ΔT = time interval during which $X(t)$ locates itself between x and $x + \Delta x$, Eq. 1
U = superficial gas velocity
U_{mf} = superficial gas velocity at minimum fluidization
$X(t)$, $Y(t)$ = random variables

Greek Letters

μ = mean
μ_r = r-th central moment about the mean
σ = standard deviation
σ^2 = variance
τ = time shift variable, Eqs. 9 and 10
ϕ_{xx} = auto-correlation function of $X(t)$
ϕ_{xy} = cross-correlation function between $X(t)$ and $Y(t)$
ϵ = voidage of the bed
ϵ_{mf} = voidage at minimum fluidization
ω = angular frequency

LITERATURE CITED

Bendat, J. S., *Principles and Applications of Random Noise Theory*, John Wiley and Sons, Inc., New York (1958).
Brown, R. G., and J. W. Nilsson, *Introduction to Linear Systems Analysis*, John Wiley and Sons, Inc., New York (1962).
Crandall, S. H., and W. D. Mark, *Random Vibrations in Mechanical Systems*, Academic Press, New York (1963).
Davenport, J. B., and W. R. Root, *An Introduction to the Theory of Random Signals and Noise*, McGraw-Hill Book Co., Inc., New York (1958).
Fan, L. T., C. J. Lee, and R. C. Bailie, "Axial Solid Distribution in Gas-Solid Fluidized Beds," *AIChE J.*, **8**, 239 (1962).
Fiocco, R. J., Sc. D. Thesis, Stevens Institute of Technology, Hoboken, N. J. (1964).
Hiby, J. W., *Proceedings of the International Symposium of Fluidization, Eindhoven*, Netherlands Univ. Press, Amsterdam, p. 99 (1967).
Kadlec, R., "The Behavior of Slugging Gas-Fluidized Solids," Ph.D. Dissertation, University of Michigan (1962).
Kang, W. K., J. P. Sutherland, and G. L. Osberg, "Pressure Fluctuations in a Fluidized Bed with and without Screen Cylindrical Packings," *I&EC Fundamentals*, **6**, 449 (1967).
Lee, Y. W., *Statistical Theory of Communication*, John Wiley and Sons, Inc., New York (1960).
Lirag, R., and H. Littman, *Statistical Study of the Pressure Fluctuations in a Fluidized Bed*, AIChE Symp. Ser., **67**(116), 11 (1971).
Littman, H., and G. A. Homolka, "Bubble Rise Velocities in Two-Dimensional Gas-Fluidized Bed from Pressure Measurements," *Chem. Eng. Prog.*, **66** (105), 37 (1970).
Shuster, W. W., and P. Kisliak, "The Measurement of Fluidization Quality," *Chem. Eng. Prog.*, **48**, 455 (1952).
Sutherland, K. S., Argonne National Laboratory, Rept. ANL-6907 (1964).
Swinehart, F. M., "A Statistical Study of Local Wall Pressure Fluctuations in Gas Fluidized Columns," Ph.D. Dissertation, University of Michigan (1966).
Tamarin, A. I., "The Origin of Self-Excited Oscillations in Fluidized Beds," *Int. Chem. Eng.*, **4**, 50 (1964).
Verloop, J., and P. M. Heertjes, "Periodic Pressure Fluctuations in Fluidized Beds," *Chem. Eng. Sci.*, **29**, 1035 (1974).
Winter, O., Density and Pressure Fluctuations in Gas Fluidized Beds," *AIChE J.*, **14**, 426 (1968).
Wong, H. W., and M. H. I. Baird, "Fluidization in a Pulsed Gas Flow," *Chem. Eng. J.*, **2**, 104 (1971).

Manuscript received September 14, 1979; revision received July 21, and accepted July 25, 1980.

Bacterial Film Growth in Adsorbent Surfaces

G. F. ANDREWS
and
CHI TIEN

Department of Chemical Engineering and Materials Science
Syracuse University
Syracuse, NY 13210

Simultaneous biological and activated-carbon treatment of organic wastewaters appears promising. The effects of bacterial film growth on adsorbent particles is investigated by laboratory work and mathematical modelling. Regeneration of the adsorbent due to film growth does occur, but faster than predicted. The discrepancy reflects uncertainty about the structure of bacterial films.

SCOPE

A promising method for removing soluble organic matter from wastewater is to combine biological treatment and activated carbon adsorption into a single unit. This is demonstrated by the PACT system (addition of powdered carbon to an activated sludge unit), the effects of bacterial growth in carbon adsorption columns, and various proposals for the biological regeneration of spent carbon.

This paper provides a mathematical model on which the design and evaluation of such systems can be based. It predicts the uptake rates of organic matter due to adsorption and biological activity when a bacterial film grows on a granular carbon particle. The predictions are compared with experimental data from a laboratory-scale, fluidized-bed reactor operated with a high-recirculation rate. The organic substrate is valeric acid, and denitrifying bacteria are used.

Unlike previous work, this model is applicable to films which are actively growing and are thick enough to cause bioregeneration. Also, all theoretical and practical work is done in a way that could be repeated on a real wastewater whose constituents are dilute, soluble, biodegradable, and adsorbable. Procedures are given for the measurement of all but one of the model's parameters. The bacterial growth rate and yield values are determined from experiments with beds of nonadsorbing coal particles.

G. F. Andrews is presently with the Department of Chemical Engineering, State University of New York at Buffalo, Buffalo, NY 14262.

CONCLUSIONS AND SIGNIFICANCE

Combined biological-activated carbon treatment systems are best studied by measuring the changes they produce in both the total carbon and dissolved organic carbon concentrations in the wastewater. The ratio of these quantities, the yield ratio, is shown here to be an important indicator of the relative significance of adsorption and bacterial growth. It equals one for pure adsorption and is related to the yield coefficient in a purely bacterial system. A low or negative value indicates that bioregeneration of the carbon is occurring.

The total carbon measurements permit the determination of the film density and the yield and decay coefficients for bacterial films growing on nonadsorbing surfaces. Because such data is rare in the literature, the procedure will be valuable in work on the secondary treatment of wastewaters by fluidized beds of biomass-coated sand or coal.

Adsorption of valeric acid on Darco carbon is reversible with similar kinetics for adsorption and desorption. Bacterial film growth on the carbon surface does cause bioregeneration. The mathematical model, based on simple rate equations, gives a reasonable description of the process but apparently under estimates the rate of bioregeneration.

This work is significant because it provides a theoretical and practical framework for the examination of ways of combining adsorption and bacterial growth. The model includes not only the individual effects of these two processes, but also the two main interactions between them; the extra mass-transfer resistance for adsorption created by the bacterial film, and the bioregeneration of the adsorbent. So, any systematic deviation between the model and experimental data probably results from a new and possibly beneficial interaction. It is believed that the observed bioregeneration rate appears high because the flow of new substrate from the adsorbent to the film base changes the composition of the film. The model is based on the assumption that the yield coefficient, film porosity, substrate diffusivity, etc. in the film, are independent of the film thickness and the type of surface it grows on. Further work is required to determine whether this is valid.

Recent studies have shown that biological treatment and adsorption on activated carbon work well together in the removal of organic matter from wastewaters. This is demonstrated by the success of the PACT system, in which powdered, activated carbon is added to an activated sludge unit (Flynn and Standick 1977), and by bioregeneration systems in which spent carbon is regenerated by contact with an active bacterial culture (Rodman and Shunney 1971). The work of Weber et al. (1972), amply supported by more recent operational experience (Guirgis et al., 1978), also showed that bacterial growth in activated carbon adsorption columns can significantly increase the apparent capacity of the carbon.

There are two main reasons for this useful, cooperative activity. First, bacteria and activated carbon tend to be complementary in the type of molecule they remove from solution (Andrews, 1979). For example, aromatic compounds generally have a higher affinity for carbon than aliphatic compounds, but they tend to be more resistant to biodegradation. The common bacterial substrates (saccharides, hydroxy- and amino-acids) are also very soluble; therefore, adsorb poorly on carbon. An important, extreme case of this effect occurs when the carbon removes from solution molecules which are toxic or inhibitory to bacteria.

The second reason is bioregeneration. Although bacteria are too large to enter the pores of activated carbon, their activities (either in the liquid phase or growing as a film on the carbon surface) reduce the concentration of biodegradable organics at the carbon surface. So, any reversibly-adsorbed, biodegradable molecules will tend to desorb and diffuse out of the carbon to the bacteria. A notable feature of this process is its selectivity for biodegradable molecules. The concentrations of nonbiodegradable and toxic organics are unaffected by bacterial activity, so they will remain safely adsorbed on the carbon. Given their generally higher adsorption affinity (suggested in the previous paragraph), they may even accelerate the bioregeneration process by displacing adsorbed biodegradable molecules from the surface.

The extent to which adsorption on activated carbon is reversible has received little attention. Mattson and Mark (1971) caution against analyzing the little that is known in terms of the classical distinction between reversible physical adsorption and irreversible chemisorption. But, they point out that low net energies of adsorption are involved so some desorption is expected. Studies at Syracuse University have shown that the adsorption of phenol on Darco carbon is approximately 50% reversible, while the adsorption of valeric acid is completely reversible.

Some authors include a third reason for the cooperation between bacteria and activated carbon. This is the stimulation of bacterial growth provided by the presence of the carbon surface. It is not included in the present list because it is not specific to adsorbent surfaces. With a dilute substrate, almost any surface stimulates growth (Dept. of the Environment, 1972). Therefore, in order to assess the true effect of adsorption on the overall removal of organic matter, a reactor containing adsorbent must be compared with one containing an equal area of nonadsorbing surface (Perotti and Redman, 1973), a requirement that is often overlooked. The same effects is achieved in this work by measuring the growth rate and yield parameters for bacteria growing on coal particles. These values are then used to predict the growth on activated carbon.

OBJECTIVE

A mathematical model capable of predicting the overall removal of organic matter by a biological/carbon system would clearly be useful. It could be used for the design of existing types of systems (PACT, adsorption columns) as well as the evaluation of new systems that take advantage of the bacteria/carbon cooperation. The objective of this work is to develop and test such a model for the case where the bacteria grow as a film on the carbon surface.

This is the first published model to incorporate the effects of a film that is actively growing over a wide range of film thicknesses. Some previous models (Jennings, 1975; Benedek, 1975) considered the film thickness as a fixed, externally defined parameter. This is obviously inadequate in, for example, an adsorption column where a cycle of operation starts with fresh carbon with few bacteria, and the adsorbate concentration and bacterial film thickness increase together. Other models (Andrews and Tien, 1974) have allowed bacterial growth, but were based on rate equations that broke down at large film thicknesses. The work of Ying and Weber (1978) was based on the plausible assumption that the maximum film thickness in an adsorption column would be controlled by regular washing and air scouring of the bed. Unfortunately, the maximum thickness is assumed to be very small (less than monolayer coverage of the surface with bacteria) and the model becomes invalid when the film is thick enough to present a significant mass transfer resistance to adsorption.

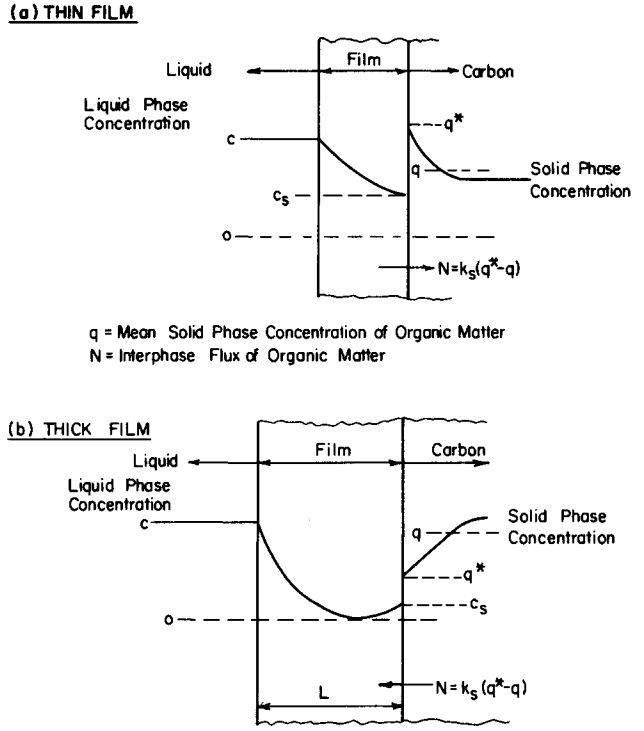

Figure 1. Growth of bacterial film on an adsorbent surface.

A general problem in modelling wastewater systems is that all waste streams are unique. The model's parameter values must, therefore, be determined by tests on the particular wastewater being considered. So, in this work the number of unknown parameters is held to a minimum (i.e., simple rate expressions are adopted), and original methods are given for their determination. Although the experimental work is done in the laboratory using synthetic wastewater, all concentrations are measured as Total Organic Carbon (TOC), a system directly applicable to real wastes.

THEORY

The basis of the model is shown in Figure 1(a). Organic substrate diffuses through, and is taken up by the bacterial film. The rate of adsorption into the carbon is based on the Glueckauf linear driving force, that is the difference between the equilibrium adsorbate concentration q^* (based on the substrate concentration at the film base C_s) and the average adsorbate concentration q. Figure 1(b) shows that bioregeneration appears naturally in this model. As time passes, the film grows thicker so C_s and q^* decreases, while q increases due to adsorption. Eventually $q^* < q$ and the Glueckauf expression predicts that substrate diffuses back into the film.

The assumptions made are:

- The organic substrate is soluble, biodegradable, and adsorbs reversibly on activated carbon.
- The film is homogeneous, i.e., its porosity, bacterial density, etc. do not vary with film thickness.
- The organic substrate is dilute and limits bacterial growth. Its uptake by the film follows first-order kinetics.
- The mass-transfer resistance of the external liquid film is negligible.
- The film grows as if on a flat surface.
- The film thickness is the same on all surfaces in the reactor.
- Bacterial activity in the liquid phase is negligible.

The substrate concentration (defined in practice in terms of the organic carbon content of the substrate) in the film is given by:

$$D\frac{d^2s}{dw^2} - k_v s = 0 \qquad (1)$$

$$s = C \qquad w = L$$

$$s = C_s \qquad w = 0$$

After solving this equation, the adsorptive and total uptake rates of substrate per unit volume of clean particles can be found:

$$N_A = \alpha D \left.\frac{ds}{dw}\right|_o = \frac{k_v}{k_1}\frac{C - C_s\cosh k_1 x}{\sinh k_1 x} \qquad (2)$$

$$N_T = \alpha D \left.\frac{ds}{dw}\right|_L = \frac{k_v}{k_1}\frac{C\cosh k_1 x - C_s}{\sinh k_1 x} \qquad (3)$$

The value of C_s is found from the continuity condition at the film base, which for a Langmuir-type isotherm is:

$$N_A = k_s\left(\frac{aC_s}{b + C_s} - q\right) \qquad (4)$$

Combining Eqs. 2 and 4 gives a quadratic equation for C_s.

The variation of film volume, x, and adsorbate concentration, q, with time is found from the conservation equations for biomass and adsorbate.

$$\frac{dx}{dt} = \frac{Y}{\rho}(N_T - N_A) - k_d x \qquad (5)$$

$$\frac{dq}{dt} = N_A \qquad (6)$$

Note that the first term on the right hand side of Eq. 5 is the growth term ($N_T - N_A$ is obviously the substrate uptake rate in the film). The second term is a decay term which accounts for both the basal metabolism (cell maintenance energy) of the bacteria and for wash-off of cells from the film.

To complete the set of equations, the type of reactor in which the particles are located must be specified. The experimental work was done in a reactor that approximated a stirred tank. The substrate conservation equation is, therefore:

$$\frac{d}{dt}[V - v(1 + x)]C = F(C_{in} - C) - v N_T \qquad (7)$$

This equation is based on the assumption that bacteria washed off the carbon remain intact. If they lyse they may contribute significantly to the dissolved organic carbon concentration (C).

The initial conditions for Eqs. 6 and 7 are $C = q = 0$ at $t = 0$. In the laboratory experiments, the carbon bed was deliberately seeded with bacteria before the start of a run. So, the initial condition for Eq. 5 is $x = x_o$, and no term is needed in Eq. 5 to describe the deposition of bacteria onto the carbon from the liquid phase (the deposition rate would be insignificant compared with the growth rate of cells already on the carbon). However, carbon in full-scale adsorption columns would be seeded by this deposition, and an exact description of this process would require some modification of Eq. 5 and the initial condition.

Eqs. 2 to 7 can provide a complete theoretical solution. It will be shown that in practice the extra information required to determine the parameter values and to answer the question "Is bioregeneration occurring?" can best be obtained by measuring the change in total carbon concentration through the reactor. Note that, when using a Beckman TOC Analyzer, this extra information comes with no extra effort since on this instrument the total carbon and inorganic carbon concentrations are measured separately, and the organic carbon is found from the difference.

Carbon enters the reactor as substrate and leaves as unused substrate, washed-out bacteria and carbon dioxide produced by bacterial respiration. Any carbon remaining in the reactor must be in the film or the adsorbate. This, if all the carbon dioxide formed remains in solution, there is an extra equation.

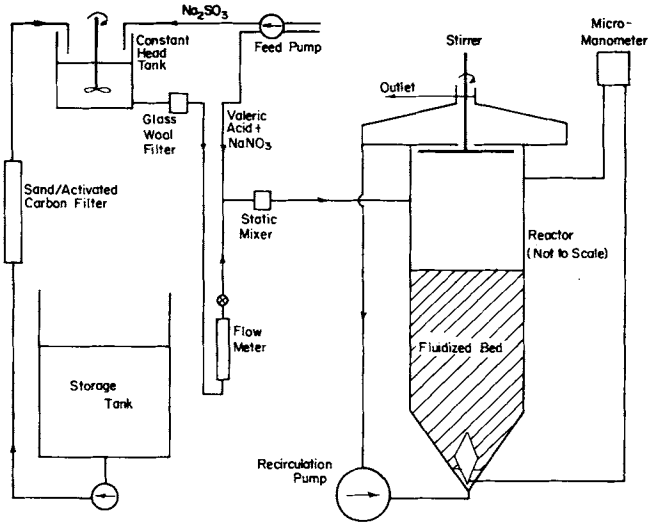

Figure 2. Equipment.

$$\frac{d}{dt}[V - v(1 + x)]\Delta TC = -F\Delta TC + v\left[\frac{dq}{dt} + \rho\frac{dx}{dt}\right] \quad (8)$$

The liquid residence time of the experimental reactor was small enough to allow the quasi-steady-state assumption. The left-hand sides of Eqs. 7 and 8 were, therefore, set to zero, and the resulting seven equations were solved numerically using a fourth order Runge-Kutta routine (Andrews, 1979).

Experiment

The apparatus is shown in Figure 2.

The reactor consists of a plexiglas column 7.62 cm diameter, 7.62 cm high containing a fluidized bed of 25 × 30 mesh coal or Darco activated carbon. The residence time is small enough so that substrate uptake by bacteria in the liquid phase is negligible. A detailed proof of this, and other details about the apparatus are given by Andrews (1979).

A mass balance at the point where the influent enters the reactor shows that the difference between the average substrate concentration in the bed ($\bar{C}$) and the effluent concentration (C) is given by $F(C_{in} - C)/2Q$. Because C_{in} is small and the flow rate through the bed (Q) is kept at a large constant value by the recirculation pump, $\bar{C} \approx C$. So, the reactor is equivalent to a stirred tank.

The reactor is fed by gravity from a constant-head tank. The feed stream consists of filtered, dechlorinated tap water containing valeric acid as the organic substrate and 2 mL/L of a nutrient/buffer solution (8.5 g KH_2PO_4, 21.75 g K_2HPO_4, 33.4 g Na_2HPO_4, 35 g NH_4Cl per liter). Sodium sulfite is added to the constant head tank to remove dissolved oxygen, and sodium nitrate (8.63 g/g of valeric acid) is then added to permit the growth of denitrifying bacteria. This system was adopted in preference to acrobic bacteria for several reasons. The low solubility of oxygen means that bacterial growth at the base of an aerobic film may be limited by oxygen rather than organic substrate. This would invalidate Eq. 1. Also, bubbling air or oxygen through the reactor may strip some of the carbon dioxide from solution, thus invalidating Eq. 8.

Bubbles of nitrogen gas produced by the denitrifying metabolism tend to adhere to the particles and carry them out with the effluent. The stirrer in the top of the reactor minimizes this problem by knocking the bubbles off. It also prevents short-circuiting of the reactor. The large-diameter chamber at the top of the reactor prevents the gas bubbles from being entrained in the recycle stream.

TABLE 1. EXPERIMENTAL CONDITIONS

Run	Particles	Particle Volume v,L	In flow F,L/h	Recirculation Ratio	Liquid Residence Time τ,h	Inlet DOC c,mg/L
1	Coal	0.369	10.9	15.0	0.351	40.0
2	Coal	0.289	10.9	14.9	0.366	26.5
3	Coal	0.239	11.5	14.6	0.348	31.7
4	Coal	0.267	11.7	15.9	0.342	23.7
5	Carbon	0.497	9.93	20.0	0.377	53.1
6	Carbon (20 × 25 mesh)	0.445	11.2	13.8	0.338	42.0
7	Carbon	0.340	8.17	22.1	0.447	30.6

TABLE 2. EXPERIMENTAL DATA: RUN 7

Time h	C_{in} mg/L	C mg/L	ΔTC mg/L	Time h	Outlet pH	Bed Height* cm	Outlet Temp. °C
2.5	30.9	9.2	22.4	3.3	7.0	24.9	24.8
5.3	30.9	14.4	15.8				
8.4	30.7	20.0	10.8				
11.6	30.7	24.2	6.4	12.3	7.1	25.1	23.8
14.2	30.4	25.7	5.2				
19.0	30.0	27.0	3.2	19.6	7.1	24.4	24.0
23.3	30.1	26.0	2.8				
26.3	30.6	26.1	3.2	26.8	7.2	23.9	25.5
31.5	30.4	24.6	2.2				
36.2	31.5	21.2	2.7	37.0	7.1	24.1	24.7
39.7	30.6	18.8	3.6				
43.7	30.4	12.6	3.0	44.3		26.9	25.0
47.1	30.5	8.1	4.7				
50.2	29.7	5.0	4.1	50.7	7.4	27.9	26.7
56.6	31.4	4.4	6.1				
62.6	30.0	3.8	7.4	61.9		31.8	26.1
70.2	30.8	3.7	8.2	71.0	7.4	36.1	26.6
79.9	31.0	3.6	7.6				
Measurement Error ±0.1	±0.5	±0.5	±0.5	±0.1	±0.05	±0.2	±0.1

*Measured from the top of the conical entrance section.

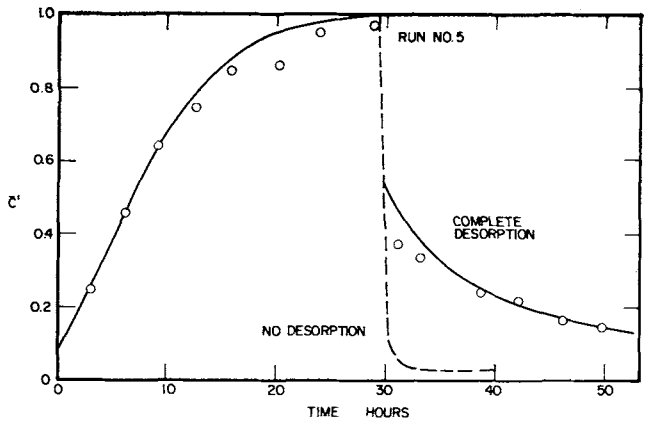

Figure 3. Comparison of theory and data—Run 5.

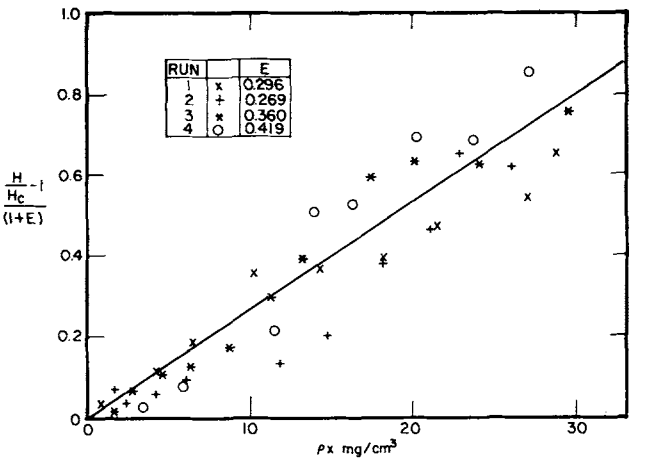

Figure 4. Variation of bed height with film volume.

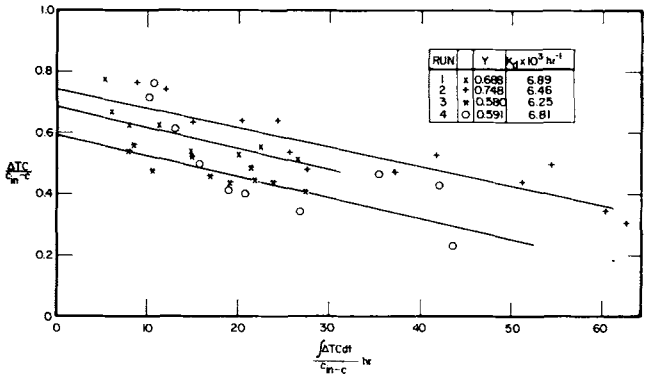

Figure 5. Variation of the yield ratio.

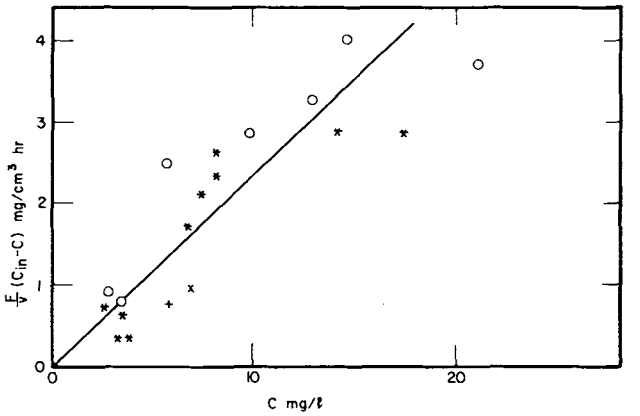

Figure 6. Substrate removal at steady state.

Before starting an experiment, the bed was washed to remove fines and seeded with a mixed culture of denitrifying bacteria. This culture was isolated from soil, and maintained on the experimental culture solution in shake flasks at room temperature. Seeding was done by filling the reactor with buffered distilled water (for experiments with activated carbon) or complete culture solution (for experiments with coal), adding a fixed volume of seed culture, and circulating this mixture slowly through the bed for 1-2 days. Attempts to measure the exact amount of bacteria deposited in the bed by this procedure were unsuccessful. The amount deposited was small, and it was masked by the natural growth or death of cells during the seeding period, and the generation of fines from the bed.

After starting the experiment, the inlet total carbon and inorganic carbon concentrations and the effluent total carbon concentration were measured every 4 to 8 hours using a Beckman 915A TOC Analyzer. An effluent sample was also taken, filtered through a 0.2μ membrane filter (which had been washed before-hand to prevent soluble organics leaching into the filtrate), acidified and sparged with nitrogen. The total carbon of the resulting solution gives the effluent-dissolved organic carbon concentration.

As a bacterial film develops, the bed expands to accommodate the extra volume. The bed height was measured at regular intervals. Experiments were terminated when the bed completely filled the column.

The conditions used in the seven completed runs are given in Table 1, and a typical data set for one run is shown in Table 2.

DETERMINATION OF PARAMETER VALUES

Adsorption Parameters

The adsorption isotherm for the organic matter in the experimental solution (valeric acid plus a small amount of phosphate buffer solution added to tap water) was measured in a batch experiment. Bacterial growth was prevented by eliminating all added nitrogen from the solution, and making it up to its original ionic strength by the addition of mercuric chloride. The isotherm was found to depend strongly on the solution pH, as is expected for a weak acid with pH = 4.82. Additional phosphate buffer was added as required to keep the pH in the range of the experiments (7.0 to 7.5). The data then showed good agreement with a Langmuir isotherm with $a = 14.8$ mg/cm^3, $b = 37.4$ mg/L (note that these are mg of organic carbon, not valeric acid).

The adsorption rate constant is estimated from the equations given by Hseih et al. (1977), which reduce to:

$$k_s = \frac{D_f \chi \, 23.3(b + C_{ref})}{ad^2[1 - 0.225r^{0.4}]} \tag{9}$$

Taking $C_{ref} = 20$ mg/L, the average concentration encountered in the experiments, gives $k_s = 0.651$ h^{-1}.

The validity of the adsorption rate equation and the reversibility of the adsorption were tested in Run 5. Bacterial growth was prevented by not seeding the bed, and by eliminating all added nitrogen from the feed stream. As soon as the carbon was saturated with adsorbate, the valeric acid in the feed was switched off. The results are compared with the theoretical predictions in Figure 3. For the desorption phase, theoretical results are shown based on the alternative hypotheses of irreversible adsorption, and completely reversible adsorption with identical kinetics for adsorption and desorption. The results show clearly that the latter hypothesis is correct.

Bacterial Parameters

The five biological parameters (Y, ρ, k_r, k_1, k_{tl}) are determined from the results of the four experiments (Runs 1-4) done with beds of nonadsorbing coal. It can be shown (Andrews, 1979) that, in the absence of adsorption, Eq. 2 to 8 reduce to:

$$\rho x = \frac{F}{v}\left[\tau \Delta TC + \int_0^t \Delta TC \, dt\right] \tag{10}$$

$$\frac{\Delta TC}{C_{in} - C} = Y - k_{tl}\frac{\int_0^t \Delta TC \, dt}{(C_{in} - C)} \tag{11}$$

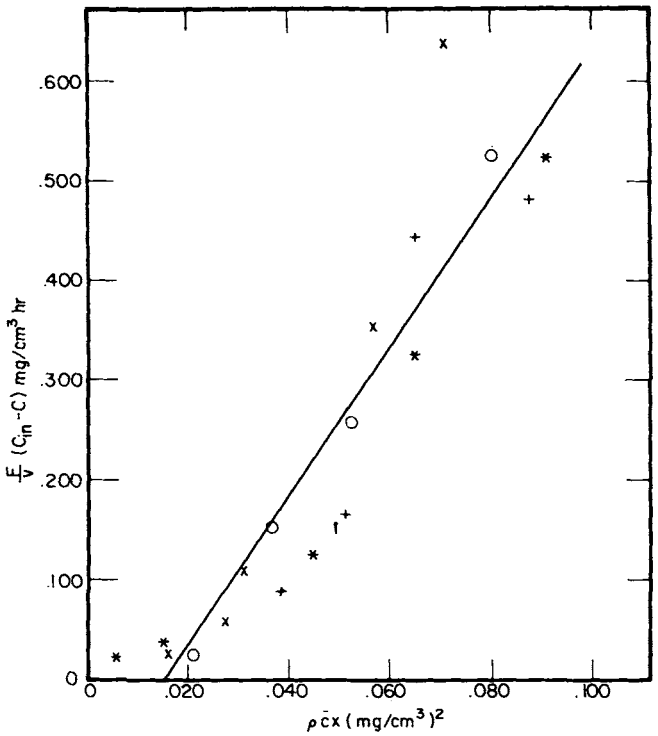

Figure 7. Substrate removal at small film volume.

$$\frac{F}{v}(C_{in} - C) = \frac{k_r C}{k_1} \tanh k_1 x \qquad (12)$$

In addition, Andrews and Tien (1979) have shown that the bed height varies with film volume as follows:

$$\frac{H}{H_C} = 1 + (1 + E)x \qquad (13)$$

E is a known constant that depends on the clean-bed porosity, the film density, the details of the bed-height, flow rate relation, etc.

The amount of bacterial organic carbon on the particles (ρx) can be found as a function of time from the total carbon measurements using Eq. 10. When the resulting data are plotted against bed height as in Figure 4, they should give a straight line of slope $1/\rho$ (see Eq. 13). In fact, the data show considerable scatter due to measurement errors in ΔTC, and the effects of particle agglomeration and nitrogen gas generation in the bed. The slope of the best line gives $\rho = 34.7$ mg/cm³, which is well within the range of 16 to 48 mg/cm³ expected for thin films from the data of Hoehn and Ray (1973) and the usual empirical formula for biomass $C_5H_7NO_2$.

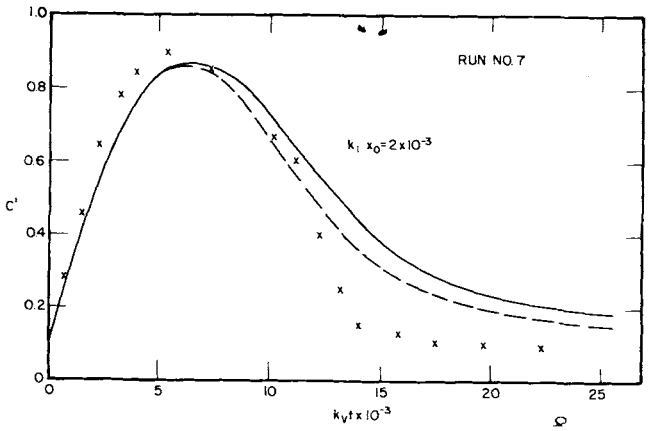

Figure 10. Theoretical and experimental substrate concentrations—Run 7.

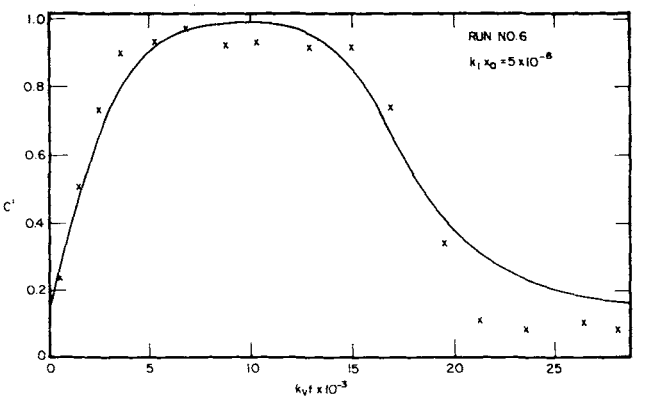

Figure 8. Theoretical and experimental substrate concentrations—Run 6.

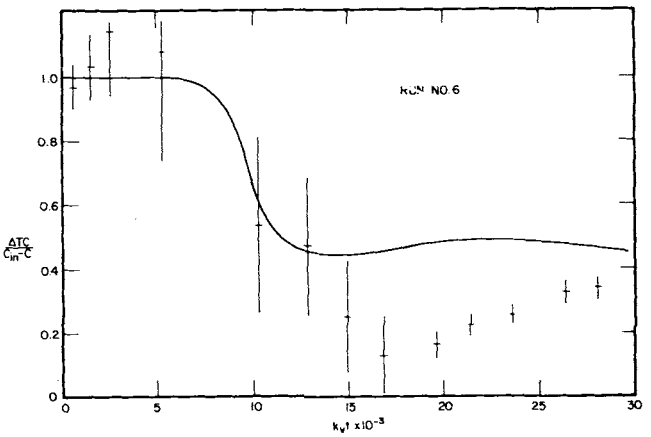

Figure 9. Theoretical and experimental yield ratio—Run 6.

The quantity $\Delta TC/(C_{in} - C)$ reappears throughout this work and will be known as the yield ratio. Eq. 11 shows that, when it is plotted as in Figure 5, the data should yield a single straight line of slope $-k_{rl}$ and intercept Y. The data are scattered due to the accumulation of measurement error in the computation of the yield ratio. Allowing for this error the data for each experimental run do fall on straight lines, and the value of k_{rl} is consistent between runs, with an average of 6.60×10^{-3} h^{-1} (note that the lines of Figure 5 are drawn allowing for the fact that the possible error in the yield ratio is different for each point). However, there is considerable variation in the yield coefficient between runs, the average being 0.652 ± 15%. The reasons for this are not understood, although it may be that the different substrate concentrations together with the slight variations in temperature (21 to 24°C) and pH (7.0 to 7.5) between runs caused differences in the composition of the biomass.

Eq. 12 shows that as the film volume grows larger $\tanh k_1 x$ approaches 1, and the substrate removal rate approaches a steady state. All the available data from this steady-state period is plotted in Figure 6. The slope of the best line gives $k_r/k_1 = 237$ h^{-1}. Unfortunately, the conflicting requirements of keeping the reactor behaving as a stirred tank and keeping the fluidized bed contained in the experimental column restrict the operating conditions under which this data can be taken to $C < 20$ mg/L. So, it is not possible to determine whether the first-order kinetics assumed for the bacteria is valid up to the highest substrate concentrations used in these experiments ($C = 40$ mg/L).

At small film thicknesses, when the mass transfer resistance of the film is negligible, $\tanh k_1 x$ approaches $k_1 x$. Eq. 12 predicts that when the data from this region are plotted as in Figure 7, they should give a straight line through the origin with slope k_r/ρ. Considering the experimental error, they do give a reasonable line, but it does not go through the origin. This may be due to nonfirst-order uptake kinetics, adsorption of some valeric acid by the coal, or incorrect estimation of the amount of biomass

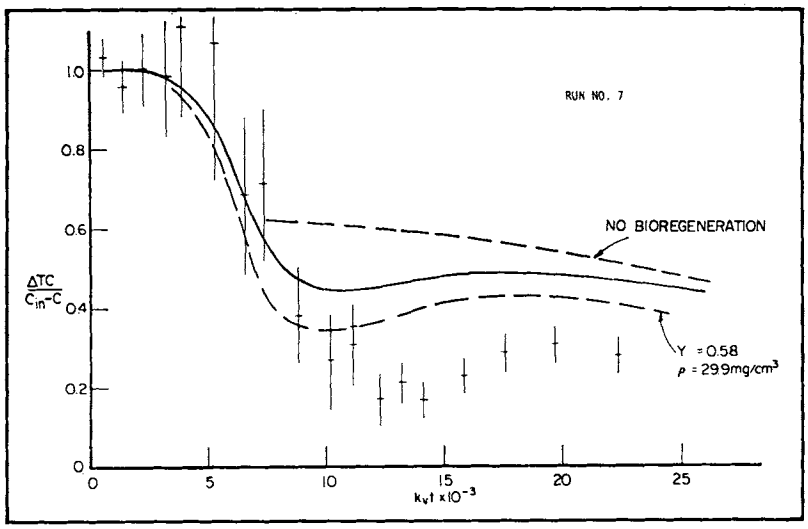

Figure 11. Theoretical and experimental yield ratio—Run 7.

deposited during the seeding period. The slope of the line in Figure 7 gives $k_v/\rho = 0.0075$ L/mg·h which compares well with the value of 0.0055 L/mg·h found by a different method in earlier work (Andrews and Tien, 1974) using a liquid-diet food substrate.

Putting the values determined above in the definition of k_1 gives the diffusion coefficient in the film as $D = 0.0099$ cm²/h. This is 34% of the free liquid value, which is certainly the correct order of magnitude.

COMPARISON OF THE MODEL WITH EXPERIMENT

With the parameter values determined above, the mathematical model is used to predict the results of two experiments (Runs 6 and 7) that involved both adsorption and bacterial growth. The value of k_1 was corrected to allow for the different sphericities of coal (0.65) and carbon (0.75). The only unknown quantity is the initial bacterial concentration x_o. This is chosen to give the best agreement between the model and the data. The existence of this one free parameter is not felt to be a serious limitation because the model must simultaneously predict two independent sets of data, the substrate concentration and the yield ratio, as functions of time.

Plots of the dimensionless substrate concentration (Figures 8 and 10) show two phases. During the initial adsorption phase the substrate concentration increases as the carbon becomes saturated with adsorbate. The increased concentration accelerates bacterial growth. Eventually, a film establishes itself, and reduces the substrate concentration back down to some steady-state value.

The most important question about the bacterial growth phase is whether bioregeneration is occurring. This is answered by the yield ratio curves (Figures 9 and 11). This ratio must be unity for pure adsorption. It falls during the bacterial growth phase because some of the substrate taken up in the reactor then reappears in the effluent as carbon dioxide or washed-off cells.

In the absence of bioregeneration, the bacterial growth phase would proceed exactly like growth on a nonadsorbing surface. This behavior, predicted from Eq. 11, is shown by the upper dashed line in Figure 11. When bioregeneration occurs, the bacterial film metabolizes substrate that was stored in the adsorbent during the adsorption phase. Part of this also appears in the effluent as carbon dioxide and washed-off cells, thus further reducing the yield ratio. [Andrews and Tien (1974) showed that this ratio could become even negative]. So, the model (solid line in Figure 11) predicts a yield ratio curve that is lower than the "no-bioregeneration" hypothesis, and that goes through a minimum. Such a minimum could be caused only by bioregeneration. The subsequent long-term decline of the yield ratio is caused by the decay term in Eq. 5.

The experimental points in Figures 9 and 11 not only show the required minimum, they also lie considerably below the theoretical curves. This indicates that bioregeneration not only occurs, it occurs much faster than is predicted by the model. This interpretation is supported by the substrate concentration data. In Figures 8 and 10, the concentration falls to the steady-state value predicted by the model, but it falls much faster than predicted, which indicates that the film grows faster than expected. A high rate of bioregeneration, that is a rapid conversion of adsorbate into biomass, would explain this discrepancy.

DISCUSSION OF RESULTS

There are several possible explanations for the rapid bioregeneration. Growth of the bacterial film may affect the adsorption equilibrium by changing the physical or chemical conditions at the carbon surface. However, this seems unlikely in the present case. The dominant effects of the film would be depletion of the phosphate buffer from solution, and the production of carbon dioxide. These would tend to reduce the pH and thus increase the carbon's capacity for valeric acid.

Other explanations were investigated by means of parameter sensitivity studies on the model. They showed that the rapid bioregeneration was not due to any type of facilitated transport within the carbon particle. Order of magnitude increases in the adsorption/desorption rate constant, k_s, causes only slight changes in the bioregeneration rate. This rate is clearly controlled by the film growth rate rather than by intraparticle transport.

The only reasonable parameter adjustments that significantly improved the fit of the theory to the data were in the values of the yield coefficient, Y, and the film density ρ. The model predictions, using the lowest values of these parameters permitted by the data in the previous section, are shown by the lower dashed lines in Figures 10 and 11. Is there any justification for using these lower values?

The simplest justification would be if the biomass on the carbon had a different composition than the biomass in the earlier experiments with coal particles. This is dismissed for two reasons. First, the growth conditions (substrate concentration, particle size, type of surface, flow velocity, etc.) were intentionally made as similar as possible in the two sets of experiments. Secondly, it is unlikely that a biomass with a high yield would be naturally replaced by one with a low yield.

A more likely explanation is that the bacterial film is not homogeneous. Films consist of cells embedded in a polysaccharide matrix. What controls the production of this polysaccharide?

Many cells produce polysaccharide slime coatings in batch cultures when they are exposed to low and declining substrate concentrations during the declining growth phase. Cells deep inside a film growing on a nonadsorbing surface are exposed to the same conditions. They may react in the same way: switching from production of new cells to production of excess polysaccharide. This would certainly be a good survival strategy for the cells, if the polysaccharide is viewed as substrate stored for later use.

It is reasonable to assume a higher yield for polysaccharide production than for cell production. So, excess polysaccharide production should give a high yield. The value $Y = 0.652$ (which corresponds to over 0.7 on a "biomass to substrate mass" basis) measured in the coal particle experiments is indeed higher than would be expected from published values for dispersed-growth cultures.

Further evidence comes from film density measurements. Characklis et al. (1974) showed that diffusion through microbial aggregates was greatly reduced when they were grown on substrates with a high carbon to nitrogen ratio, conditions that favor polysaccharide production. This implies that excess polysaccharide leads to films with a low porosity and high density (as dry weight or organic carbon per unit volume).

So, if there is excess polysaccharide production deep inside the film, the film density would be expected to increase with film thickness. The increase would continue until the film was so thick that no substrate reached the film base. Cells at the base would then use the polysaccharide as substrate to provide their maintenance energy requirement, thus reducing the film density again. This is precisely the type of density variation observed experimentally by Hoehn and Ray (1973).

Now, consider a cell deep in a film growing on an adsorbent surface undergoing bioregeneration. It does not experience a low and declining substrate concentration, because it receives fresh substrate from the adsorbent. It, therefore, produces new cells rather than excess polysaccharide, giving both a lower yield and a lower film density. So, variations in the polysaccharide production in the film may justify the use of the lower values of Y and ρ required to obtain agreement between the data and the theoretical model. (The values of k_r and k_1 would, of course, be affected by changes in the film composition. However, studies show that the theoretical predictions are relatively insensitive to these parameters).

ACKNOWLEDGMENT

This study was performed under Grant No. ENG 79-08893, National Science Foundation.

NOTATION

a,b = Langmuir isotherm constant
C' = C/C_{in}
C = concentration of dissolved organic carbon in liquid, mg/L
C_{in} = value of C at reactor inlet, mg/L
C_{ref} = a reference concentration, mg/L
C_S = value of C at carbon surface, mg/L
$\bar{C}$ = average value of C in bed, mg/L
D = effective substrate diffusion coefficient in film, cm²/h
D_f = substrate diffusion coefficient in water: cm²/h
d = carbon particle diameter
E = constant in Eq. 13
F = inflow rate to reactor, L/h
H = bed height, cm
H_c = height of a bed containing no biomass, cm
k_d = film decay rate constant, h^{-1}
k_s = adsorption rate constant, h^{-1}
k_r = substrate uptake rate per unit volume of film, h^{-1}
k_1 = $(k_r/D\alpha^2)^{1/2}$
N_A = adsorptive uptake rate of organic carbon per unit particle volume, mg/h · cm³
N_T = total uptake rate of organic carbon per unit particle volume: mg/h · cm³
Q = volumetric flow rate through bed, L/h
q = concentration of adsorbed organic carbon, mg/cm³
q^* = equilibrium value of q, mg/cm³
r = separation factor
s = concentration of organic carbon in substrate in the bacterial film, mg/L
t = time, h
V = volume of empty reactor, L
v = volume of clean (biomass-free) particles, L
w = distance from film base, cm
x = film volume/clean particle volume
Y = yield coefficient

Greek Letters

α = surface to volume ratio of clean particles, cm^{-1}
χ = internal porosity of carbon
ΔTC = inlet total carbon conc.—outlet total carbon conc.
ρ = concentration of organic carbon in bacterial film, mg/cm³
τ = reactor residence time, h

LITERATURE CITED

Andrews, G. F., "Bacterial Growth in Fluidized Beds of Activated Carbon," Ph.D. Dissertation, Dept. of Chem. Eng., Syracuse Univ., Syracuse, NY (1979).

Andrews, G. F., and C. Tien, "The Expansion of a Fluidized Bed Containing Biomass," *AIChE J.*, **25**, (4) 720 (1979).

Andrews, G. F., and C. Tien, "The Interaction of Bacterial Growth, Adsorption, and Filtration in Carbon Columns Treating Liquid Wastes," *AIChE Symp. Ser. (Water)*, **71**, (152) 164 (1974).

Benedek, A., "The Role of Biological Activity in Activated Carbon Adsorbers," 30th Annual Industrial Waste Conf., Purdue Univ., Lafayette, IN (1975).

Characklis, W. G., J. V. Matson, and D. M. Pipes, "Diffusion in Microbial Aggregates," Proceedings AIChE—G.V.C. Joint Meeting, Munich (1974).

Department of the Environment, "Water Pollution Research, 1971," H.M.S.O. London (1972).

Flynn, B. P., and J. C. Standick, "State of the Art: Powdered Activated Carbon Addition to Activated Sludge," 70th AIChE Annual Meeting, NY (1977).

Guirges, W., T. Cooper, J. Harris, and R. Ungar, "Improved Performance of Activated Carbon by Pre-Ozonation," *J. of the Water Poll. Control Fed.*, **50**, 308 (1978).

Hoehn, R. C., and A. D. Ray, "Effects of thickness on Bacterial Film," *J. of the Water Poll. Control Fed.*, **45**, 302 (1973).

Hseih, J., R. M. Turian, and C. Tien, "Multicomponent Liquid Phase Adsorption in a Fixed Bed," *AIChE J.*, **23**, 263 (1977).

Jennings, P., "A Mathematical Model for Biological Activity in Expanded Beds," Ph.D. Dissertation, Dept. of Civil Eng., Univ. of Illinois, Urbana (1975).

Mattson, J. S., and H. B. Mark, "Activated Carbon—Surface Chemistry and Adsorption of Solution," Marcel Dekker, NY (1971).

Perrolti, A. E., and C. A. Rodman, "Enhancement of Biological Waste Treatment by Activated Carbon," *Chem. Eng. Prog.*, **69**, (11), 63 (1973).

Rodman, C. A., and E. L. Shunney, "Bioregenerated Activated Carbon Treatment of a Textile Dye Wastewater," E.P.A. Water Poll. Control Res. Series No. 12090 DWM (1971).

Weber, W. J., L. D. Friedman, and R. Bloom, "Biologically Extended Physiochemical Treatment," Advances in Water Poll. Control Research, Proc. of the 6th International Conference, Jerusalem, S. H. Jenkins, ed., Pergamon Press, Oxford (1972).

Ying, W., and W. J. Weber, "Biophysiochemical Adsorption Systems for Wastewater Treatment: Predictive Modelling for Design and Operation," 33rd Industrial Waste Conference, Purdue Univ., Lafayette, IN (1978).

Manuscript received February 22, 1980, revision received June 7, and accepted July 25, 1980.