horizontal (approximately) and the intersection of these characteristics with the new β characteristics would form a rectangular grid in absolute time and space coordinates. Although output was obtained directly from this grid, the time and space increments could not be independently chosen because of their unique relationship as defined by the β characteristic. Calculations showed that the no vapor holdup model was accurate to three significant figures.

Since neglecting the vapor holdup led to neglecting transients for the time period prior to the arrival of a new vapor composition from the reboiler, it was expected that larger values of A/B as well as larger initial composition gradients in the column would result in larger error. Further calculations showed that for either an H increase from 3 to 6 or an A/B increase from $1/20$ to $1/4$, the no vapor holdup assumption led to as much as 15% error.

SUMMARY AND CONCLUSIONS

The numerical results of the examples used can be seen to be efficient since iterative or interpolation techniques were not required. High accuracy was obtained with increments, as large as $\Delta h \doteq 0.1$, as indicated by the rapid convergence of the numerical solutions as the size of the increments was decreased and by comparison to analytical solutions.

The coding sequence described in Part I was found to be applicable without change for the specific examples used. For more generalized problems the coding would be somewhat lengthier than that used with conventional methods. However, the proposed methods are expected to be more efficient and accurate.

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Bilayer Film Model for the Interaction between Adsorption and Bacterial Activity in Granular Activated Carbon Columns

Part I: Formulation of Equations and Their Numerical Solutions

S-C P. WANG and CHI TIEN

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

The diffusion-reaction film model proposed by Andrews and Tien (1981) for the interaction between adsorption and bacterial activities in carbon columns was generalized. The microbial film was assumed to be composed of two regions of distinctively different microbial activity, depending on the presence or absence of dissolved oxygen. Governing equations were derived to describe the dynamics of the carbon columns in which the interaction between adsorption and bacterial growth and methods for solving these equations were developed.

SCOPE

The application of granular activated carbon columns for treating water and waste water has become a standard treatment technology. When the dissolved organics present in the waste are both adsorbable and biodegradable, bacterial growth in the column becomes almost unavoidable. When the growth may create operating difficulties, its presence has been viewed more recently as beneficial because of the synergistic and complementary nature of adsorption and bacterial activity in the treatment process. The present study is concerned with the formulation of a model which can predict the essential features of the interaction.

The model for the interaction is a generalization of an earlier study by Andrews and Tien (1981) and allows the bacterial activity to be either aerobic or anoxic depending on the film thickness. Equations describing column operations incorporating this interaction model were derived and algorithms for their solution were developed. Sample calculations which demonstrate the effect of various process variables were made as part of this study.

S-C P. Wang is presently with W. R. Grace, Inc., Columbia, MD.

CONCLUSIONS AND SIGNIFICANCE

The analysis presented in this work represents a significant improvement over the earlier work of Andrews and Tien (1981). By considering the bacterial film to be composed of two regions with different bacterial activity, the model more realistically approximates the conditions encountered in the application of activated carbon in waste treatment.

Inspite of the apparent complexities of the equation describing the carbon processes, these equations can be solved using the algorithms developed in this work. The availability of the model and its solution make it possible to consider the design and operation of carbon process for waste treatment in terms of fundamental parameters and, therefore, on a more rational basis.

It is known that bacterial films may develop on the surface of carbon particles in adsorption columns treating water or waste water. The bacterial growth results from the fact that some or all of the dissolved organics present in the solution are biodegradable. While, in the past, bacterial growth has been considered inconvenient because of the bed clogging it causes, its presence makes a carbon bed both a bioreactor and an adsorption column. Thus, in a carbon bed with bacterial growth, dissolved organic substances are removed by way of two separate but often complementary mechanisms, adsorption and biological degradation.

During the past decade, several attempts have been made to analyze the carbon process for waste treatment taking into account the effect of bacterial growth. The first effort was made by Andrews and Tien (1974). They showed that the problem can be most conveniently analyzed in terms of the transport, transformation and conservation of organic carbon among the solution, adsorbent, and bacterial film. The simplifications introduced in their work dictate the use of a particular form of expression for microbial growth, which is valid only for thin films.

Jennings (1975) considered the type of waste with biodegradable but nonadsorbable contaminates. His work assumed a fixed film thickness. This assumption, in fact, has been used in most biofilm kinetics studies (Atkinson and Daoud, 1968; Williamson and McCarty, 1976; Harris and Hansford, 1976; Reimer and Harremoes, 1978). On the other hand, in a real column, fresh carbon begins with virtually no bacteria. The film develops at a rate which varies along the bed height and depends on a number of variables.

Ying and Weber (1978) recognized this condition. In their analysis of the carbon process, the microorganisms are allowed to grow until they reach a certain level, whereafter they are kept at this externally-defined steady-state level by periodically washing and air-scouring the bed. Since the steady-state level of biofilm is assumed to be less than a monolayer of microorganisms, the presence of the biofilm provides no extra mass transfer resistance for adsorption; the rate of the substrate uptake by microorganisms is a function of the substrate concentration at carbon surface. Thus, the Ying-Weber model is applicable to conditions of low microbial growth rate and with frequent and effective bed washing.

A more complete model, suggested recently by Andrews (1979) and Andrews and Tien (1981), predicts the uptake rate of dissolved organics as a result of adsorption and of bacterial activity of the growing bacterial films covering carbon particles. The model was formulated in such a way that it can be readily applied to real waste systems whose exact composition may not be known. Two main features of interaction between adsorption and microbial growth are considered in the model, namely, the extra mass transfer resistance to adsorption resulting from the microbial film and the bioregeneration of saturated adsorbent. Analysis of carbon column performance using this conceptual framework has been done by Tien and Wang (1982) and Andrews and Tien (1982).

The Andrews-Tien model assumes that the rate of the degradation of dissolved organics is limited by the substrate concentration in the absence of dissolved oxygen. The model, therefore, is applicable to denitrifying bacteria under anoxic conditions. In actual waste systems, a certain amount of dissolved oxygen is likely to be present. Thus, for a thin film, the corresponding bacterial activity is likely to be aerobic. On the other hand, as the film thickness increases, oxygen becomes available only at the outer portion of the film. It is, therefore, necessary to recognize the difference between the bacterial activity at the outer part of the film and that at the inner part. An analysis of the carbon column's performance based on this bilayer film concept is the objective of the study.

BILAYER MICROBIAL FILM MODEL

The basis of the model is shown in Figures 1a–1c. A homogeneous growing film is present outside the surface of a carbon particle immersed in a liquid solution containing appropriate amounts of organic substrate; inorganic nutrients, i.e., nitrates and dissolved oxygen (DO). These substances diffuse through and are taken up by the film in accordance with the nature of the bacterial growth. Once having reached the base of the film and depending on the local concentration gradient at the film base, the organic substrate may further diffuse into the interior of the carbon particle and become adsorbed.

Initially, the film is relatively thin, and the DO is available throughout the film. The film activity is, therefore, aerobic. As shown in Figure 1a, only the organic substrate and DO display concentration profiles across the film.

As the film thickness increases beyond a certain value (L_I), the DO is only available at the outer portion of the film ($L_I < x < L$). If one assumes that the bacteria are facultative anaerobes, the activity of the inner portion of the film becomes anoxic denitrifying. A declining concentration profile of nitrate must, therefore, exist across the film. By definition, the concentation of DO vanishes in the region $O < x < L_I$. This situation is given in Figure 1b.

As time progresses, both the film thickness and the degree of saturation of the carbon particles increase. When the carbon is completely saturated, the organic substrate is removed by bacterial activity only. If the film is sufficiently thick, the consumption of the organic substrate by bacteria within the film may cause the organic substrate concentration there to fall below that of the corresponding concentration within the carbon. This situation initiates the bioregeneration effect, that is, the desorption of the organic substrate from the carbon back to the solution phase of the film. The concentration profiles of such a case are demonstrated in Figure 1c.

The assumptions in formulating the model are:

1. The organic substrate is soluble and biodegradable and adsorbs reversibly an activated carbon.
2. The film is homogeneous: the characteristics for each part (inner and outer) remain constant.
3. The nature of bacterial activity is either aerobic or anoxic, depending on the availability of DO.
4. The organic substrate concentration is dilute and limits

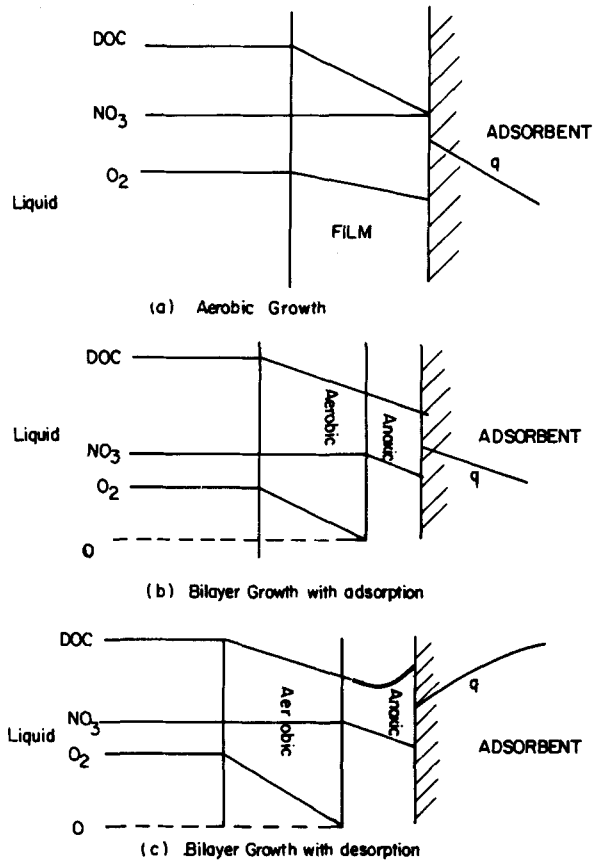

Figure 1. Schematic representation of biofilm outsider adsorbent.

bacterial growth for either type of bacterial activity. The respective reaction kinetics are first order.

5. In both aerobic and anoxic growth, the biological pathways are invariant. Therefore, the consumption of substrate follows a fixed stoichiometric relationship.

6. The pseudosteady-state assumption is used on account of the relatively slow film growth rate.

7. The effect of diffusion and possible adsorption by carbon of biological end products is negligible.

8. The film grows as if on a flat surface.

9. The resistance to mass transfer from the bulk liquid to the surface of the film is negligible.

The concentration profiles of the organic substrate, DO, and nitrate (S_c, S_0, and S_n) are given by

(For $L_I < x < L$)

$$D_c \frac{d^2S_c}{ds^2} = kS_c \tag{1}$$

$$D_0 \frac{d^2S_0}{dx^2} = \beta kS_c \tag{2}$$

$$D_n \frac{d^2S_n}{dx^2} = 0 \tag{3}$$

(For $0 < x < L_I$)

$$D_c \frac{d^2S_c}{dx^2} = \alpha kS_c \tag{4}$$

$$S_0 = 0 \tag{5}$$

$$D_n \frac{d^2S_n}{dx^2} = \gamma kS_c \tag{6}$$

The boundary and the interphase conditions are:

(A) At the liquid-film interface, i.e., $x = L$

$$S_c = [C] \tag{7a}$$

$$S_0 = [0_2] \tag{7b}$$

$$S_n = [NO_3] \tag{7c}$$

(B) At the film base, i.e., $x = 0$

$$D_c \frac{dS_c}{dx} = \frac{a_p}{3}\frac{dq}{d\theta} = k_p(q_i - q) \tag{8a}$$

$$q_i = f(S_0|_{x=0}) \tag{8b}$$

$$\frac{dS_n}{dx} = 0 \tag{8c}$$

(C) At the boundary between the aerobic and anoxic regions, i.e., $x = x_I$

$$S_c|_{L_I^+} = S_c|_{L_I^-} \tag{9a}$$

$$S_0|_{L_I^+} = S_0|_{L_I^-} \tag{9b}$$

$$S_n|_{L_I^+} = S_n|_{L_I^-} \tag{9c}$$

$$\left.\frac{dS_c}{dx}\right|_{L_I^+} = \left.\frac{dS_c}{dx}\right|_{L_I^-} \tag{9d}$$

$$\left.\frac{dS_0}{dx}\right|_{L_I^+} = \left.\frac{dS_0}{dx}\right|_{L_I^-} = 0 \tag{9e}$$

$$\left.\frac{dS_n}{dx}\right|_{L_I^+} = \left.\frac{dS_n}{dx}\right|_{L_I^-} \tag{9f}$$

The solutions of the concentration profiles across the film are:

(*For* $L_I < x < L$)

$$S_c = y_{11}\sinh\sqrt{k/D_c}\,x + y_{12}\cosh\sqrt{k/D_c}x \tag{10}$$

$$S_0 = \frac{\beta D_c}{D_0}(y_{11}\sinh\sqrt{k/D_c}\,x + y_{12}\cosh\sqrt{k/D_c}\,x) + ax + b \tag{11}$$

$$S_n = a_1x + b_1 \tag{12}$$

(*For* $0 < x < L_I$)

$$S_c = y_{21}\sinh\sqrt{\alpha k/D_c}x + y_{22}\cosh\sqrt{\alpha k/D_c}\,x \tag{13}$$

$$S_0 = 0 \tag{14}$$

$$S_n = \frac{\gamma D_c}{\alpha D_n}(y_{21}\sinh\sqrt{\alpha k/D_c}\,x + y_{21}\cosh\sqrt{\alpha k/D_c}\,x) + a_2x + b_2 \tag{15}$$

The coefficients of the concentration profiles, y_{11}, y_{12}, etc., and the anoxic film thickness, L_1, can be obtained for a specified set of substrate concentrations in liquid phase, a given degree of adsorbent saturation (i.e., q) and a given film thickness from the above set of boundary conditions. In particular, at the film base, assuming that the adsorption isotherm is linear, from Eq. 8b and 13 one has

$$q_i = f(S_c/_{x=0}) = f(y_{22}) = \Lambda y_{22} \tag{16}$$

when

$$\Lambda = q^*/[C]_i \qquad q^* = f([C]i) \tag{17}$$

The determination of the profile coefficients can be greatly simplified if the bacterial growth is either aerobic or anoxic. For the former case, which occurs during the initial growth period, $L_I = 0$ and $y_{21} = y_{22} = 0$. Furthermore, in Eq. 16, the coefficient y_{22} is replaced by y_{12}. On the other hand, if the bacterial activity is anoxic, $L_I = L$ and $Y_{11} = Y_{12} = 0$.

The emergence of an anoxic region within the film is determined by the condition that the concentration of D_o cannot be negative. From Eq. 11, one has

$$S_0|_{x=0} = \frac{\beta D_c}{D_0}y_{12} + b \geq 0 \tag{18}$$

which, in turn, can be rewritten, upon application of the boundary conditions of Eqs. 7b, 9e and 16 to be

$$y_{12} = \frac{[C] + \frac{k_p q}{\sqrt{kD_c}} \sinh\sqrt{k/D_c}L}{\cosh\sqrt{k/D_c}L + \frac{k_p \Lambda}{\sqrt{kD_c}} \sinh\sqrt{k/D_c}L}$$

$$\geq \frac{[C] + \frac{k_p L}{D_c} q - \frac{D_0}{\beta D_c}[0_2]}{1 + k\frac{k_p L \Lambda}{D_c}} \quad (19)$$

As stated previously (Andrews and Tien, 1974), the carbon process can best be analyzed in terms of the transport and transformation of organic carbon. To express the film thickness, L, on such a basis, let B denote the amount of the microbial organic carbon of the film per unit mass of the activated carbon and ρ be the organic carbon density of the film. If L is sufficiently small as compared with the radius of the carbon particle, a_p, one has

$$L = \left(\frac{1}{\rho}\right)\frac{a_p \rho_p}{3} B \quad (20)$$

Assuming that the film washoff and the basal metabolism in the biofilm are negligible, the film growth as measured by $dB/d\theta$ can be related with the microbial activity throughout the film as following:

In the aerobic region, $L_I < x < L$

$$\frac{4}{3}\pi a_p^3 \rho_p \frac{dB_1}{d\theta} = Y_1(4\pi a_p^2)\int_{L_I}^{L} kS_c dx \quad (21)$$

In the anoxic region, $0 < x < L_I$

$$\frac{4}{3}\pi a_p^3 \rho_p \frac{dB_2}{d\theta} = Y_2(4\pi a_p^2)\int_{0}^{L_I} \alpha k S_c dx \quad (22)$$

and

$$B = B_1 + B_2 \quad (23)$$

where subscripts 1 and 2 denote the regions of $L_I < x < L$ (aerobic) and $0 < x < L_I$ (anoxic), respectively, and Y the yield coefficient. Substituting Eq. 10 (or Eq. 13) into Eq. 21a (or Eq. 21b), the rates of the biofilm growth are found to be

$$\frac{a_p}{3}\rho_p \frac{dB_1}{d\theta} = y_1\sqrt{kD_c}\,[y_{11}(\cosh\sqrt{k/D_c}\,L - \cosh\sqrt{k/D_c}\,L_I) + y_{12}(\sinh\sqrt{k/D_c}\,L - \sinh\sqrt{k/D}\,L_I)] \quad (24a)$$

$$\frac{a_p}{3}\rho_p \frac{dB_2}{d\theta} = y_2\sqrt{\alpha k D_c}\,[y_{21}(\cosh\sqrt{\alpha k/D_c}\,L_I - 1) + y_{22}\sinh\sqrt{\alpha k/D_c}\,L_I] \quad (24b)$$

The increase in the degree of saturation of the carbon particle can be found from the solution of Eq. 8a, namely,

$$\frac{dq}{d\theta} = \frac{3k_p}{a_p}[\Lambda y_{22} - q] \quad (25)$$

Also from the substrate concentration profiles, the uptake fluxes of the bacterial film are found to be

$$N_c = D_c \frac{dS_c}{dx}\bigg|_{x=L} = \frac{a_p}{3}\left(\frac{\rho_p}{Y_1}\frac{\partial B_1}{\partial\theta} + \frac{\rho_p}{Y_2}\frac{\partial B_2}{\partial\theta} + \frac{\partial q}{\partial\theta}\right) \quad (25a)$$

$$N_0 = D_0 \frac{dS_0}{dx}\bigg|_{x=L} = \beta\frac{a_p}{3}\frac{\rho_p}{Y_1}\frac{\partial B_1}{\partial\theta} \quad (25b)$$

$$N_n = D_n \frac{dS_n}{dx}\bigg|_{x=L} = \frac{\gamma}{\alpha}\frac{a_p}{3}\frac{\rho_p}{y_2}\frac{\partial B_2}{\partial\theta} \quad (25c)$$

GOVERNING EQUATIONS

The most common mode of operation in the application of granular carbon for waste treatment is to pass the waste upward through a carbon bed. The upward flow mode allows carbon granules to accommodate bacterial growth, thus avoiding the bed clogging problem. Since the bed expands continuously, it is convenient to describe the bed axial distance not by the actual volume, z, but its equivalent value, z', on the basis of no nacterial growth. The conservation equations of the substitutes are:

$$\frac{u}{1-\epsilon}\frac{\partial[C]}{\partial z'} + \frac{\partial}{\partial\theta}\left[\frac{\rho_p}{Y_1}B_1 + \frac{\rho_p}{Y_2}B_2 + q\right] = 0 \quad (26a)$$

$$\frac{u}{1-\epsilon}\frac{\partial\left(\frac{1}{\beta}[0_2]\right)}{\partial z'} + \frac{\partial}{\partial\theta}\left[\frac{\rho_p}{Y_1}B_1\right] = 0 \quad (26b)$$

with the following initial boundary conditions:

at the inlet, $z' = 0$

$$[C] = [C]i$$

$$[O_2] = [O_2]_i$$

$$[NO_3] = [NO_3]_i \quad (27)$$

and, initially, $\theta < 0$, $z > 0$, $q = 0$

$$B = B_0 \quad (28)$$

The two independent z' and θ variables are defined as

$$z = (1-\epsilon_c)\int_0^{z'}\frac{1+v}{1-\epsilon}dz' \quad (29a)$$

$$\theta = t - \int_0^{z'}\frac{\epsilon}{u}dz' \quad (29b)$$

The bed height and pressure drop are given as

$$H = (1-\epsilon_c)\int_0^{H_c}\frac{1+v}{1-\epsilon}dz' \quad (30a)$$

and

$$-\Delta p = \int_0^{H_c}\left(1 + \frac{3L}{a_p}\right)\frac{37.5}{(a_p+L)^2}\mu u\frac{(1-\epsilon)^2}{\epsilon^3}dz' \quad (31a)$$

where v, the film coverage defined as the volume of film per unit volume of clean carbon granules is given as

$$v = \frac{3}{a_p}L = \frac{\rho_p}{p}B \quad (32)$$

METHOD OF SOLUTION

The following is a brief discussion of the numerical method used to solve the governing equations. Detailed results can be found in Wang's dissertation (1982).

First, for convenience, Eqs. 26a through 26c, 23 through 25 can be written into dimensionless form or

$$\frac{\partial[C]^+}{\partial z^+} = -\frac{\partial K}{\partial\theta^+} = -P_c = -P_0 - P_n - m_2\frac{\partial q^+}{\partial\theta^+} \quad (33a)$$

$$m_3\frac{\partial[O_2]}{\partial z^+} = -\frac{\partial(B_1^+/Y_1)}{\partial\theta^+} = -P_0 \quad (33b)$$

$$m_4\frac{\partial[NO_3]^+}{\partial z^+} = -\frac{\partial(B_2^+/Y_2)}{\partial\theta^+} = P_n \quad (33c)$$

$$B^+ = B_1^+ + B_2^+ \quad (34)$$

$$\frac{1}{Y_1}\frac{\partial B_1^+}{\partial\theta^+} = y_{11}^+(\cosh B^+ - \cosh B_2^+) + y_{12}^+(\sinh B^+ - \sinh B_2^+) \quad (35a)$$

$$\frac{1}{Y_2}\frac{\partial B_2^+}{\partial\theta^+} = \sqrt{\alpha}[y_{21}^+(\cosh\sqrt{\alpha}B_2^+ - 1) + y_{22}^+\sinh\sqrt{\alpha}B_2^+] \quad (35b)$$

$$m_2\frac{\partial q^+}{\partial\theta^+} = \sqrt{\alpha}y_{21}^+ \text{ if } B_2^+ > 0 \quad (36a)$$

On the other hand, if the film is entirely aerobic, Eq. 36a is replaced by

$$m_2\frac{\partial q^+}{\partial\theta^+} = y_{11}^+ \text{ if } B_2^+ = 0 \quad (36b)$$

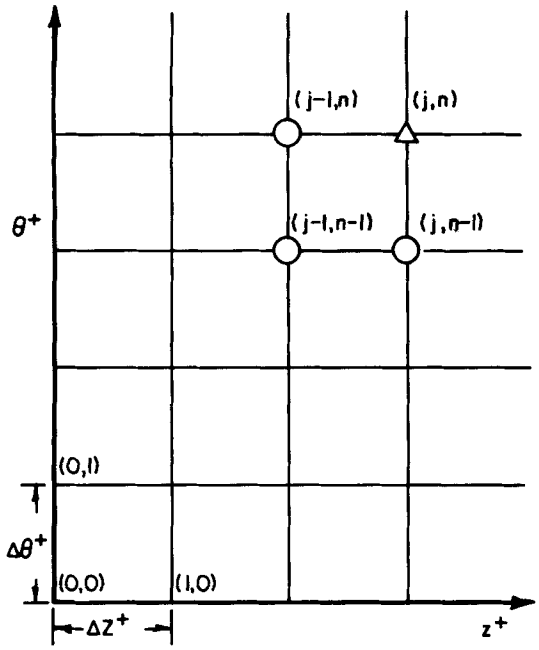

Figure 2. Computation grids for the numerical solution.

The corresponding dimensionless boundary conditions and the expressions of bed height and pressure drop become,

$$\text{at } z^+ = 0,\ [C]^+ = [O_2]^+ = [NO_3]^+ = 1 \text{ if } [O_2]_i > 0$$
$$[C]^+ = [NO_3]^+ = 1 \quad \text{if } [O_2]_i = 0 \tag{37}$$

$$\text{at } \theta^+ = 0,\ B^+ = B_0^+ \text{ and } q^+ = 0 \tag{38}$$

and the bed height and pressure drop become

$$H = \frac{ua_p}{3(1-\epsilon)\sqrt{kD_c}} \int_0^{H_c^+} \left(1 + \frac{3B^+\sqrt{D_c/k}}{a_p}\right) dz^+ \tag{30b}$$

$$-\Delta p = \frac{ua_p}{3(1-\epsilon)\sqrt{kD_c}} \frac{37.5\,\mu u(1-\epsilon)^2}{\epsilon^3} \times \int_0^{H_c} \left(1 + \frac{3B^+\sqrt{D_c/k}}{a_p}\right) \frac{dz^+}{(a_p + B^+\sqrt{D_c/k})^3} \tag{31b}$$

The governing equations derived above are of the type of differential equations (semilinear hyperbolic) characteristic of fixed-bed processes, such as adsorption, heat regeneration, deep-bed filtration, etc. The method of solution presented here is a combination of algorithms for the solution of first-order initial value problems and those for the solution of semilinear hyperbolic equations. The scheme of computation is reflected in Figure 2, where the $z^+ - \theta^+$ plane is divided by a network, with interval Δz^+ in the z^+ direction and $\Delta\theta^+$ in the θ^+ direction. The first step of computation is to initialize along the θ^+ and z^+ axes.

Along z^+ Axis

The initial condition of Eq. 38 gives $B^+ = B_0^+$ and $q^+ = 0$. The condition given by Eq. 19 becomes

$$\frac{[C]^+}{\cosh B_0^+ + m_1 \sinh B_0^+} \geq \frac{[C]^+ - D_0^+ m_3 [0_2]^+}{1 + m_1 B_0^+} \tag{39}$$

Three cases, namely, aerobic growth, bilayer growth, and anoxic growth, are considered as follows.

Aerobic Growth. If Eq. 34 can be satisfied, $L_I = 0$, $B_2^+ = 0$, and $y_{21}^+ = y_{22}^+ = 0$. The concentration gradients of substrate in liquid phase can be expressed (i.e., from Eqs. 33a–36b) as

$$\frac{\partial [C]^+}{\partial z^+} = -\frac{m_1 \cosh B_0^+ + \sinh B_0^+}{\cosh B_0^+ + m_1 \sinh B_0^+} [C]^+ \tag{40a}$$

$$\frac{\partial [O_2]^+}{\partial z} = \frac{m_1(\cosh B_0^+ - 1) + \sinh B_0^+}{m_3(\cosh B_0^+ + m_1 \sinh B_0^+)} [C]^+ \tag{40b}$$

$$\frac{\partial [NO_3]^+}{\partial z^+} = 0 \tag{40c}$$

which, upon integration with the initial condition of Eq. 37, yields

$$[C]^+ = \exp\left(-\frac{m_1 \cosh B_0^+ + \sinh B_0^+}{\cosh B_0^+ + m_1 \sinh B_0^+} z^+\right) \tag{41a}$$

$$[O_2]^+ = \frac{m_1(\cosh B_0^+ - 1) + \sinh B_0^+}{m_3(m_1 \cosh B_0^+ + \sinh B_0^+)} ([C]^+ - 1) + 1 \tag{41b}$$

$$[NO_3]^+ = 1 \tag{41c}$$

Bilayer Growth. If Eq. 39 is not satisfied, it means that the anoxic layer exists even initially. The governing equations, Eqs. 33a–33c, become

$$\frac{\partial [C]^+}{\partial z^+} = -P_c = -P_n - P_0 \tag{42a}$$

$$m_3 \frac{\partial [O_2]^+}{\partial z^+} = -P_0 = -y_{11}^+(\cosh B_0^+ - \cosh B_2^+) - y_{12}^+(\sinh B_0^+ - \sinh B_2^+) \tag{42b}$$

$$m_4 \frac{\partial [NO_3]^+}{\partial z^+} = -P_n = -\sqrt{\alpha}[y_{21}^+(\cosh\sqrt{\alpha}B_2^+ - 1) + y_{22}^+ \sinh\sqrt{\alpha}B_2^+] \tag{42c}$$

The coefficients $y_{11}^+, y_{12}^+, y_{21}^+, y_{22}^+$, and the anoxic biofilm coverage B_2^+, can be determined from the application of the boundary conditions given by Eqs. 7a–9f. With these coefficients and b_2^+ known, one can solve the above first-order differential equations by using the fourth-order Runge-Kutta method.

Anoxic Growth. Since $[O_2]_i = 0$, $y_{11}^+ = y_{12}^+ = 0$ and the substrate concentration gradients in the liquid phase can be expressed as

$$\frac{\partial [C]^+}{\partial z^+} = -\frac{m_1 \cosh\sqrt{\alpha}B_0^+ + \sqrt{\alpha}\sinh\sqrt{\alpha}B_0^+}{\cosh\sqrt{\alpha}B_0^+ + \dfrac{m_1 \sinh\sqrt{\alpha}B_0^+}{\sqrt{\alpha}}} [C]^+ \tag{43a}$$

$$\frac{\partial [NO_3]^+}{\partial z^+} = -\frac{m_1(\cosh\sqrt{\alpha}B_0^+ - 1) + \sqrt{\alpha}\sinh\sqrt{\alpha}B_0^+}{m_4\left(\cosh\sqrt{\alpha}B_0^+ + \dfrac{m_1 \sinh\sqrt{\alpha}B_0^+}{\sqrt{\alpha}}\right)} [C]^+ \tag{43b}$$

which, upon integration with the initial condition of Eq. 37, yield

$$[C]^+ = \exp\left(-\frac{m_1 \cosh\sqrt{\alpha}B_0^+ + \sqrt{\alpha}\sinh\sqrt{\alpha}B_0^+}{\cosh\sqrt{\alpha}B_0^+ + \dfrac{m_1 \sinh\sqrt{\alpha}B_0^+}{\sqrt{\alpha}}} z^+\right) \tag{44a}$$

$$[NO_3]^+ = \frac{m_1(\cosh\sqrt{\alpha}B_0^+ - 1) + \sqrt{\alpha}\sinh\sqrt{\alpha}B_0^+}{m_4(m_1 \cosh\sqrt{\alpha}B_0^+ + \sqrt{\alpha}\sinh\sqrt{\alpha}B_0^+} ([C]^+ - 1) + 1 \tag{44b}$$

Along θ^+ Axis

The bulk-phase substrate concentrations are given by the boundary conditions of Eq. 37. By applying these conditions and using the fourth-order Runge-Kutta method, the values of B_1^+, B_2^+, B^+, and q^+ along the θ axis can be determined from Eqs. 34–36. The initial conditions are given by Eq. 38. Similar to the procedure for initialization along the z^+ axis, procedures for integrating along the θ^+ axis for the three cases can be readily developed.

Interior Points

For the interior points (j,n), the fourth-order algorithm developed by Vanier (1970) can be used to obtain values $[C]^+$, $[O_2]^+$, $[NO_3]^+$, K, B_1^+, B_2^+, B^+, and q^+. Assuming the values of all vari-

ables—substrate concentrations, film coverage q^+, coefficients of substrate profiles in biofilm—are known at points $(j-1, n-1)$, $(j-1, n)$, and $(j, n-1)$, the following procedures are used:

(1) A first estimate of $[C]^+$, $[O_2]^+$, $[NO_3]^+$, K, B_1^+, and B_2^+ is found to be

$$[C]_{j,n}^{+(1)} = [C]_{j-1,n}^{+} + [C]_{j,n-1}^{+} - [C]_{j-1,n-1}^{+} + \Delta z^+(-P_{c_{j-1,n}} + P_{c_{j-1,n-1}}) \quad (45a)$$

$$[O_2]_{j,n}^{+(1)} = [O_2]_{j-1,n}^{+} + [O_2]_{j,n-1}^{+} - [O_2]_{j-1,n-1}^{+} + \frac{\Delta z}{m_3}(-P_{o_{j-1,n}} + P_{0_{j-1,n-1}}) \quad (45b)$$

$$[NO_3]_{j,n}^{+(1)} = [NO_3]_{j-1,n}^{+} + [NO_3]_{j,n-1}^{+} - [NO_3]_{j-1,n-1}^{+} + \frac{\Delta z^+}{m_4}(-P_{n_{j-1,n}} + P_{n_{j-1,n-1}}) \quad (45c)$$

$$K_{j,n}^{(1)} = K_{j-1,n} + K_{j,n-1} - K_{j-1,n-1} + (P_{c_{j,n-1}} - P_{c_{j-,n}})\Delta\theta^+ \quad (45d)$$

$$B_{1j,n}^{+(1)} = B_{1j-1,n}^{+} + B_{1j,n-1}^{+} - B_{1j-1,n-1}^{+} + Y_1(P_{0_{j,n-1}} - P_{0_{j-1,n-1}})\Delta\theta^+ \quad (45e)$$

$$B_{2j,n}^{+(1)} = B_{2j-1,n}^{+} + B_{2j,n-1}^{+} - B_{2j-1,n-1}^{+} + Y_2(P_{n_{j,n-1}} - P_{n_{j-1,n-1}})\Delta\theta^+ \quad (45f)$$

Also, from the definitions of B^+ and K, one has

$$q_{j,n}^{+(1)} = (K_{j,n} - B_{1j,n}^{+(1)}/Y_1 - B_{2j,n}^{+(1)k}/Y_2)/m_2 \quad (45g)$$

$$B_{j,n}^{+(1)} = B_{1j,n}^{(1)} + B_{2j,n}^{+(1)} \quad (45h)$$

(2) An iterative calculation is then carried out as follows:

$$[C]_{j,n}^{+(i)} = [C]_{j,n}^{+(i-1)} + (P_{cj,n}^{(i-1)} - P_{cj-1,n-1} + P_{cj,n-1} + P_{cj-1,n})\Delta z^+/2 \quad (46a)$$

$$[O_2]_{j,n}^{+(i)} = [O_2]_{j,n}^{+(i-1)} + (-P_{0j,n}^{(i-1)} - P_{0_{j-1,n-1}} + P_{0j-1,n} + P_{0_{j-1,n}})\Delta z^+/2m_3 \quad (46b)$$

$$[NO_3]_{j,n}^{+(i)} = [NO_3]_{j,n}^{+(i-1)} + (-P_{nj,n}^{(i-1)} - P_{nj-1,n-1} + P_{nj,n-1} + P_{nj-1,n})\Delta z^+/2m_4 \quad (46c)$$

$$K_{j,n}^{(i)} = K_{j,n}^{(i-1)} + (P_{cj,n}^{(i-1)} + P_{cj-1,n-1} - P_{cj,n-1} - P_{cj-1,n})\Delta\theta^+/2 \quad (46d)$$

$$B_{1j,n}^{+(i)} = B_{1j,n}^{+(i-1)} + Y_1(P_{0j,n}^{(i-1)} + P_{0_{j-1,n-1}} - P_{0j,n-1} - P_{0_{j-1,n}})\frac{\Delta\theta^+}{2} \quad (46e)$$

$$B_{2j,n}^{+(i)} = B_{2j,n}^{+(1)} + Y_2(P_{nj,n}^{(i-1)} + P_{nj-1,n-1} - P_{nj,n-1} - P_{nj-1,n})\frac{\Delta\theta^+}{2} \quad (46f)$$

$$q_{j,n}^{+(i)} = (K_{j,n}^{(i)} - B_{1j,n}^{+(i)}/Y_1 - B_{2j,n}^{+(i)}/Y_2)/m_2 \quad (46g)$$

$$B_{j,n}^{+(i)} = B_{1j,n}^{+(i)} + B_{2j,n}^{+(i)} \quad (46h)$$

After the ith iterative values of $[C]^+$, $[O_2]^+$, $[NO_3]^+$, B^+, and q^+ have been determined, the corresponding substrate profile coefficients, y_{11}^+, y_{12}^+, y_{21}^+, y_{22}^+, and the anoxic biofilm, B_2^+ are determined in accordance with the boundary conditions of Eq. 7a–9f. The ith iterative values of P_c, P_o, and P_n can then be calculated from Eqs. 35a–36b and used to calculate the next iterative values of $[C]^+$, $[O_2]^+$, etc. The iteration stops when the desired degree of convergence is achieved and the last iterative values are taken to be the values of the variables at point (j,n).

The large number of parameters involved makes it impractical to obtain a criterion selecting optimum increments for the numerical solution. From a fairly large number of sample calculations using parameters similar to those obtained in the experimental work reported in Part II, however, the values of $\Delta z^+ = 0.2$ and $\Delta\theta^+ = 0.02$ were found to be adequate. As a check of the accuracy of the method developed, the numerical values of $[C^+]$ for the special case of pure adsorption (i.e., $B_0^+ = 0$] were calculated. The results were found to agree with the exact solutions given by Thomas (1948) to within 1%.

RESULTS AND DISCUSSION

The formulation presented above defines the dynamics of the adsorption-microbial growth interaction in terms of nine parameters (D_0^+, B_0^+, α, Y_1, Y_2, m_1, m_2, m_3, and m_4). The significance of these parameters can be discerned from their definitions. For example, the oxygen diffusion parameter, D_0^+, defined as D_0/D_c is expected to have an influence on the onset of the anoxic region. An increase in D_0^+ will delay the denitrifying bacterial activity within the microbial film. The quantity B_0^+ represents the extent of the initial bacterial film coverage. If $B_0^+ = 0$, the column is operating under sterile conditions. No bacterial growth will be possible and the process is pure adsorption. On the other hand, the microbial growth and biodegradation rate increases with the increase of B_0^+. The parameter, α is the ratio of the *DOC* uptake rate under anoxic growth to that under aerobic growth. Since the aerobic respiration is more efficient, the value of α is less than 1 and a smaller value of α leads to a greater difference between column performance under anoxic and aerobic conditions.

The significance of the two yield coefficients Y_1 and Y_2 can be stated as follows. A greater value of Y_1 leads to a higher aerobic film growth, a faster DOC consumption and *DO* depletion and an earlier onset of anoxic region. Similarly, a higher value in Y_2 implies a greater anoxic film growth rate and higher rates in *DOC* consumption, denitrification and bioregeneration. The two parameters m_1 and m_2 represent the solid phase (i.e., absorbent) mass transfer resistance and adsorption capacity, respectively. An increase in m_1 will increase the rates of both adsorption and desorption while a larger m_2 means a greater adsorption capacity. Consequently, the achievement of carbon saturation will require a longer time. The parameters m_3 and m_4 involve the various substrate concentrations in the liquid phase as well as the ratio of the rates of substrate utilizations. For example, a larger value of m_3 implies that the oxygen depletion will occur at a later time.

The results of sample calculations made in this study corresponding to a typical set of parameter values (roughly that used for the experimental work described in Part II) are shown in Figures 3–10. In Figure 3, the histories of effluent concentrations of the organic substrate [expressed as dissolved organic carbon (*DOC*)], dissolved oxygen (*DO*), and nitrate for two column heights are shown.

Initially, the bacterial film coverage of carbon granules is slight. The removal of the organic substrate is largely due to adsorption. The initial part of *DOC* curve, in fact, is very similar to breakthrough curves observed in fixed-bed absorption. Both the degrees

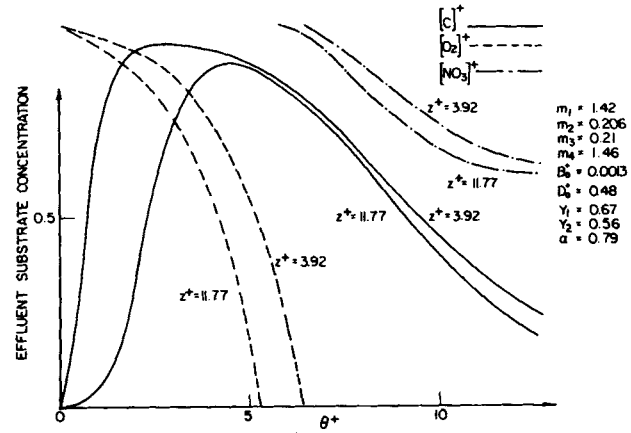

Figure 3. Substrate concentration histories at different bed heights—bi-layer growth.

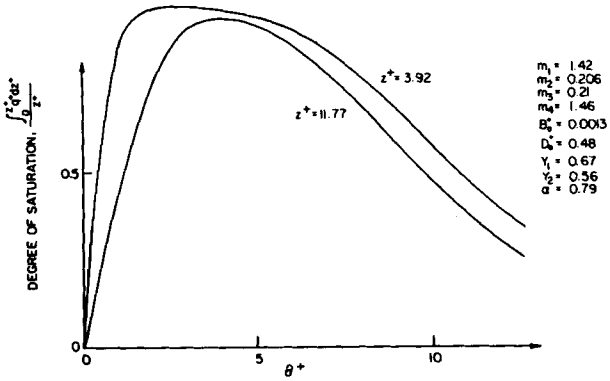

Figure 4. Adsorption histories of different bed heights—bi-layer growth.

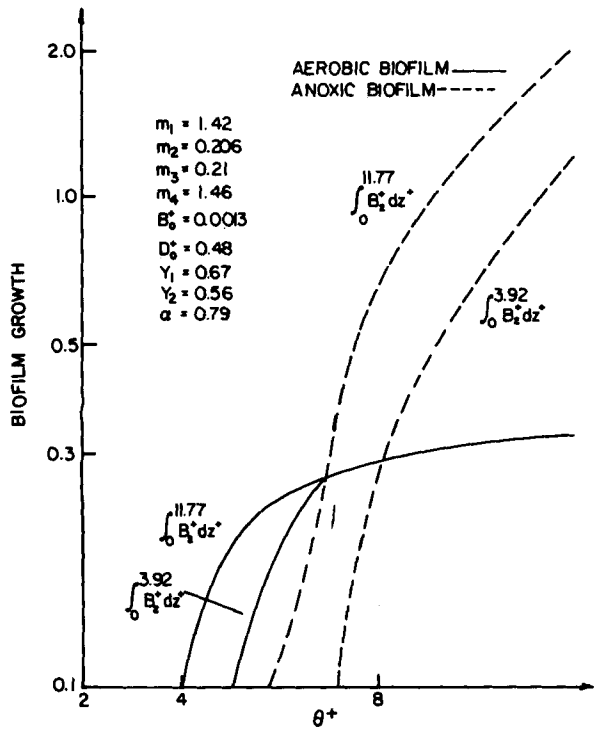

Figure 5. Aerobic and anoxic biofilm growth of different bed heights—bi-layer growth.

of carbon saturation and film coverage increase with time. Eventually, a significant film coverage retards adsorption. This factor, is however, compensated for by the increase in the removal of the organic substrate as a result of biodegradation. The reason for this change is that biological activity is directly proportional to the extent of film coverage.

This fact explains the behavior exhibited by the second part of the *DOC* curve, which shows a steady decrease with time. The depletion of the *DO* occurs shortly after the effluent concentration of the organic substrate reaches its maximum. As expected, the removal of nitrate occurs only after the depletion of the *DO*.

The degree of saturation of adsorbents varies with both time and axial distance. The degree of saturation of the column as a whole can be determined by evaluating the integral $\int_0^{z^+} q^+ dz^+$. This situation is shown in Figure 4, in which the values of $1/z + \int^{z+} q^+ dz^+$ for two column heights are shown as functions of time, θ^+. By comparing Figure 3 with Figure 4, one can see that the maximum degree of saturation occurs at approximately the time when the value of $[C^+]$ reaches its maximum. The decrease of the degree of saturation occurs when the *DOC* concentration at the film base is less than that in the adsorbed phase. As expected, because of bioregeneration, the maximum degree of saturation achieved in a shallow bed is greater than that of a lengthier column.

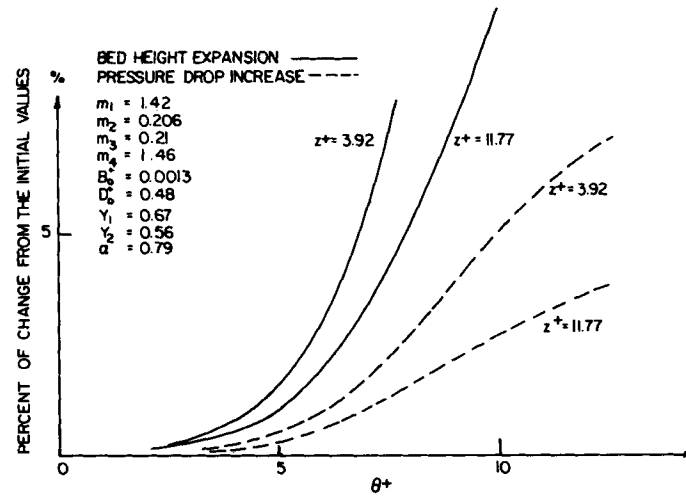

Figure 6. Bed height expansions and pressure drop increase at different bed heights—bi-layer growth.

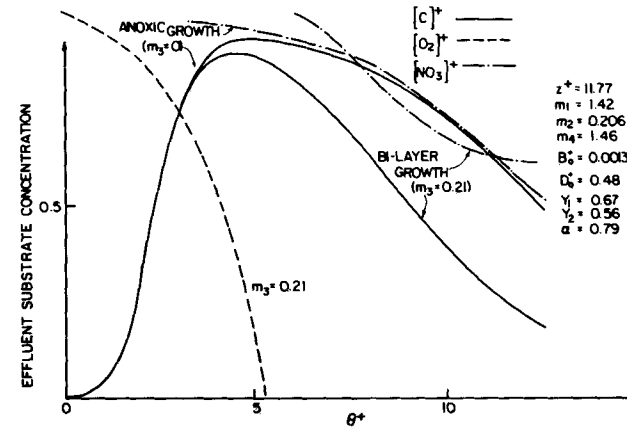

Figure 7. Substrate concentration histories—comparison between anoxic and bi-layer growth.

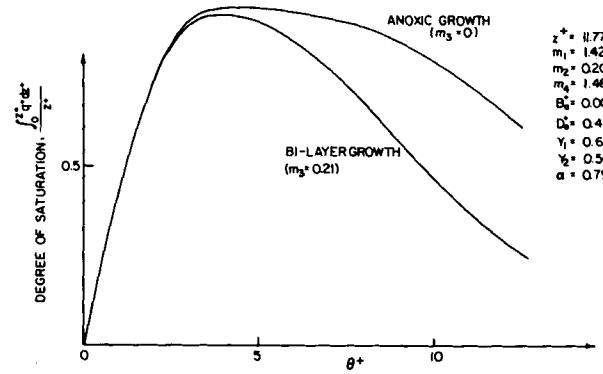

Figure 8. Adsorption histories—comparison between anoxic and bi-layer growth.

The extent of film growth throughout the column can be described by the quantity $\int_0^{z^+} B_1^+ dz^+$ and $\int_0^{z^+} B_2^+ dz^+$, as shown in Figure 5. The relative importance of aerobic growth vs. anoxic growth can be seen by comparing the magnitude of these two quantities. It is also evident that the time at which the value of $\int_0^{z^+} B_2^+ dz^+$ becomes comparable to $\int_0^{z^+} B_1^+ dz^+$ coincides with the beginning of significant denitrification, as shown by the nitrate concentration curves in Figure 3.

As is evidenced by Figure 6, neither bed height expansion nor pressure drop increase is found to be significant in these particular examples. For both cases, the increases in bed height and in pressure drop are found to be less than 10% and 5%, respectively.

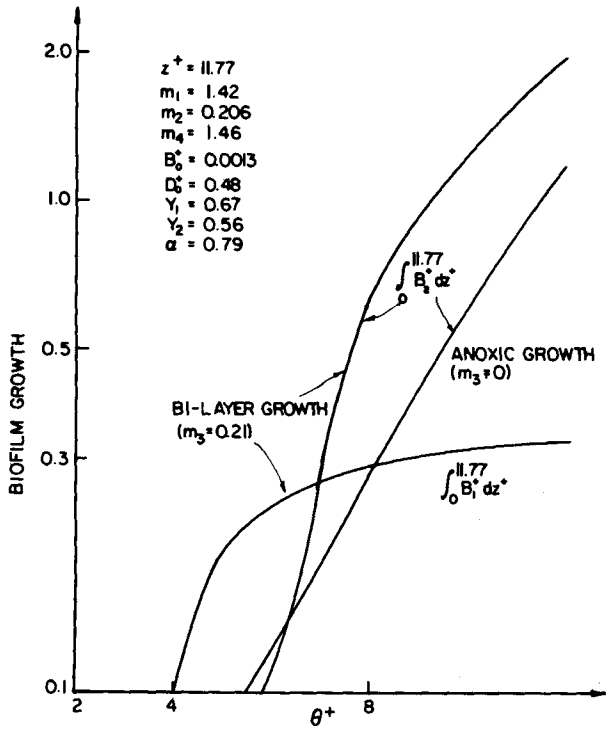

Figure 9. Aerobic and anoxic biofilm growth—comparison between anoxic and bi-layer growth.

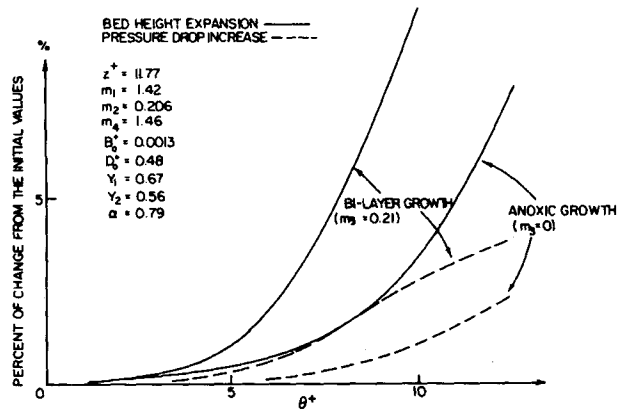

Figure 10. Bed height expansions and pressure drop increases—comparison between anoxic and bi-layer growth.

The effect due to the presence of *DO* is shown in Figures 7–10. In terms of the removal of the organic substrate, the effect of the microbial activity for the bilayer case is more pronounced than that of anoxic growth case, as seen from the *DOC* concentration curves in Figure 7. The same behavior is also shown in the extent of bioregeneration (Figure 8) and the film coverage values (Figure 9). As a consequence, the extent of bed height expansion and pressure drop increase is greater if *DO* is present in the influent (Figure 10).

ACKNOWLEDGMENT

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NOTATION

a,b = constants in Eq. 11
a_1,b_1 = constants in Eq. 12
a_2,b_2 = constants in Eq. 15
a_p = particle radius, cm
a_s = radius of biofilm attached particle, cm
B = biofilm organic carbon/weight of clean particle
B' = defined as $\sqrt{k/D_c}\,\frac{1}{\rho}\,\frac{a_p\rho_p}{3}\,B$
$[C]$ = dissolved organic carbon concentration, g/cm^3
$[C]_i$ = initial value of $[C]$
$[C]^+$ = defined as $[C]/[C]_i$
D_c = diffusivity of *DOC* in biofilm, cm^2/s
D_f = free-liquid diffusivity, cm^2/s
D_n = diffusivity of nitrate in biofilm, cm^2/s
D_0 = diffusivity of *DO* in biofilm, cm^2/s
D_0^+ = defined as D_o/D_c
g = acceleration of gravity, cm/s^2
H = bed height, cm
j = index of distance from column inlet
K = defined as $(B_1^+/Y_i) + (B_2^+/Y_1) + m_3q^+$
k = *DOC* uptake rate constant in aerobic respiration, s^{-1}
k_p = particle-phase mass transfer coefficient, cm/s
L = biofilm thickness, cm
L_I = anoxic biofilm thickness, cm
m_1 = defined as $\Lambda k_p/\sqrt{kD_c}$
m_2 = defined as $(q^*a_p/3\rho)\sqrt{k/D_c}$
m_3 = defined as $[O_2]_i/\beta[C]_i$
m_4 = defined as $\dfrac{\alpha[NO_3]_i}{\gamma[C_i]}$
N_c = *DOC* flux at biofilm surface, g/s·cm^2
N_n = nitrate flux at biofilm surface, g/s·cm^2
N_0 = *DO* flux at biofilm surface: g/s·cm^2
$[NO_3]$ = nitrate concentration
$[NO_3]_i$ = initial value of $[NO_3]$
$[O_2]$ = dissolved oxygen concentration
$[O_2]_i$ = initial value of $[O_2]$
$[O_2]^+$ = defined as $[O_2]/[O_2]_i$
n = index of time elapsed
P_c = function defined by Eq. 33a
P_n = function defined by Eq. 33b
P_0 = function defined by Eq. 33c
q = concentration of adsorbed organic carbon, g/cm^3
q_i = value of q at adsorbent-film interface
q^* = equilibrium value of q, g/cm^3
S_c = *DOC* concentration in biofilm, g/cm^3
S_n = nitrate concentration in biofilm, g/cm^3
S_0 = *DO* concentration in biofilm, g/cm^3
t = time,
u = superficial velocity, cm/s
v = biofilm volume/clean particle volume
$\bar{v}$ = average value of v
x = distance from biofilm base, cm
Y = yield coefficient: biofilm organic carbon generation/*DOC* consumption
$y_{11},y_{12},y_{21},y_{22}$ = constants in Eqs. 11 and 13
$y_{11},y_{12},y_{21},y_{22}$ = defined as $y/[C]_i$
z = distance from inlet of reactor, cm
z' = equivalent distance if there is no biofilm, cm
z^+ = defined as $3z'(1-\epsilon)\sqrt{kD_i}(ua_p)$

Subscripts

1 = aerobic region
2 = anoxic region
c = value for clean particles
e = effluent
i = influent
0 = condition at time zero

Superscripts

$+$	= dimensionless quantity
(i)	= ith iteration

Greek Letters

α	= DOC uptake rate ratio of anoxic growth to aerobic growth
β	= uptake rate ratio of DO reduction to aerobic DOC degradation
γ	= uptake rate ratio of nitrate reduction to aerobic DOC degradation
ϵ	= bed porosity
ϵ_c	= clean bed porosity
θ	= corrected time defined by Eq. 29, s
θ^+	= defined as $[C]_t k\theta/\rho$
Λ	= partition coefficient defined by Eq. 17
μ	= liquid viscosity, poise
ρ	= organic carbon density of biofilm, g/cm^3
ρ_b	= biofilm density, g/cm^3
ρ_f	= fluid density, g/cm^3
ρ_p	= particle density, g/cm^3
ρ_s	= density of biofilm attached particle, g/cm^3

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Bilayer Film Model for the Interaction between Adsorption and Bacterial Activity in Granular Activated Carbon Columns

Part II: Experiment

Experiments were conducted on the degradation of valeric acid in aqueous solutions by bacteria in attached growth and on the removal of valeric acid from aqueous solutions in granular activated carbon columns. The first type of experiment was intended to obtain results necessary to determine the values of the relevant parameter of biofilm kinetics. These parameters were then used in conjunction with the model developed in Part I to predict the performance of carbon columns for removing valeric acid. Comparisons between experiments and predictions constitute the necessary model validation.

S-C P. WANG and CHI TIEN

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

SCOPE

The experimental work conducted in this study is of two kinds: (a) the degradation of valeric acid in aqueous solutions in a fluidized reactor and (b) the removal of valeric acid and denitrification of the aqueous solution in granular carbon columns with significant microbial growth.

The analysis of Part I has shown that the interaction between

S-C. Wang is presently with W. R. Grace Inc., Columbia, Md.