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A MODEL OF A FIXED-FILM TRICKLE-FILTER BIOREACTOR FOR TCE DEGRADATION

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ABSTRACT

A mechanistically based model of a fixed-film trickle-filter bioreactor for cometabolic degradation of TCE has been developed. This model incorporates diffusional and kinetic resistances and generates estimates of TCE stripped from the liquid by gas as well as the extent of biological degradation of TCE. The model is consistent with a limited amount of experimental data. Further experience with this modeling approach is necessary in order to determine if this is a useful procedure for correlating bioreactor performance for design and scale-up.

INTRODUCTION

Contamination of groundwater by organic compounds is a major environmental problem. An attractive new treatment technology is the fixed-film

bioreactor; this technology utilizes immobilized microorganisms to oxidize organic species to carbon dioxide, water, and simple acids and bases. The use of methanotrophic microorganisms (bacteria that metabolize methane) to degrade trichloroethylene (TCE) has recently been demonstrated by Strandberg et al. (1) and others (2-11); these aerobic microorganisms were immobilized in a fixed-film trickle-filter bioreactor hereafter referred to as the FFTFBR and required methane as a primary carbon source.

The overall chemical reactions for the degradation of TCE by methanotrophic microorganisms are shown in Figure 1. In the FFTFBR, methane and oxygen (air) are provided in the gas phase with the biofilm supported on a packing material. The TCE-contaminated liquid is distributed over the packing material at the top of the column and allowed to come in contact with the biofilm and the gas phase as it flows down the column. Methane and oxygen are absorbed into the liquid and then diffuse with the TCE to the biofilm, where absorption and reaction occur. TCE can also desorb from the liquid to the gas phase. The goal is to develop a mechanistically based mathematical model describing these phenomena. Such a model can provide insight into the rate-controlling phenomena as well as provide a rational basis for scale-up of this technology for application.

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The mathematical model of the FFTFBR utilizes information on mass-transfer phenomena obtained from several sources. Since TCE is quite volatile, the inclusion of gas-phase resistance in this model is important. The model provides for gas and liquid mass-transfer resistances at the gas-liquid interface, the liquid-phase mass-transfer resistance at the liquid-microorganism interface, and the kinetics of the biooxidation reaction. After estimation of the mass-transfer resistances from procedures found in the literature, the kinetic resistance was determined by an iterative procedure in which this parameter was adjusted until the predicted removal of TCE agreed with that from the experimental data.

BACKGROUND

The ability of methane-utilizing bacteria to cometabolize short-chain chlorinated hydrocarbons such as TCE has been reported by several groups (1-

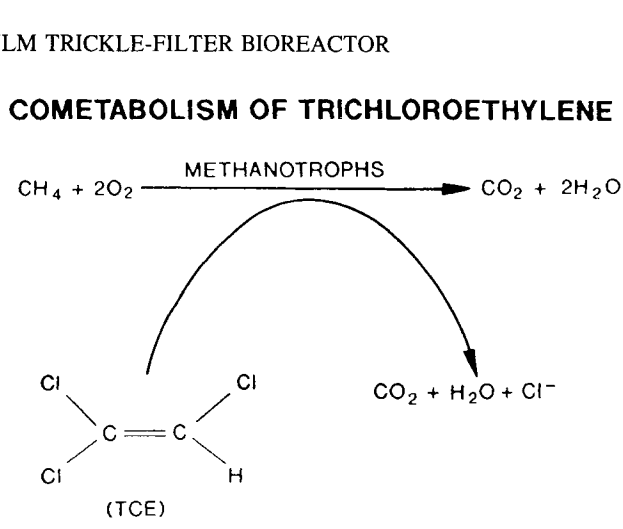

FIGURE 1. Biochemical reactions for degradation of TCE by methanotrophic microorganisms.

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11). Little et al. (4) recently reported the mineralization of TCE by a pure culture of a methane-oxidizing organism isolated from TCE-contaminated groundwater. It has been established that the enzyme methane monooxygenase oxidizes these chloroalkenes to epoxides that spontaneously degrade to intermediates that can be further metabolized.

Strandberg et al. (1) and Garland et al. (2) conducted exploratory studies with a fixed-film packed-bed bioreactor to evaluate the technical feasibility of bioremediation of TCE-contaminated groundwater using methanotrophic microorganisms. The performance of their bench-scale bioreactor system for TCE degradation is the basis for the model development described here. Their work yielded a TCE removal rate that appeared to be first order in TCE concentration; hence the present model was generated assuming first-order kinetics.

The bioreactor is shown in Figure 2; it consisted of a 5-cm-ID glass column packed with 0.6-cm ceramic Berl saddles as a support matrix for the biofilm. In these studies, a concentrated feed solution containing mineral salts and TCE was continuously bled into a stream of process water (nonchlorinated tap water meeting potable water standards). In some experiments, trans-1,2

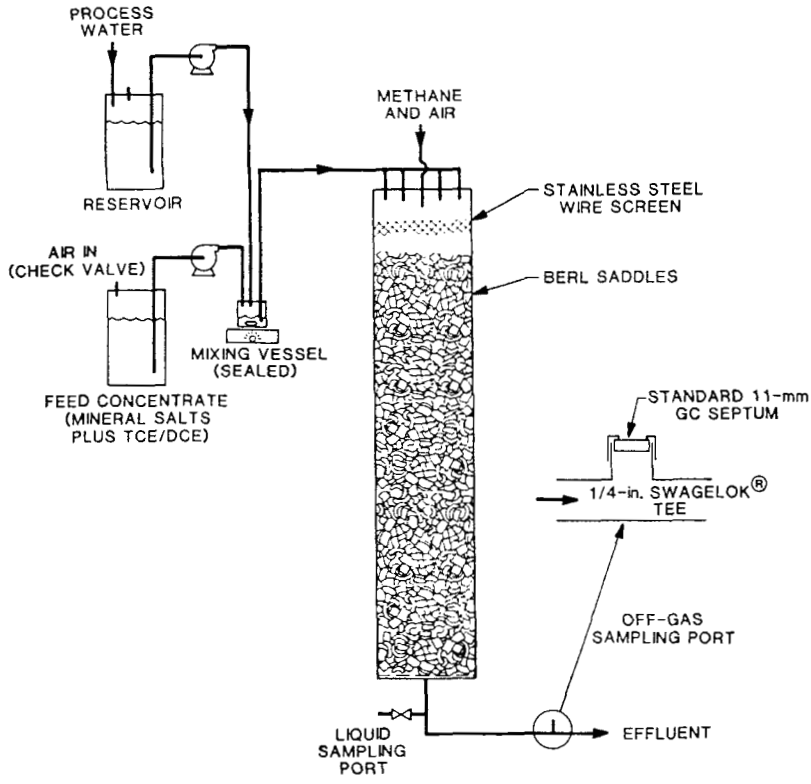

FIGURE 2. Schematic of experimental system used by Strandberg et al. (1) and Garland et al. (2).

dichloroethylene (DCE) was also fed to the bioreactor. The liquid was distributed over the top of the packing at 10 mL/min unless noted otherwise. Bioreactor performance in terms of TCE and DCE degradation was measured at liquid flow rates of 5, 10, 20, 35, and 50 mL/min.

The influent concentration of TCE (typically 1 mg/L) was controlled by adjusting the concentration of TCE in the feed concentrate and by varying the dilution with process water. A concurrent gas stream containing methane (4 vol % unless noted otherwise) and air was introduced at the top of the bioreactor at 20 mL/min. The system was operated at ambient temperature (22-24°C).

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MODEL DEVELOPMENT

The development of the model describing biooxidation of TCE in the bioreactor is based on a steady-state mass balance around an incremental volume of the reactor. Mass balances are determined for the flow of liquid and gas through the incremental volume. For the gas flow:

moles of component A entering increment	=	moles of component A exiting increment	+	moles of component A absorbing into liquid phase

This may be represented in a differential form as:

$$\frac{dy}{dz} = - \frac{N_A a}{G} \quad . \tag{1}$$

Equation (1) is the governing equation for mass transfer of component A to and from the gas phase. Utilizing the film theory for mass transfer, the gas-phase flux of the absorbing component may be reasonably represented by:

$$N_A a = k_G a P_T (y - y_i) \; . \tag{2}$$

Similarly, the flux through the liquid film adjacent to the gas-liquid interface may also be reasonably represented by:

$$N_A a = k_L a C_L (x_i - x) \; . \tag{3}$$

By definition, the overall gas-liquid mass transfer coefficient $K_G a$ is:

$$\frac{1}{K_G a P_T} = \frac{1}{k_G a P_T} + \frac{m}{k_L a C_L} \quad , \tag{4}$$

where m is equal to y_i/x_i. Equations (2), (3), and (4) are combined to give:

$$N_A a = K_G a P_T (y - mx) \; . \tag{5}$$

Equation (5) defines the overall flux across the gas-liquid interface. Substitution of Eq. (5) into Eq. (1) yields:

$$\frac{dy}{dz} = - \frac{K_G a P_T}{G} (y - mx) \quad . \tag{6}$$

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The mass balance equation for flow of liquid through the incremental volume is developed similarly to that for the gas phase:

moles of component A entering increment	+	moles of component A absorbing from gas	=	moles of component A exiting increment	+	moles of component A absorbing into biomass

This may be represented as:

$$Lx_{in} + N_A a\, dz = Lx_{out} + N'_A a' dz\,, \tag{7}$$

where N'_A is the flux of component A at the surface of the biofilm and a′ is the interfacial area of biofilm per volume of bioreactor. The interfacial area of the biofilm was assumed to be equal to that of the gas-liquid interfacial area:

$$a = a'\,. \tag{8}$$

The wetted area was assumed to be completely covered with biofilm.

By applying assumptions similar to those used in the development of Eq. (1), Eq. (7) becomes:

$$\frac{dx}{dz} = \frac{N_A a}{L} - \frac{N'_A a}{L}\,. \tag{9}$$

Again, utilizing the film theory for mass transfer, the flux through the liquid film region adjacent to the biofilm surface is reasonably represented by:

$$N'_A a = k_S C_L (x - x_S)\,. \tag{10}$$

The reaction rate is postulated to be first order in TCE concentration and may be defined in terms of biomass surface area and related to the flux as:

$$N'_A a = k C_L x_S\,. \tag{11}$$

This definition of k includes any diffusional resistance within the biofilm and the effective biofilm loading for the bioreactor.

Utilizing the definition

$$\frac{1}{K_S a C_L} = \frac{1}{k_S C_L} + \frac{1}{k C_L}\,. \tag{12}$$

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Eqs. (10) and (11) may be reasonably represented as:

$$N'_A a = K_S a C_L x \ . \tag{13}$$

The mass-transfer correlations used in this study were selected based on their applicability at conditions resembling those under which the FFTFBR was operated. The important operating conditions were temperature, pressure, flow rates, and packing size. Trickle-bed reactors are most commonly used in the petrochemical industry (12). A search of the literature produced the following correlations whose applicable conditions best represented those of the FFTFBR. These correlations from Shende and Sharma (13), Mahajani and Sharma (14) and Satterfield et al. (15), respectively, are:

$$k_G a = 0.0000610 V_G^{0.866} V_L^{0.34} \ , \tag{14}$$

$$k_L a = 8.08(L'/\mu)^{0.41} Sc^{0.5} D_L \ , \text{ and} \tag{15}$$

$$k_S = 0.266(D_L/d_p\alpha)Re^{1.15} Sc^{-1/3} \ . \tag{16}$$

The value of the Henry's Law constant for TCE was estimated to be about 140,000 mm Hg (10,16). Experimental performance data and operating conditions from Strandberg et al. (1) were used to define the conditions needed to estimate k_G, k_L, k_S, and m. The set of first-order differential equations represented by Eqs. (1) and (9) is an initial-value problem and was solved by 7th-order Runge-Kutta integration with step-size control. A value of the reaction rate constant, k, was calculated for each experimental data point as that necessary for the model-predicted bioreactor performance to match that of the experiment in terms of removal of TCE.

MODEL-DATA COMPARISON

The results of the determination of the individual kinetic rate constant, k, for each run are presented along with the experimental conditions from Strandberg et al. (1) in Table 1. The average fractional kinetic resistance, estimated as $(1/k)/(1/K_S a)$, was greater than 0.90 for the data set, indicating little

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TABLE 1. INDIVIDUAL KINETIC RATE CONSTANT AND ORIGINAL DATA BASE FROM STRANDBERG ET AL. (1) AND GARLAND ET AL. (8)

Run	Liquid Rate (L/min)	Gas Rate (L/min)	Influent Methane Concentration (%)	Influent Liquid Phase TCE (mole fraction)	Reaction Rate Constant (min^{-1})
1	0.01	0.025	10	5.6E-08	16E-03
2	0.01	0.036	5	6.7E-07	15E-03
3	0.01	0.036	5	4.3E-08	23E-03
4	0.012	0.036	5	7.1E-07	56E-04
5	0.01	0.036	5	1.1E-07	97E-04
6	0.01	0.013	2	1.1E-07	17E-04
7	0.01	0.02	4	1.1E-07	21E-04
8	0.01	0.02	4	7.3E-08	17E-04
9	0.01	0.02	4	8.9E-08	22E-04
10	0.01	0.02	4	6.7E-08	40E-04
11	0.01	0.02	4	9.0E-08	25E-04
12	0.01	0.02	4	8.4E-08	26E-04
13	0.01	0.02	4	1.2E-07	58E-04
14	0.01	0.02	4	6.0E-08	40E-04
15	0.01	0.02	4	8.1E-08	43E-04
16	0.01	0.02	4	9.9E-08	68E-04
17	0.01	0.02	4	1.1E-07	28E-04
18	0.01	0.02	4	1.1E-07	27E-04
19	0.005	0.02	4	1.2E-07	37E-04
20	0.01	0.02	4	1.4E-07	56E-04
21	0.01	0.02	4	1.5E-07	30E-04
22	0.02	0.02	4	1.4E-07	59E-04
23	0.035	0.02	4	1.5E-07	41E-04
24	0.05	0.02	4	1.4E-07	11E-03

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liquid-phase diffusional resistance. Substantial gas-phase resistance, $(1/k_Ga)/(1/K_Ga)$, is present, especially for conditions involving low gas velocities through the bioreactor.

Strandberg et al. (1) also reported first-order rate constants for the last six experiments in Table 1. However, the model used to deduce the rate constants was somewhat different from the present model in that all the rate-limiting phenomena were lumped into one rate constant and the actual liquid residence time was used, as estimated from salt pulse experiments. The present model separates the extracellular mass transfer resistance from the intracellular (biofilm) mass transfer and reaction kinetics, and is based on the superficial liquid flow rate through the bioreactor column instead of the actual liquid residence time.

To compare the rate constants of Strandberg et al. (1) with those in Table 1, it is necessary to compensate for the different residence time basis. The actual liquid residence times for the last six experiments in Table 1 were estimated to range from 11 to 75 minutes, and the liquid holdup in the bioreactor was thus about 0.50 to 0.65 L, depending on the flow rate. The present model is based on the geometrical volume of the bioreactor, which was about 2.2 L. These different bases lead to a factor of 4.4 to 3.4 difference in the rate constants. Most of the data in Table 1 pertain to a liquid flow rate of 0.01 L/min; for this flow rate, the Strandberg rate constants are 0.024 and 0.016 min^{-1} for two different experiments that correspond to Runs 20 and 21 in Table 1. Dividing the Strandberg rate constants by 4.4 for these conditions gives 0.0055 and 0.0036 min^{-1}, respectively, which are consistent with the rate constants derived from the present model for runs 20 and 21 shown in Table 1. This good agreement between the rate constants from the two models is consistent with the model prediction noted earlier of little liquid-phase diffusional resistance.

The experiments reported in Table 1 were conducted over a period of time from late April to mid-August 1988. The individual kinetic constants regressed using the model are displayed in Figure 3 according to the date of the experiment. The first six experiments, conducted in April and May, utilized a prototype 30-cm packed bioreactor. The packing material and biofilms were then transferred to a 110-cm column of the same diameter. New packing was added to fill the

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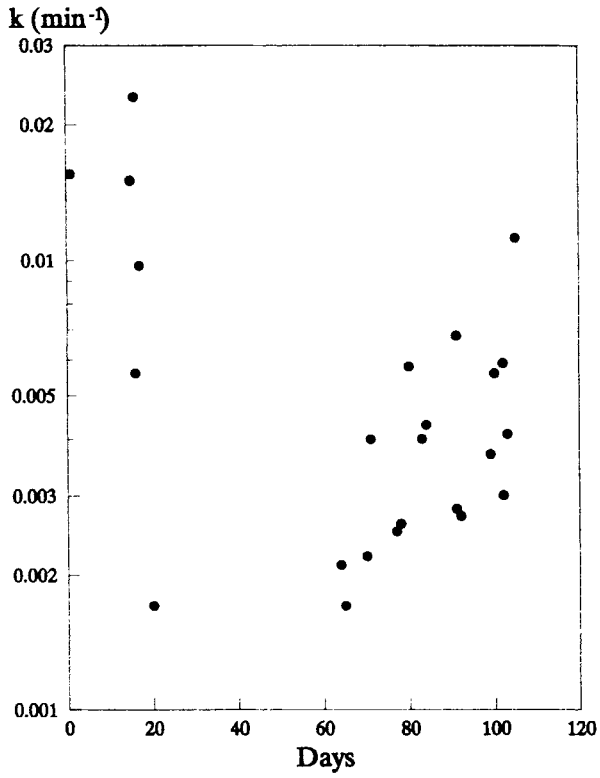

FIGURE 3. Kinetic rate constant vs day of experiment.

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bottom of the column, and the established "seed" biofilms and packing were placed on the top of the new column. After an acclimation period in May and June, data were then collected again and are represented by the rate constants on the right side of Figure 3.

Both groups of data obviously have considerable scatter; nevertheless, the earlier group appears to have generally larger values of k than the later group. This result is consistent with the two different bioreactors described above. The 30-cm bioreactor was visually observed to have a higher biofilm loading per unit volume of bioreactor (or per unit surface area of packing) than did the 110-cm

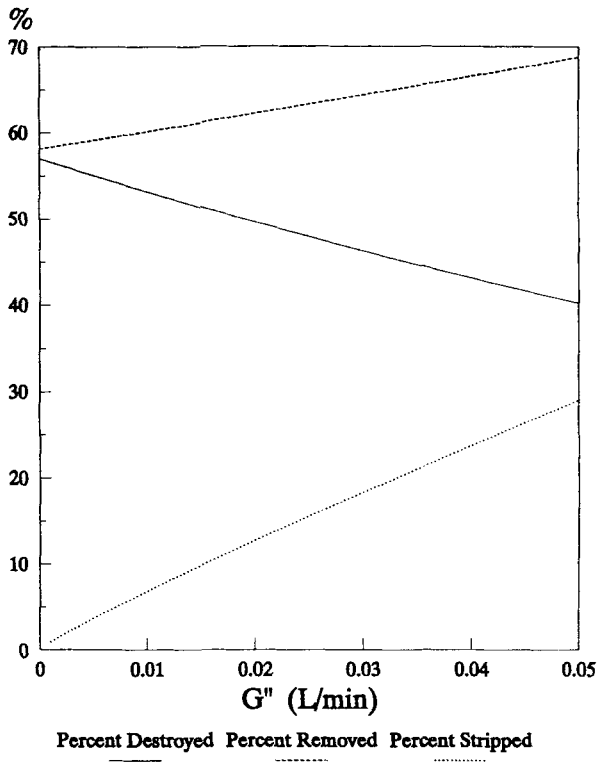

FIGURE 4. Model-predicted TCE removal by bacterial destruction and removal via stripping vs gas rate; other variables held constant.

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bioreactor. This condition would yield a smaller rate constant for the 110-cm bioreactor than for the 30-cm bioreactor under the model conditions for which the specific bioreactivity was assumed to be constant and uniform. No independent information is available to assess the intrinsic bioactivity of the biofilm over time. It may have varied, which would contribute to the scatter in the values of k.

The removal of the TCE from the liquid phase involves two simultaneously occurring phenomena. TCE is removed from the liquid phase by destruction--that is, oxidation by the biofilm--and by stripping, which is the

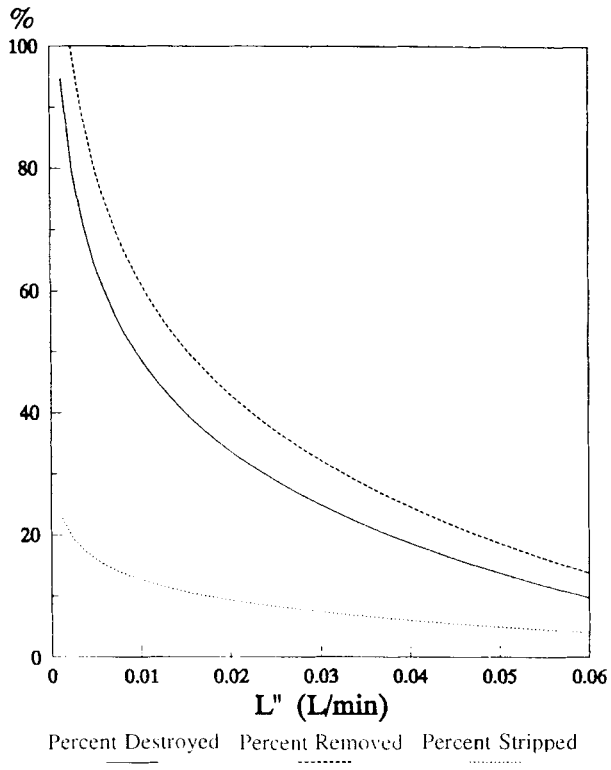

FIGURE 5. Model-predicted TCE removal by bacterial destruction and removal via gas stripping vs liquid rate; other variables held constant.

transfer of TCE from the liquid phase to the gas phase. The relative removals by these phenomena are displayed in Figures 4 and 5, which show the effect of the gas rate and the liquid rate on the model predictions of TCE destroyed by the biofilm, stripped into the gas phase, and total removed from the liquid phase. A typical kinetic constant, 0.004 min^{-1}, was used in the predictions. The effects of variations of gas and liquid rates are as expected. Increased gas rate produces an increase in stripping and affects total removal very little. Although the dominant removal mechanism is destruction by the biofilm, stripping reduces destruction by the biofilm by reducing the bulk liquid-phase TCE concentration. Increased

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liquid rate produces a decrease in both destruction by the biomass and total removal. Since the dominant removal mechanism is destruction by the biofilm, the increased liquid rate reduces the liquid-phase residence time and thus decreases total removal substantially.

Insufficients measurements were made of TCE content in the off-gas for comparison of model-predicted stripping versus actual stripping. Subsequent work with a pilot plant study will include measurement of the off-gas for TCE content, providing an additional means to measure the model's accuracy.

SUMMARY

The mechanistically based mathematical model reasonably correlates the performance of bench-scale results and trends in this data. The model appears useful in locating optimal conditions for minimizing the stripping of components of interest from the reactor. Further development of the model by comparison with the results from larger-scale bioreactors will be helpful in establishing this approach as a useful design tool. Future work with larger-scale reactors will determine if other parameters such as surface loading rate, hydraulic retention time, and volumetric loading rate should be incorporated into the model. The simplicity of the model will allow easy incorporation of these parameters. Additionally, as larger-scale reactors with increased gas and liquid flow rates are built and operated, more suitable correlations for the mass-transfer coefficients should be explored.

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NOMENCLATURE

a	gas-liquid interfacial area, area/volume
a′	liquid-biofilm interfacial area, area/volume
C_L	liquid phase total molar concentration, mole/volume
D_L	diffusivity coefficient, area/time
G	total superficial molar gas flow rate, mole/area time
G"	gas flow rate, liters/minute

k	reaction rate constant, 1/time
$k_G a$	gas phase mass transfer coefficient, mole/volume time pressure
$k_L a$	liquid phase mass transfer coefficient, 1/time
k_S	liquid phase mass transfer coefficient at the surface of the biofilm, 1/time
$K_G a$	overall gas-liquid mass transfer coefficient, mole/volume time pressure
$K_S a$	overall liquid-solid mass transfer coefficient, 1/time
L	total superficial molar liquid flow rate, mole/area time
L′	total superficial mass liquid flow rate, mass/area time
L"	liquid flow rate, liters/minute
m	slope of equilibrium line or equilibrium constant
Na	gas-liquid molar flux, mole/volume time
N′a	liquid-solid molar flux, mole/volume time
P_T	total pressure, pressure
Re	Reynolds number
Sc	Schmidt number
V	reactor volume
V_G	gas velocity, length/time
V_L	liquid velocity, length/time
x	mole fraction in liquid phase; x_i-mole fraction at gas-liquid interface; x_S- mole fraction at biomass surface; x_{in}-mole fraction entering increment; x_{out}-mole fraction exiting increment;
y	mole fraction in gas phase; y_i-mole fraction at gas-liquid interface; y_{in}-mole fraction entering increment; y_{out}-mole fraction exiting increment
z	column length, length
α	fraction of packing that is wetted
τ	residence time, time
μ	liquid viscosity, mass/length time

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