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.

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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

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adsorption and bacterial growth can be described by two sets of parameters: adsorption parameters and bacterial parameters. In this study procedures consistent with the bilayer model framework were developed for evaluating these parameters from fluidized reactor data. From the carbon column experiments, effluent concentration histories of the organic substrate, the dissolved oxygen, and the nitrate as well as bed height change were obtained. These results were compared with predictions from the model developed in Part I for the purpose of model validation.

CONCLUSIONS AND SIGNIFICANCE

The validity of the bilayer model is demonstrated through the agreement between model predictions and the experimental results. The fluidized reactor experiments also indicate that the fluidized reactor is, indeed, a versatile apparatus in obtaining biofilm kinetic parameters. Moreover, the parameters obtained under restricted conditions (either aerobic or anoxic with no adsorption) can be applied to a more general situation.

This study substantially extends the earlier work of Andrews and Tien (1981). It provides a broader and more useful framework for examining not only the ways of combining adsorption and bacterial growth in waste treatment but also and equally important, the new possibilities of analyzing attached growth systems of biological treatment.

PRINCIPLES OF DETERMINING BACTERIAL PARAMETERS

The model formulated in Part I involves the use of: the adsorption parameters, including the partition coefficient, Λ, and the particle-phase mass transfer coefficient, k_p; and the bacterial parameters, including the yield coefficients, Y_1 and Y_2, the film density, ρ, the rate constant and reaction rate ratio, k, α, β, and γ, and the diffusivities, D_c, D_0, and D_n. Procedures used in determining the adsorption parameters are well known and adequately documented elsewhere (Hsieh et al., 1977; Andrews and Tien, 1981). The principles applied in determining the bacterial parameters, however, are discussed below.

Generally speaking, in order to investigate the dynamics of bacterial growth, continuous culture provides a convenient method of maintaining the culture over prolonged periods of time. A chemosat is widely used in studying microbial activities in dispersed phase. A chemosat, in fact, functions as a completely stirred tank reactor (CSTR). When used in the study of attached biofilm growth, it has to meet three requirements:

(1) A sufficient quantity of inert support must be present to produce the required surface for biofilm growth.

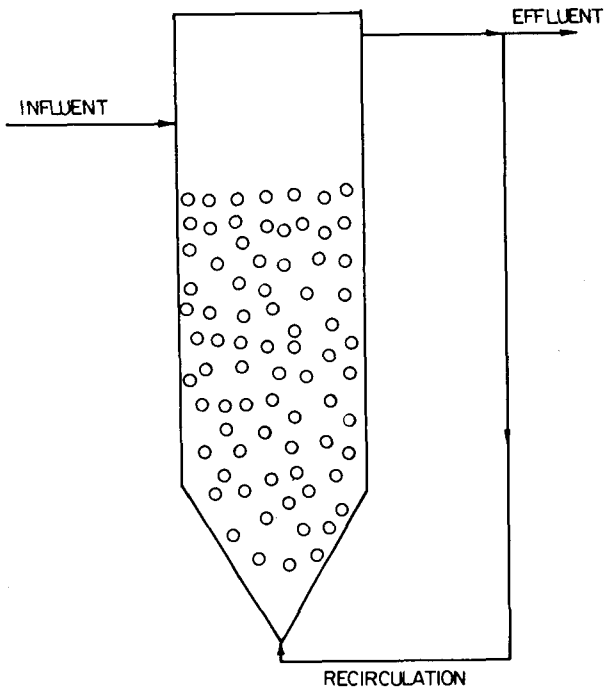

Figure 1. Modified continuous stirred tank reactor for determining bacterial parameters in biofilm.

(2) The reactor holding time should be kept close to or less than the microbial generation time in order to minimize the microbial activity in the dispersed phase.

(3) The reactor should be operated with a high recycle ratio to achieve perfect fluid mixing.

Assuming that a fluidized reactor with nonadsorbing particles is employed to determine the bacterial parameters, Figure 1, one can monitor the influent and effluent concentrations [*DOC* (dissolved organic carbon), *IC* (inorganic carbon), *TC* (total carbon), O_2, and NO_3] and the bed height as functions of time. From the results of these measurements, the biological parameters can be obtained according to the procedures described below.

Anoxic Growth

The conservation equations of the *DOC*, the *IC*, the NO_3, and the *TC* for a fluidized reactor with nonabsorbing paticles are:

$$V\frac{d[C]}{dt} = F([C]_i - [C]) - \frac{W}{Y_2}\frac{dB_2}{dt} \tag{1a}$$

$$V\frac{d[IC]}{dt} = F([IC]_i - [IC]) + \frac{W(1-Y_2)}{Y_2}\frac{dB_2}{dt} \tag{1b}$$

$$V\frac{d[NO_3]}{dt} = F([NO_3]_i - [NO_3]) - \frac{\gamma W}{\alpha Y_2}\frac{dB_2}{dt} \tag{1c}$$

$$V\frac{d\Delta TC}{dt} = W\frac{dB_2}{dt} - F\Delta TC \tag{1d}$$

where V is the liquid phase volume of the reactor, F is the flow rate through the reactor, W is the weight of the particles, and $\Delta TC = (TC)_i - TC$.

With $\Lambda = 0$ (nonabsorptive), Eq. 24a of Part I renders the anoxic biofilm growth expression as

$$\frac{dB_2}{dt} = \frac{3Y_2}{a_p\rho_p}\sqrt{\alpha k D_c}[C]\tanh\sqrt{\alpha k/D_c}\,\frac{1}{\rho}\frac{a_p\rho_p}{3}B_2 \tag{2}$$

The following points should be noted about these equations. The effect due to the activities of the microorganisms in the dispersed phase is ignored, and a complementary relationship between the production of biomass and oxidative product is assumed.

It can be shown (Wang, 1981) that, after a short transient period, the following relationships can be obtained from Eqs. 1a–1c:

$$Y_2 = 1 - \frac{[IC] - [IC]}{[C]_i - [C]} \tag{3a}$$

$$\frac{\gamma}{\alpha} = \frac{[NO_3]_i - [NO_3]}{[C]_i - [C]} \tag{3b}$$

One can, therefore, determine the values of Y_2 and γ/α from the concentration histories of the organic substrate, the *IC*, and the NO_3, in the reactor.

For the determination of the organic carbon density of biofilm, ρ, consider an initially sterilized reactor and then seeded with bacteria culture and substrates. At the end of the inoculating period, the microbial film present in the bed (B_0, expressed in terms of its organic carbon equivalent) can be obtained as:

$$V\Delta TC_0 = WB_0 \tag{4}$$

where ΔTC_0 is the change in the total carbon concentration of the solution present in the reactor. Accordingly, Eq. 4 can be used as the initial condition for the determination of B from Eq. 1d, or

$$B_2 = \frac{F}{W}\left(\frac{V}{F}\Delta TC + \int_0^t \Delta TC\, dt\right) = B_0 + \frac{\rho}{\rho_p}v \tag{5}$$

The quantity v, the volume of film per unit volume of clean particles, can be found from the data on bed height increase. The relationship among v, the bed height, H, and the bed porosity, ϵ, for a fluidized bed operated as a CSTR is found to be (Wang, 1981)

$$\frac{H}{H_c} = \frac{1-\epsilon_c}{1-\epsilon}(1+v) \tag{6}$$

$$\left(\frac{\epsilon}{\epsilon_c}\right)^{-4.7} = \frac{4.5 + C_R}{4.5 + C_R(1+v)^{0.229}} \frac{1 + \dfrac{\rho_b - \rho_f}{\rho_p - \rho_g}v}{(1+v)^{1/3}} \tag{7}$$

where $C_R = 1.087\,(a_p u \rho_f/\mu)^{0.687}$

Thus, from bed height measurements and total carbon concentration measurements, corresponding values of ρv and v can be calculated. The quotient of these two quantities yields the value of ρ.

Finally, to determine αk and D_c, Eqs. 1a and 2 are applied. If a quasisteady-state assumption is invoked, Eq. 1a can be simplified to give

$$[C]_i - [C] = \frac{W}{FY_2}\frac{dB_2}{dt} \tag{8}$$

Substituting Eq. 2 into Eq. 8, one has

$$\frac{[C]_i}{[C]} - 1 = \frac{W}{F}\frac{3}{a_p\rho_p}\sqrt{\alpha k D_c}\tanh\sqrt{\alpha k/D_c}\,\frac{1}{\rho}\frac{a_p\rho_p}{3}B_2 \tag{9}$$

At small film thickness (small B_2), Eq. 9 becomes

$$\frac{[C]_i}{[C]} - 1 = \frac{\alpha k W B_2}{F\rho} \tag{10a}$$

αk, therefore can be determined from the concentration histories of the TC (to determine the value of B_2 from Eq. 5) and the DOC during the initial experimental period.

At large, B_2, Eq. 9 becomes

$$\frac{[C]_i}{[C]} - 1 \simeq \frac{W}{F}\frac{3}{a_p\rho_p}\sqrt{\alpha k}\sqrt{D_c} \tag{10b}$$

One can, therefore, determine the value of D_c from the ratio of the DOC concentration of influent to that of the effluent.

Aerobic Growth

Under the condition of aerobic growth, the conservation equations of the organic carbon, the IC, the DO, and the TC are

$$V\frac{d[C]}{dt} = F([C]_i - [C]) - \frac{W}{Y_1}\frac{dB_1}{dt} \tag{11a}$$

$$V\frac{d[IC]}{dt} = F([IC]_i - [IC]) + \frac{W(1-Y_1)}{Y_1}\frac{dB_1}{dt} \tag{11b}$$

$$V\frac{d[O_2]}{dt} = F([O_2]_i - [O_2]) - \frac{\beta W}{Y_1}\frac{dB_1}{dt} \tag{11c}$$

$$V\frac{d\Delta TC}{dt} = W\frac{dB_1}{dt} - F\Delta TC \tag{11d}$$

With $\Lambda = 0$ (nonadsorptive), Eq. 24b of Part I gives the aerobic biofilm growth expression as

$$\frac{dB_1}{dt} = \frac{3Y_1}{a_p\rho_p}\sqrt{kD_c}\,[C]\tanh\sqrt{k/D_c}\,\frac{1}{\rho}\frac{a_p\rho_p}{3}B_1 \tag{12}$$

Similar to the case of anoxic growth, after a short period of transiency, Eqs. 11a–11b can be combined to give

$$Y_1 = 1 - \frac{[IC] - [IC]_i}{[C]_i - [C]} \tag{13}$$

$$\beta = \frac{[O_2]_i - [O_2]}{[C]_i - [C]} \tag{14}$$

One can, therefore, determine the values of Y_1 and β from the concentration histories of the organic carbon, IC, and DO in the reactor.

Similar to Eqs. 5 and 9, one can show

$$B_1 = \frac{F}{W}\left(\frac{V}{F}\Delta TC + \int_0^t \Delta TC\, dt\right) + B_0 \tag{15}$$

$$\frac{[C]_i}{[C]} - 1 = \frac{W}{F}\frac{3}{a_p\rho_p}\sqrt{kD_c}\tanh\sqrt{k/D_c}\,\frac{1}{\rho}\frac{a_p\rho_p}{3}B_1 \tag{16}$$

At thin film, i.e., B_1, Eq. 16 becomes

$$\frac{[C]_i}{[C]} - 1 = \frac{Wk}{F\rho}B_1 \tag{17}$$

The reaction rate constant, k, therefore, can be determined from the concentration histories of the TC and the DOC.

When the aerobic biofilm has developed to its transition state, which is defined as $s_0|_{x=0} = 0$ and $L_I = 0$ (i.e., the onset of the anoxic layer), Eq. 19 of Part I provides the following relationship:

$$\frac{[C]}{\cosh\sqrt{k/D_c}\,\dfrac{1}{\rho}\dfrac{a_p\rho_p}{3}B_1} = [C] - \frac{D_0}{\beta D_c}[O_2] \tag{18}$$

Thus, the diffusivity, D_0, of the DO in the biofilm can be determined from the values of $[C]$, $[0]$, and B_1, according to Eq. 18. The achievement of the transition state can be easily detected experimentally by the emergence of a noticeable degree of denitrification.

The discussions presented above enable the determination of nine of the ten biological model parameters. The only undetermined parameter is D_n. On the other hand, since nitrate is not the limiting nutrient, the value of D_n is, therefore, not required in the theoretical prediction.

EXPERIMENTAL WORK

Determination of Bacterial Parameters (Fluidized-Bed Reactor Experiments)

Equipment. The experimental apparatus used in this work (Figure 2) was essentially the same as that designed by Andrews (1979, 1981) with the addition of a temperature control unit. The storage tank held a 24-hour supply of tap water at room temperature. Air was constantly sparged through the water to strip off chlorine. The constant head tank was fed via an upflow filter that removed impurities from the water. This filter was washed between each experiment.

The actual reactor was a plexiglass column, 7.62×10^{-2} m i.d., and 0.762 m high, calibrated for bed height measurement. It was fed by gravity from a constant head tank. The nutrient solution (with its composition given in Table 1) was injected into the influent stream by a feed pump, at a point downstream of the flow meter.

Flow through the reactor was maintained with the use of a Manostat peristaltic pump. The recirculation was kept at a large, constant rate, so that the reactor functioned as a stable fluidized bed. With its high recirculation rate, the reactor could be considered a completely stirred tank reactor. The temperature control unit consisted of a heat exchanger connected to a constant temperature bath. This control unit was capable of maintaining the reactor temperature at 23 ± 1°C. Short circuiting was prevented by the use of a small stirrer at the top of the reactor.

The nitrogen bubbles produced by anoxic denitrification tended to adhere to the coal particles and, in turn, to carry them out of the reactor. The top of the reactor was designed to minimize this problem. The stirrer section knocked the bubbles off the particles and returned the particles to the bed.

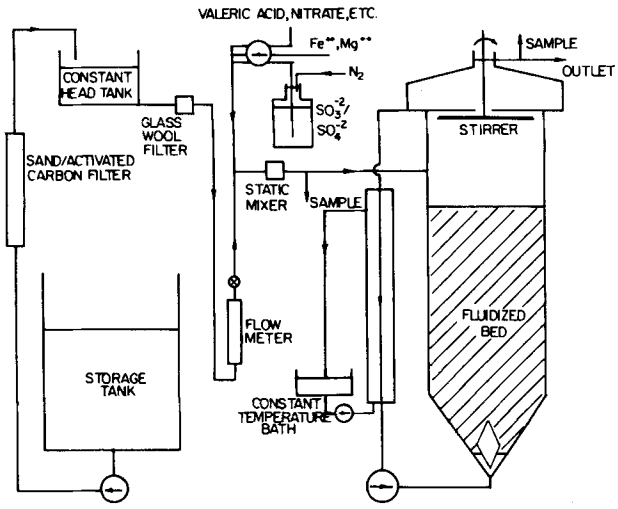

Figure 2. Fluidized reactor (not to scale).

The upper section was a radial-flow gas bubble separator that prevented the bubbles from being recirculated. The baffled conical entrance section was designed to minimize entrance effects. The operating conditions used in this experiment are listed in Table 1.

Procedure. Eight runs were completed with the equipment described above. Four were made under anoxic growth conditions; the other four were conducted under aerobic conditions. The procedures are as follows:

Before each run, the reactor was washed and disinfected using a 3% Lysol solution. Coal particles of the size range $0.595 \sim 0.707$ cm were obtained from sieving and washed at least ten times in distilled water in order to remove fines and soluble organic matter before they were loaded into the reactor. Further removal of coal fines was completed by back-washing the bed with distilled water.

Coal beds were seeded with bacteria by first filling the reactor with a solution which was similar in composition to the influent stream. A small amount of seed culture of mixed denitrifying bacteria was added, and this mixture of denitrifying bacteria and nutrients was circulated slowly through the bed for 1 to 2 days. Assuming that the coal particles were sterile initially, a carbon balance over this seeding period gave the initial film coverage, B_0, by the expression

$$V\Delta TC_0 = WB_0$$

After the influent stream was started, measurements of total carbon (*TC*), dissolved organic carbon (*DOC*), dissolved inorganic carbon (*DIC*), and dissolved oxygen (*DO*) concentrations of both the influent and effluent were made by taking samples at 8- to 12-hour intervals.

Throughout this work, Beckman 915A Total Organic Carbon (TOC) Analyzer was used to measure the carbon concentrations. The influent samples were taken from a point between the static mixer and the reactor (Figure 2), and the effluent samples were taken from the top of the reactor. The total carbon (*TC*) concentration was measured directly by injecting the sample into the TOC Analyzer. The dissolved carbon (*DC*) concentration was measured by collecting a large sample (from either the influent or effluent of the reactor) and filtering it through a membrane filter of 0.2 μm pore size. The measured *TC* concentration of the filtrate gave the *DC* concentration of the sample. If this filtrate was first acidified and sparged with nitrogen to remove the presence of dissolved carbon dioxide, the *TC* concentration of the resulting solution became the same as the *DOC* concentration. The *IC* concentration could then be obtained by subtracting the *DOC* concentration from the *DC* concentration.

For the analysis of the nitrate concentration, an Orion Model 701A digital ionalyzer, Model 93-07 nitrate electrode, and a Model 90-02 double-junction reference electrode were used. The unacidified filtrate was used in this measurement.

An Extech Model 8012 dissolved oxygen probe was connected to the Orion Mode 701A digital ionalyzer to measure the *DO* concentrations in the samples. For the *DO* concentration measurements, influent samples were taken from the head tank, and effluent samples were collected through a 50 mL syringe at the reactor's outlet. This sampling procedure eliminated the possible adsorption of oxygen from the atmosphere.

The bed height was also measured. Prior to taking the measurement, any particles that had settled in the upper section of the reactor were recirculated to the base of the bed. Spot checks were also made of the effluent flow rate, temperature, and pH.

Anoxic runs were normally continued until the production of nitrogen bubbles became vigorous and caused a significant loss of coal particles from the fluidized reactor. In the aerobic measurements, runs were discontinued when nitrogen bubbles were observed to adhere to the coal particles.

Equipment Experiments

Equipment. The experimental apparatus for the column experiments is shown in Figure 3. The auxiliary equipment for the supply of tap water and nutrients was the same as that described previously. Three identical plexiglass columns, 2.54×10^{-2} m i.d. and 0.9144 m high with calibration (for bed height measurement), were used as test columns. They were employed simultaneously and fed by a Cole-Parmer Masterflex pump. A static mixer was placed before the pump to mix the treated tap water with required concentrated streams of nutrients.

The presence of denitrifying bacteria in the activated carbon bed during experiments produced nitrogen gas. Although most of the nitrogen bubbles formed would eventually escape out of the bed, they tended to remain within the bed for a considerable time if unaided. This production of nitrogen had a two-fold effect on the experiment. First, the presence of considerable bubbles reduced the contact time and contact surface between liquid (test solution) and solid (carbon granules) phases. Second, the bubbles tended to carry carbon particles out of the bed (by flotation). To overcome these difficulties, a stainless steel rod (4.7625×10^{-3} m diameter and 0.6096 m in height) with attached fins was placed into the center of the plexiglass column. The rod was made to move axially in a reciprocating manner (0.8333 Hz, 1.5875×10^{-3} m axial displacement) with the use of a cam

TABLE 1. EXPERIMENTAL CONDITIONS FOR THE FLUIDIZED REACTOR

Run #	1	2	3	4	5	6	7	8
Particle Volume (cm^3)	246	246	246	247	246	181	181	181
Clean Bed Height (cm)	21.9	23.7	23.4	24.4	21.4	15.5	15.3	14.4
Clean Bed Porosity	0.754	0.772	0.770	0.778	0.748	0.744	0.741	0.724
Reactor Volume (10^{-3} m^3)	4.57	4.57	4.57	4.57	1.55	1.55	1.55	1.55
Superficial Velocity (cm/s)	1.07	1.07	1.07	1.07	0.978	1.07	1.07	1.07
$[C]_f$ (ppm)	33.6	34.9	35.8	32.9	22.5	22.7	22.4	22.4
$[NO_3]_f$ (ppm)	290	380	400	190	110	110	110	110
$[O_2]_f$ (ppm)	0	0	0	0	9.5	9.8	9.6	9.6

Type of Particle: Coal, $a_p = 0.033$ cm; $\rho_p = 1.38$ gm/cm^3
Flow Rate through the Reactor: 3 mL/s; Reactor Radius: 3 cm
Temperature: 23 ± 1°C; pH: 7.2 ± 1.

Substrate Concentration of Test Solutions: Basis 1 L tap water

KH_2PO_4	17.0 mg	$Co(NO_3)_2 \cdot 6H_2O$	0.23 mg
K_2HPO_4	43.5 mg	$MgSO_4 \cdot 7H_2O$	15.0 mg
$Na_2HPO_4 \cdot 7H_2O$	66.8 mg	$FeSO_4 \cdot 7H_2O$	10.0 mg
NH_4Cl	70.0 mg	Valeric Acid $CH_3(CH_2)_3COOH$	Varied
Na_2SO_3	94.5 mg (Anoxic Growth)	$NaNO_3$	Varied
Na_2SO_4	106.5 mg (Aerobic Growth)		

TABLE 2. EXPERIMENTAL CONDITIONS FOR THE COLUMN EXPERIMENTS

Run #	1	2	3	4	5	6	7	8	9	10	11	12
Particle Radius (mm)	0.49	0.38	0.33	0.49	0.38	0.33	0.49	0.38	0.33	0.49	0.38	0.33
Weight of Carbon (g)	60	40	50	40	50	60	40	50	60	40	50	60
Initial Bed Height (cm)	28.4	20.6	27.0	19.0	25.0	32.6	18.8	24.7	31.6	18.6	24.7	31.7
Initial Bed Porosity, × 10	3.55	4.07	4.34	3.57	3.89	4.38	3.50	3.82	4.20	3.43	3.82	4.22
Volumetric Flow Rate (cm^3/min)	32.0	31.5	30.5	30.5	30.5	30.5	31.0	30.5	30.5	31.0	30.5	30.5
$[C]_{ni}$ (ppm)	31.3	31.3	31.3	23.4	23.4	23.4	31.9	31.9	31.9	22.8	22.8	22.8
22.8												
$[NO_3]_i$ (ppm)	250	250	250	140	140	140	190	190	190	130	130	130
$[O_2]_i$ (ppm)	0	0	0	0	0	0	8.9	8.9	8.9	8.4	8.4	8.4
B_0 (10^{-6})	8.54	23.0	41.6	10.5	29.3	45.5	15.8	38.4	55.4	14.1	33.9	47.6

Type of Particle: Darco Activated Carbon, ρ_p = 0.67 g/cm^3
Reactor Radius: 1.247 cm
Temperature: 23 ± 1°C pH: 7.2 ± 0.1

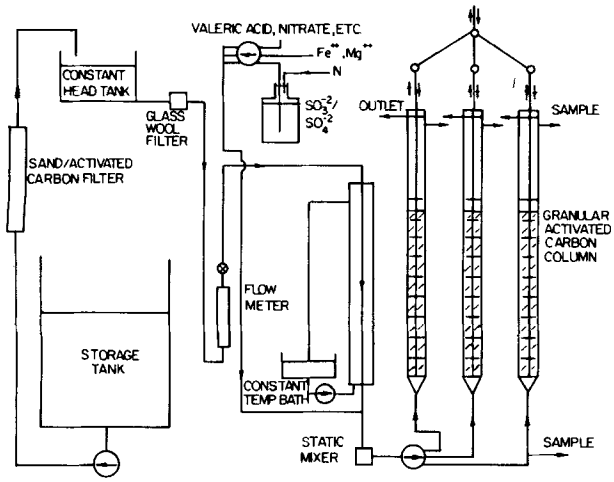

Figure 3. Equipment for column experiments (not to scale).

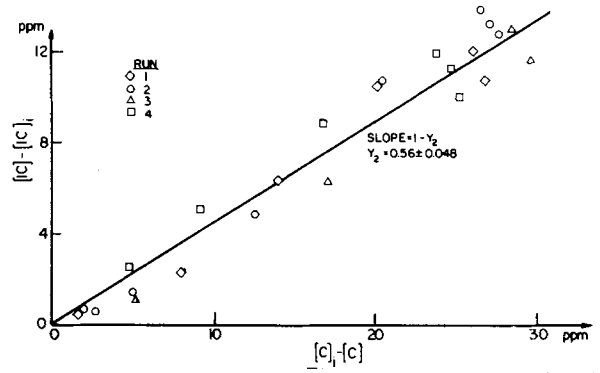

Figure 4. Dissolved inorganic carbon production vs. dissolved organic carbon degradation.

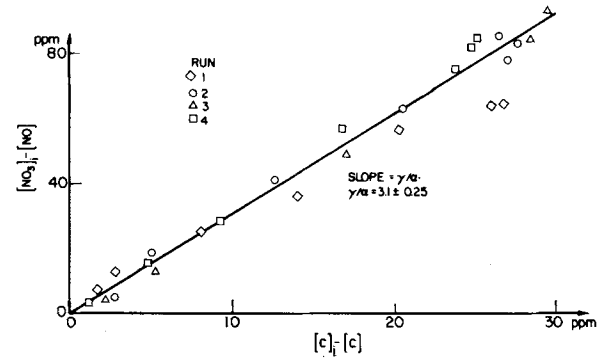

Figure 5. Nitrate reduction vs. dissolved organic carbon degradation—anoxic growth.

arrangement. The movement produced also prevented the agglomeration of carbon particles. The operating parameters used in these experiments are shown in Table 2.

Procedure. Four sets of experiments were completed with the equipment described above. Two sets were made with test solutions devoid of *DO*, while the other two were made with test solutions with *DO*. Since three columns were operated in each set of experiments, twelve runs were accomplished.

Using the procedure described above, Darco Activated Carbon Particles (Atlas Chemical Industries) of three different sizes were prepared. Seeding was accomplished by injecting a fixed amount of seeding culture into the lower part of the bed immediately after the influent stream was started. The determination of the initial film coverage of carbon, B_0, follows the established procedures (Wang, 1981; Tien and Wang, 1982).

The test solution was passed through the carbon bed in an upward manner, thus minimizing bed clogging, as mentioned earlier. The influent and effluent concentrations (valeric acid expressed in *DOC*, *DO*, and NO_3) were measured periodically using the methods previously described. Bed heights and flow rates were also measured at the same time. Spot checks were also made of the effluent temperature and pH.

Runs were normally continued until the DOC concentrations of the effluents reached steady-state values for all three columns. This condition depended on substrate concentrations, bed heights, and bacteria seeding. Two to three days were generally required under the conditions studied in this work.

RESULTS

Bacterial Parameters for Anoxic Growth

Four runs were made with the fluidized bed reactor. The data obtained are the histories of the total carbon (*TC*), dissolved organic carbon (*DOC*), dissolved inorganic carbon (*DIC*) and dissolved oxygen (*DO*) concentrations and bed height.

The anoxic biological parameters were determined from these data according to Eqs. 3c, 3b, 5–7, 10a, and 10b. In Figure 4, the data of $[IC] - [IC]_i$ were plotted against $[C]_i - [C]_0$. According to Eq. 3a, the data should yield a straight line with the slope being $1 - Y_2$. The best fitted line gives $Y_2 = 0.56 \pm 0.048$, with 95% confidence interval. Similarly, according to Eq. 3b, the plot shown in Figure 5 yields $\gamma/\alpha = 3.1 \pm 0.25$ (95% confidence interval).

The organic density of the bacterial film, ρ, was determined on the basis of Eqs. 5–7. From Eqs. 6 and 7 together with the bed height history, values of v as a function of time were established. Similarly based on Eq. 5, the concentration history of *TC* enabled the calculation of ρv at specified times. When the latter quantity was plotted against the former (Figure 6), a straight line passing through the origin was expected. The value of ρ was found to be 37 ± 5.5 mg/cm^3.

Figure 7 illustrates the determination of the parameter αk. The procedure was based on Eqs. 5 and 10a, which suggested that a plot of

$$([C]_i/[C] - 1 \text{ vs. } \frac{1}{\rho}\left(\frac{V}{F}\Delta TC - \int_0^t \Delta TC\, dt\right)$$

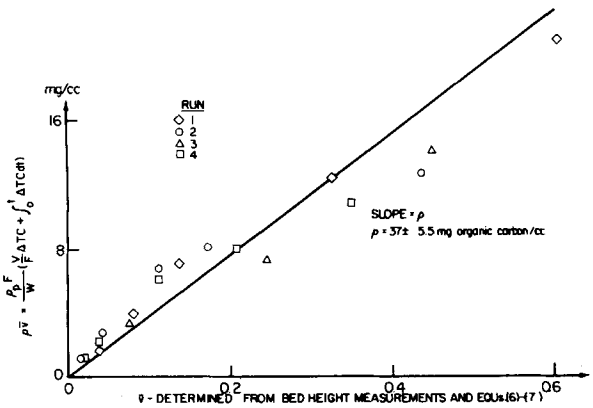

Figure 6. Estimate of the organic carbon density of biofilm—anoxic growth.

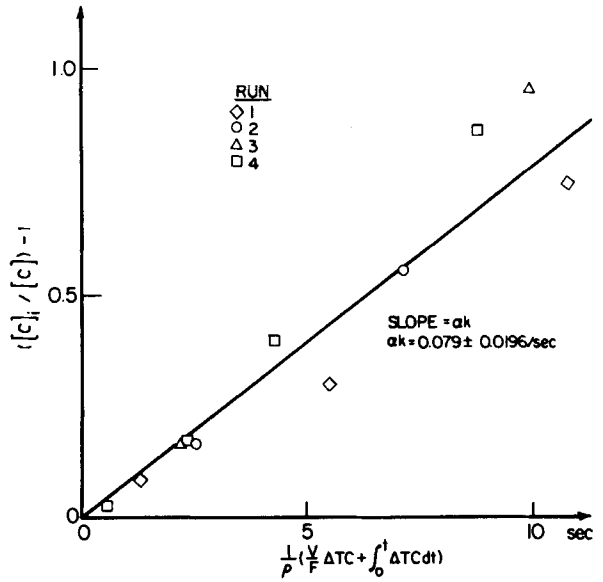

Figure 7. Dissolved organic carbon removal with small film volume—anoxic growth.

should yield a straight line. The results give $\alpha k = 0.079 \pm 0.0196$ L/s (95% confidence interval).

The value of the diffusivity of the organic substrate, D_c, was found from these data according to Eq. 10b. Equation 10b applies when the film is relatively thick. Under such conditions, the *DOC* value was low (4.5 ~ 7 ppm), and the error of measurements became more significant. The average value of $[C]_i/[C]$ of the last two sample measurements for each run was used to calculate D_c from Eq. 10b. The results are given in Table 3.

Bacterial Parameters of Aerobic Growth

The determination of Y_1, k, and α was based on Eq. 13–17 and followed procedures similar to those of the anoxic case described above. The results are shown in Figures 8–10.

D_0 was determined from experimental data on the basis of Eq. 18, and the results are shown in Table 3. The values of $[C]$, $[O_2]$ and B_1 used were those at the transition state (i.e., at the onset of the anoxic layer). The variation of the values of D_0 obtained from run to run is fairly significant (by a factor of approximately 1.5) and is mainly due to the relatively large errors encountered in analyzing samples with low D_0 concentrations.

Column Experiment

For illustration, two sets of column experiments are shown in Figures 11 and 12. The substrate concentrations shown in these figures include those of *DOC*, *DO* (for the aerobic case), and nitrate. Also included in these figures are predictions based on the models presented in Part I. The predictions were made using the bacterial parameters reported on this work. The adsorption parameters used were then reported by Wang (1981). The initial film thickness, B_0, was estimated according to a previously established procedure (Tien and Wang, 1982) as stated earlier. A summary of the parameter values used in making the predictions are summarized in Table 4.

As shown in these two figures, the *DOC* concentration curves have two phases. The first is the adsorption phase, during which

TABLE 3. VALUES OF VALERIC ACID AND DISSOLVED OXYGEN DIFFUSIVITIES IN BIOFILMS

Run #	1	1	2	2	3	3	4	4
$\frac{[C]_i}{[C]} - 1$	4.07	5.75	4.79	5.58	4.01	5.73	4.12	4.63
Average Value of $\frac{[C]_i}{[C]} - 1$				4.84				
$\frac{W}{F}\frac{3}{a_p\rho_p}\sqrt{\alpha k}$				2,095				

* $D_c = 5.4 \times 10^{-6}$ cm²/s

Run #	5	6	7	8
$[C]$ (ppm)	10.2	14.5	14.9	10.1
$[O_2]$ (ppm)	1.0	1.5	1.4	1.4
$\sqrt{k/D_c}\frac{a_p\rho_p B_1}{3\rho}$	0.234	0.259	0.232	0.239
** $D_0 \times 10^{-6}$ (cm²/s)	2.65	3.07	2.72	1.96
Average Value of D_0 (cm²/s)		2.6×10^{-6}		

* Based on Eq. 10b: $\sqrt{D_c} = \dfrac{([C]_i/[C]) - 1}{\frac{W}{F}\frac{3}{a_p\rho_p}\sqrt{\alpha k}}$

** Based on Eq. 13: $D_0 = \dfrac{\beta D_c[C]}{[O_2]}\left(1 - 1/\cosh\sqrt{k/D_c}\,\dfrac{a_p\rho_p B_1}{3\rho}\right)$

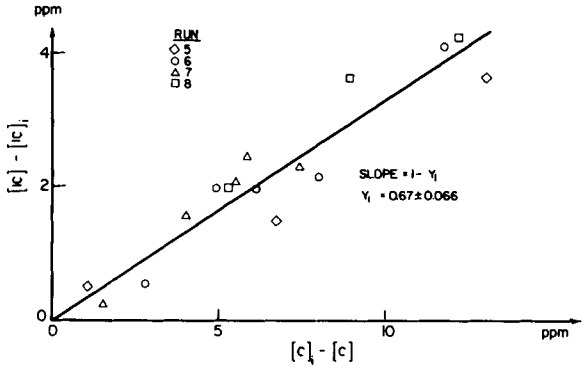

Figure 8. Dissolved inorganic carbon production vs. dissolved organic carbon degradation.

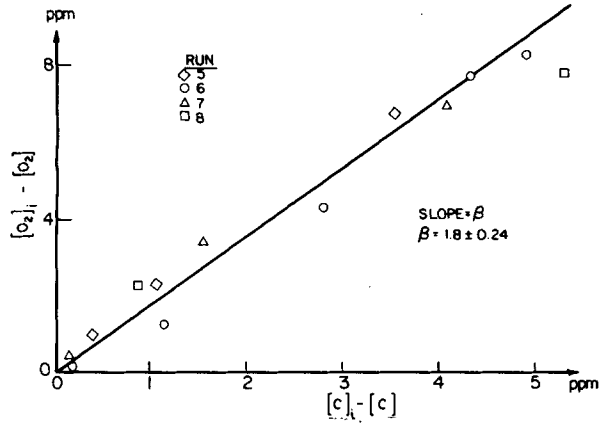

Figure 9. Oxygen reduction vs. organic carbon degradation—aerobic growth.

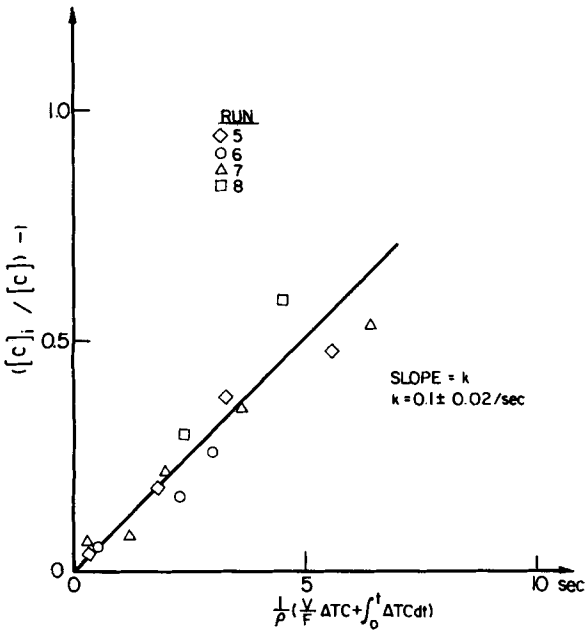

Figure 10. Dissolved organic carbon removal with small film volume—aerobic growth.

the *DOC* concentration increases as the carbon becomes more saturated with valeric acid. The agreement between the data and the model during this phase is good, although the experimental data are almost always higher than the predictions. These discrepancies may be due to a number of assumptions which were made in the formulation of the model of Part I. First, the model neglects the liquid-phase mass transfer resistance, which results in predicting a slower breakthrough behavior. Second, Glueckauf's linear driving

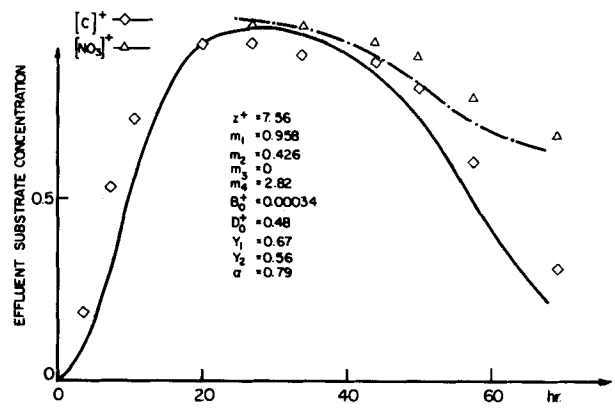

Figure 11. Theoretical and experimental effluent concentrations in column experiment—run 1.

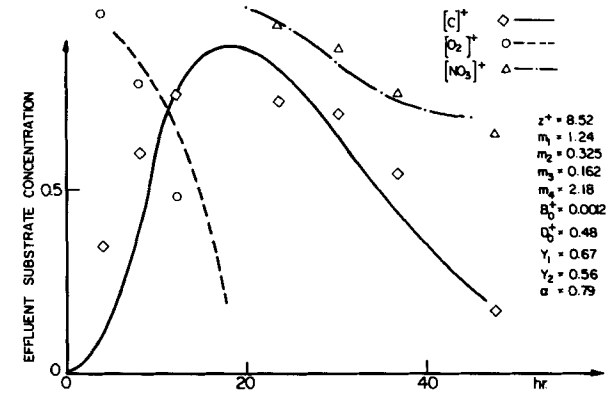

Figure 12. Theoretical and experimental effluent concentrations in column experiment—Run 8.

TABLE 4. PARAMETERS USED IN PREDICTING BREAKTHROUGH CURVES OF CARBON COLUMNS

Biological Parameters	
Y_1	0.67
Y_2	0.56
k_1	0.1
α	0.79
β	1.8
γ	2.44
ρ	37 mg/cm^3
D_0	2.6×10^{-6} cm^2/s
D_c	5.4×10^{-6} cm^2/s
Λ	230
k_p	4.5×10^{-6} cm/s (a_p = 0.033 cm)

force expression, used in the model for the intraparticle diffusion, is only an approximation of the actual intraparticle diffusion. Third, the linear equilibrium behavior does not adequately describe the isotherm data (Wang, 1981). In light of the use of these significant simplifications, the agreement must be considered satisfactory.

The second part of the breakthrough curve is the microbial growth phase during which the *DOC*, *DO*, and nitrate concentrations are reduced because of their uptakes by the developing films. It is clear from the experiments that unless the *DO* is completely eliminated from the solution, the initial bacterial growth is that of aerobic respiration. As a result, the necessity of viewing the film as a bilayer rather than according to the simpler version proposed earlier (Andrews and Tien, 1981) becomes rather obvious. The validity of the bilayer concept is also confirmed by the fact that the occurrence of denitrification takes place only after the *DO* is depleted, Fig. 12.

TABLE 5. PARAMETERS OBTAINED UNDER ANOXIC CONDITIONS VS. THOSE BY ANDREWS AND TIEN

	This Study	Andrews and Tien (1981)
Yield Coefficient	0.56	0.56
Substrate Uptake Rate Constant (s^{-1})	0.79	0.072
Organic Carbon Film Density (mg/cm^3)	37	37.4
Substrate Diffusivity (cm^2/s)	5.4×10^{-6}	2.7×10^{-6}

DISCUSSION

Bacterial Parameters

The accuracy of the bacterial parameters determined in this can be seen by comparing the results obtained under anoxic conditions with the earlier work of Andrews and Tien (1981), Table 5. Among the parameters a significant difference was observed only in the case of D_e (5.4×10^{-6} cm^2/s vs. 2.7×10^{-6} cm^2/s). Considering the inherent difficulty in determining carbon concentrations using the total carbon analyzer, this degree of agreement must be judged satisfactory.

A direct comparison between the parameters obtained in this work with those available in literature is difficult, since the interpretation of biofilm kinetics data was often made without considering the growing nature of the film. Nevertheless, some approximate comparisons can be made. For example, the biofilm volatile solids density was estimated to be 65 mg/cm^3 according to the data of Mulcahy and LaMotta (1978). Using the formula, $C_5H_7NO_2$ for the volatile solids, ρ becomes 34.5 mg/cm^3 and agrees well with the value obtained in this work. Similarly, D_e was found to be approximately two-thirds of the value of the corresponding diffusivity in water, a figure which compares favorably with that of glucose as reported by Atkinson (1974).

Tomlinson and Snaddon (1966) measured the diffusivity of oxygen through slime and found it to be two-thirds of the diffusivity of oxygen in water. On the other hand, the measured value of the oxygen diffusivity through attached slime with the use of an oxygen microprobe was found to be only 2% of the value in water (Bungay et al., 1969). The value determined in this study, which is 12% of the oxygen diffusivity in water, therefore, does not appear to be unreasonable.

The validity of the experimentally determined stoichiometric ratio values can be discerned from the following argument. With the yield coefficient of the aerobic growth estimated to be 0.67, the oxidation of valeric acid by oxygen can be considered as

$$6\ C_5H_{10}O_2 + 4\ NH_3 + 19\ O_2 \rightarrow 4\ C_5H_7NO_2 + 10\ CO_2 + 22\ H_2O$$

B should be equal to 1.7 according to the above reaction, a figure which compares well with the determined value of β (1.8). Similarly, with $Y_2 = 0.56$, the oxidation of valeric acid by nitrate can be assumed to be

$$25\ C_5H_{10}O_2 + 14\ NH_3 + 74\ Na\ NO_3 \rightarrow 14\ C_5H_7NO_2 + 37\ N_2 + 19\ Na_2CO_3 + 36\ NaHCO_3 + 79\ H_2O$$

The stoichiometric ratio of the denitrification to the biooxidation of valeric acid by oxygen, according to the above equations, is 3.1, which is essentially the experimentally determined value of γ/α (3.1 ± 0.25).

Validity of the Bilayer Model

The validity of the bilayer model proposed in Part I is demonstrated through the column experiment results. As shown in Figures 11 and 12, the main features of the effluent concentration history curves (*DOC*, *DO*, and NO_3) predicted by the model are largely substantiated by experimental data. In addition, dual phase behavior of the organic substrate breakthrough curve is clearly shown. The occurrences of denitrification after the depletion of the dissolved oxygen is also confirmed by experiments. The quantitative agreement between experiment and prediction is comparable to that observed in fixed-bed adsorption. Considering the complexities of biological processes in general, the accuracy of the model can be judged satisfactory.

ACKNOWLEDGMENT

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NOTATION

F = flow rate through the fluidized reactor
V = liquid-phase volume of the reactor
W = weight of particles in the reactor

For other letter symbols not defined above, see Part I of this paper.

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