10^{-3}) corresponds to roughly $\frac{1}{5}$ of complete monolayer coverage with cells of 1 μ diameter. Procedures for evaluating the other parameters for a wastewater were given by Andrews and Tien (1981).

The breakthrough curves predicted for these conditions are shown in Figure 5. There is an initial absorption phase, during which adsorption keeps the substrate concentration low so that film growth is inhibited. Then as the carbon saturates, the substrate concentration rises, the bacterial film grows rapidly and bacterial removal causes the substrate concentration to fall again to a steady-state value. The shape of the curve for the stratified bed during the adsorption phase is similar to that observed for packed beds. This happens because the different values of x imposed on the particles at time zero creates stratification and thus keeps the relative positions of the particles constant. The sharp rise in the curve happens at the point that the bed becomes disordered. Given even coverage at time zero ($x_0 = 10^{-3}$) the bed is always disordered and the stratification and solids-mixing cases are virtually indistinguishable. (Only one line is shown for this case in Figure 5.)

Figure 6 shows that the speed and extent of film growth are strongly dependent on the value of the parameter S. This depends on the biodegradability of the substrate, the inlet concentration and the film decay processes (cell maintenance requirements, wash-off, etc.). Since it determines whether bacterial activity will be significant in the bed, estimates of S are important for the designers of adsorption columns.

The breakthrough curves measured by Weber et al. (1972) did not have the bell shape of Figure 5, but rose slowly from $c = 0.04$ to $c = 0.50$ (approximately) over a period of months. This difference appears because they used a bed of 8 × 35 mesh carbon, not monosized particles. Stratification of this bed would be based on particle size, and would not be greatly affected by film growth (i.e., the bed would never become completely disordered). Once the carbon at the base of the bed was saturated it would be exposed to the inlet substrate concentration, so film growth would be rapid. Consequently bacterial uptake could replace adsorption as the main removal mechanism before breakthrough could occur at the top of the bed.

The effect of the solids mixing condition on the development of the bacterial film is shown in Figure 7. Once the adsorption phase is over, the mean value of the distribution $g(x)$ increases to a steady-state value determined by the film decay processes. The solids mixing condition has little effect on the mean of $g(x)$ but a dramatic effect on the variance. For a stratified bed the variance drops to zero as expected as the bed becomes disordered. For a completely mixed bed the variance rises rapidly. This happens because the film rate depends on substrate concentration and on the amount of film present. When all particles are exposed to the same average substrate concentration the thickest films will grow fastest.

So complete mixing, like complete stratification, is a self-destructive condition. The variance of $g(x)$ (more exactly, the variance of the distribution of settling velocities) is the driving force for bed stratification so, if complete mixing goes on long enough and the variance of $g(x)$ gets large enough, a bed would tend to stratify. It follows that a real bed must achieve a stable operating point at which random mixing (which increases the variance of $g(x)$ and thus the tendency towards stratification) is balanced by stratification (which reduces the variance of $g(x)$ and thus allows more mixing). This operating point will be characterized by a certain value of the variance of $g(x)$.

Figure 8 shows the variation with time of the distribution of the adsorbate concentration in the particles. The mean value rises to a maximum during the adsorption phase. However, as the bacterial film develops, the substrate concentration at the film/carbon interface drops causing some adsorbate to desorb. This bioregeneration causes the mean adsorbate concentration to drop to a steady-state level. It also causes the non-zero variance in the distribution of q during the bacterial growth phase.

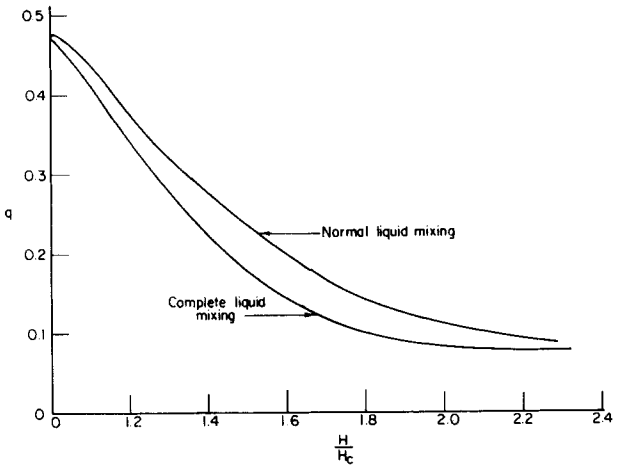

Figure 9. Adsorbate concentration at the top of a stratified bed.

In a stratified bed the bioregenerated particles, that is those heavily coated with film, will be near the top of the bed. This raises the possibility that particles could be taken from the bed, washed clean of film, and returned to the bed for further adsorption. Figure 9 shows how the value of q at the top of the bed varies as the bed expands. Clearly, particles removed after the bed height had doubled would have significant adsorption capacity remaining.

This idea is obviously limited by the way bed stratification destroys the conditions that create it. But this does not happen in all possible operating conditions. Given complete mixing of the liquid (a condition approximated by a high liquid recycle ratio) a particle will be exposed to the same substrate concentration wherever it is located in the bed. So the solids mixing condition becomes irrelevant and the variance of $g(x)$ increases even for a completely stratified bed (Figure 7). So stratification will be maintained and the adsorbate concentration at the top of the bed will be low (Figure 9).

A similar result would appear if the substrate uptake rate on the film were zero-order instead of first order in substrate concentration. The dependence of the film growth rate on the position of the particle in the bed would be reduced and stratification could be maintained. The model is currently being expanded to explore this possibility.

ACKNOWLEDGMENT

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NOTATION

A = $Ka \tanh k_1 x$
a = maximum capacity of carbon for adsorbate k_1/s_{in}
B = buoyant density of bacterial film/buoyant density of clean carbon
b = Langmuir isotherm parameter/s_{in}
c = s/s_{in}
c_s = (substrate concentration at film-carbon interface)/s_{in}
D = diffusion coefficient of substrate in bacterial film, cm^2/h
D_d = axial dispersion coefficient, cm^2/s
d_c = diameter of carbon particle
e = exponent in drag coefficient correlation
$F(x)$ = $(1 + x)/(1 - \epsilon)$
Ga = Galileo number for a clean particle
$g(x)$ = distribution function of film volume over the particles
H = bed height
K = (adsorption rate constant)/k_v
k_1 = (volume to surface area ratio of a clean particle) $(k_v/D)^{1/2}$
k_v = substrate uptake rate constant in the film, h^{-1}
M = linearization 'constant" in Eq. 9
n = exponent in bed porosity correlation
N_A = dimensionless rate of adsorption (normalized like N_{Tc})
N_T = dimensionless substrate uptake rate onto particle (normalized like N_{Tc})
$\overline{N}_{Tc}$ = total substrate uptake rate (per unit clean particle volume) averaged over all particles exposed to substrate concentration c, mgL·h
N_{Tc} = $k_1 \overline{N}_{Tc}/k_v s_{in}$
P = $2\beta A/(b + A + \beta)^2$
Pe = $uv F(x)/D_d \epsilon$
q^* = dimensionless adsorbate concentration in equilibrium with C_s
q = $\dfrac{\text{average adsorbate concentration in a carbon particle}}{\text{maximum capacity of carbon for adsorbate}}$
R = $k_v v/uk_1$
Re = particle Reynolds number
S = (Film decay rate constant) ρ/k_v
s = substrate concentration, mg/L
t = time
u = superficial liquid velocity, cm/s
u_s = particle settling velocity, cm/s
v = clean particle volume per unit area of bed, cm
x = film volume/clean particle volume
y = fraction of the total clean particle volume that is below a point in the bed
z = distance into bed, cm

Greek Symbols

β = $c\ sech\ k_1 x + qA$
γ = parameter defined by Eq. 10
ϵ = bed porosity
ρ = (cell density in film)/(cell yield coefficient) × s_{in}
τ = $k_v t$
$\Delta\tau$ = increment of τ used in numerical solution

Subscripts

o = value at time zero
in = value at column inlet
c = value for a clean particle (no film)

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A Dynamic Method for Liquid-Particle Mass Transfer in Trickle Beds

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Previous investigations of liquid-to-particle mass transfer in trickle beds have used non-porous particles. However, the applications of trickle beds have been for reactions or adsorption employing porous catalysts as adsorbents. In this study a method of dynamic adsorption with porous particles is developed. The procedure is to extrapolate the response to a step-function input of non-volatile adsorbate to a short time where intraparticle diffusion and adsorption do not affect the overall process.

The method is applied to the adsorption of benzaldehyde from aqueous solutions in a bed of granular, activated carbon particles. Measurements were made for three particle sizes, in adsorbers of two diameters, at 298K and 1 atm. The gas flow rate had no discernible effect on the mass transfer coefficients, $k_{Ls}a_{Ls}$, over a superficial velocity range of 1.47 to 8.0×10^{-2} m/s, but $k_{Ls}a_{Ls}$ increased with liquid rate. The results, correlated as Sherwood vs. Reynolds number, agree well with the non-porous particle data of Van Krevelen and Krekels (1948), but suggest larger Sherwood numbers than similar data from later investigations.

The wide range of mass transfer results for either liquid-to-particle or liquid-to-gas in trickle beds seems to be due in large measure to the difficulty in reproducing the rivulent flow pattern of liquid from bed to bed.

SCOPE

Van Krevelen and Krekels (1948) used the dissolution technique (benzoic acid particles dissolving in water and glycol solutions) in one of the first studies of mass transfer in trickle beds. They measured liquid-particle transfer coefficients in downflow of liquid over the particles; a gas phase was present but there was no gas flow. Since then all published data have been obtained by the same dissolution method using various kinds of non-porous particles. The dissolution technique has several advantages, but the time required to reach steady state (Satterfield et al., 1978) and particle shrinkage may affect the results. However, the most important reason for seeking another method is that most applications of trickle beds employ porous catalyst particles.

A critical requirement of a method for porous, catalyst-type particles is that a minimum of rate parameters be involved. To eliminate rate constants for catalytic reaction (and associated problems, such as variable catalyst activity) an adsorption process is desirable. However, the process now becomes a dynamic one. If the adsorption is of the rapid, physical type, equilibrium may be assumed at the adsorption site within the particle. A non-volatile adsorbate is necessary if mass transfer from liquid to gas is to be avoided. A system that meets these and other requirements reasonably well is the adsorption of benzaldehyde (vapor pressure at 298K = 127 Pa) from aqueous solutions in a bed of activated carbon particles. In this system intraparticle diffusion in the liquid-filled pores, as well as the desired mass transfer process from liquid to particle, may affect the concentration of benzaldehyde in the effluent liquid. However, intraparticle diffusion can be eliminated from dynamic adsorption results by extrapolating the data to essentially zero time.

This paper reports mass transfer coefficients measured in this way at 298K and atmospheric pressure. Results were obtained for gas and liquid flow rates in the gas-continuous flow regime.

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