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Extension of Anaerobic Digestion Model No. 1 with Processes of Sulfate Reduction

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Abstract

In the present work, the Anaerobic Digestion Model No. 1 (ADM1) for computer simulation of anaerobic processes was extended to the processes of sulfate reduction. The upgrade maintained the structure of ADM1 and included additional blocks describing sulfate-reducing processes (multiple reaction stoichiometry, microbial growth kinetics, conventional material balances for ideally mixed reactor, liquid-gas interactions, and liquid-phase equilibrium chemistry). The extended model was applied to describe a long-term experiment on sulfate reduction in a volatile fatty acid–fed upflow anaerobic sludge bed reactor and was generally able to predict the outcome of competition among acetogenic bacteria, methanogenic archaea, and sulfate-reducing bacteria for these substrates. The computer simulations also showed that when the upward liquid velocity in the reactor exceeds 1 m/d, the structure of the sludge becomes essential owing to bacterial detachment.

Index Entries: Mathematical modeling; sulfate reduction; methanogenesis; competition; Anaerobic Digestion Model No. 1.

Introduction

The Anaerobic Digestion Model No. 1 (ADM1) is a structured model that includes disintegration and hydrolysis, acidogenesis, acetogenesis, and methanogenesis as the steps in anaerobic biodegradation. A detailed description of ADM1 is given in ref. *1*. At present, ADM1 does not account for the processes of sulfate reduction, and, hence, it is invalid to describe an important part of the anaerobic degradation processes. The reasonable upgrading procedure should incorporate a minimal number of equations to ADM1, which describe the main features of the sulfate-reducing processes.

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The fact that sulfate-reducing bacteria are capable of using many of the intermediates formed during the methanogenic breakdown of organic matter results in competition for these substances. In general, substrate competition in anaerobic systems is possible on three levels: between sulfate-reducing bacteria and fermentative (acidogenic) bacteria for sugars and amino acids; between sulfate-reducing bacteria and acetogenic bacteria for syntrophic substrates, such as volatile fatty acids (VFA) and ethanol; and between sulfate-reducing bacteria and methanogenic archaea for the direct methanogenic substrates—acetate and hydrogen.

The competition of the first level is won by the very fast growing fermentative (acidogenic) bacteria *(2)*. Therefore, this part of ADM1 as well as the disintegration/hydrolysis will be not modified. The Monod kinetic data of sulfate-reducing bacteria, acetogenic bacteria, and methanogenic archaea for growth and conversion on VFA and hydrogen indicate that sulfate-reducing bacteria successfully compete with acetogenic bacteria and methanogenic archaea. This was confirmed experimentally for hydrogen *(3–6)* and for propionate/butyrate *(3)*. Different situations can appear for acetate utilization. In some situations, sulfate-reducing bacteria could successfully outcompete methanogenic archaea for acetate *(3,7)*, whereas some other results showed that the latter is preferentially degraded to methane *(4,8–10)*. These facts indicate that the mass balance equations of ADM1 should be supplemented with additional members, which describe VFA and hydrogen removal via sulfate reduction. In addition, the kinetic expressions should be upgraded by taking into account hydrogen sulfide inhibition, especially in its undissociated form *(2,4,6)*.

Basic Principles of ADM1 Extension to Sulfate-Reducing Processes

Stoichiometry of Sulfate-Reducing Processes

The methanogenic conversions of VFA are well described by ADM1 *(1)*. In particular, in molar basis, they are the following:

$$C_3H_7COOH + 2H_2O \xrightarrow{X_1} 2CH_3COOH + 2H_2 \quad (1)$$

$$C_2H_5COOH + 2H_2O \xrightarrow{X_2} CH_3COOH + CO_2 + 3H_2 \quad (2)$$

$$CH_3COOH \xrightarrow{X_3} CH_4 + CO_2 \quad (3)$$

$$4H_2 + CO_2 \xrightarrow{X_4} CH_4 + 2H_2O \quad (4)$$

in which X_1 and X_2 are the groups of syntrophic acetogenic bacteria, and X_3 and X_4 are the groups of methanogenic archaea.

Extension of the ADM1 reaction sequences for the sulfate reduction process was done by incorporation of the following reactions *(11–13)*:

$$C_3H_7COOH + 0.5H_2SO_4 \xrightarrow{X_5} 2CH_3COOH + 0.5H_2S \quad (5)$$

$$C_2H_5COOH + 0.75H_2SO_4 \xrightarrow{X_6} CH_3COOH + CO_2 + H_2O + 0.75H_2S \quad (6)$$

$$CH_3COOH + H_2SO_4 \xrightarrow{X_7} 2CO_2 + 2H_2O + H_2S \quad (7)$$

$$4H_2 + H_2SO_4 \xrightarrow{X_8} H_2S + 4H_2O \quad (8)$$

Thus, according to the proposed stoichiometric scheme (Eqs. 5–8), the sulfate reduction process is carried out by four groups of microorganisms: the group X_5 comprises all butyrate-degrading sulfate-reducing bacteria; X_6, all propionate-degrading sulfate-reducing bacteria; X_7, all acetotrophic sulfate-reducing bacteria; and X_8, all hydrogenotrophic sulfate-reducing bacteria.

Kinetics and Mass Balances

In this section, only expressions that correspond directly to the extension of ADM1 model are introduced. All others are referenced in the detailed description of ADM1 *(1)*. The kinetics of sulfate reduction processes was introduced following the principles of ADM1 taking into account both the concentration of electron donor (organic substrate or hydrogen) and concentration of electron acceptor (SO_4^{2-}):

$$\rho_i = \frac{k_{max} S_i}{K_S + S_i} \cdot \frac{S_{SO_4}}{K_{SO_4} + S_{SO_4}} \cdot X \cdot I_{pH} \cdot I_{sulfide} \quad (9)$$

The first two terms on the right side of Eq. 9 are uninhibited Monod-type uptake. The *I* functions are the inhibition functions that describe the influence of excessive amounts of sulfide. The I_{pH} function was used in the form analogous to that applied in ADM1 *(1)*:

$$I_{pH} = \frac{1 + 2 \times 10^{0.5(pK_1 - pK_2)}}{1 + 10^{(pH - pK_2)} + 10^{(pH - pK_1)}} \quad (10)$$

Undissociated H_2S inhibition is assumed to proceed according to first-order inhibition kinetics *(14)* for all bacteria. Because little reliable information about H_2S inhibition kinetics is available, the inhibition factor $I_{sulfide}$ as given in Eq. 11 can be considered a reasonable approximation:

$$I_{sulfide} = 1 - \frac{H_2S}{K_I} \qquad (\text{if } H_2S > K_I,\ I_{sulfide} = 0) \quad (11)$$

For calculation of pH values and concentrations of undissociated forms of VFA and other species during the process, the corresponding formulas 4.1–4.7 of ADM1 were applied *(1)*. Material balances in the liquid phase were described according to formulas 5.2–5.3 of ADM1 accounting for ideal mixing conditions *(1)*. For dissolved gas components, additional terms according to formula 4.10 of ADM1 were used to describe mass transfer between gas bubbles and liquid *(1)*.

The general mass balance equation used to describe the behavior of each microbial group in the reactor is presented in the form of Eq. 12 following formula 5.3 in the description of AMD1 *(1)*:

$$\frac{dX_{liq,i}}{dt} = \frac{qX_{in,i}}{V_{liq}} - \frac{X_{liq,i}}{SRT} + \sum_j \rho_j \nu_{i,j} \tag{12}$$

In ADM1, the solids retention time (SRT) function was accepted as

$$\mathrm{SRT} = \mathrm{HRT} + t_{i,X} \tag{13}$$

in which $t_{i,X}$ is the residence time of the solids above the hydraulic retention time (HRT) *(1)*. Following the aim of this work, the function for SRT was taken to be dependent not only from the HRT but also from the upward liquid velocity (V_{up}):

$$\frac{1}{\mathrm{SRT}} = \frac{[1 - ER_i(V_{up})]}{\mathrm{HRT}} \tag{14}$$

in which ER_i characterizes the efficiency of the retention of bacterial group X_i in the reactor. These parameters are functions of both the upward liquid velocity, V_{up}, and the reactor design. The same description of the efficiency of biomass retention was used previously for modeling upflow anaerobic sludge bed (UASB) reactors *(11,15)*. Thus, the mass balance in the reactor for bacterial group X_i can be expressed as

$$\frac{dX_i}{dt} = -\frac{X_i}{\mathrm{HRT}} \cdot [1 - ER_i(V_{up})] - b_i \cdot X_i + \sum_j \rho_j \nu_{i,j} \qquad (i = 1, 8) \tag{15}$$

$$\frac{dX_9}{dt} = -\frac{X_9}{\mathrm{HRT}} \cdot [1 - ER_9(V_{up})] + \sum_{i=1}^{i=8} b_i \cdot X_i \tag{16}$$

where

$$ER_i(V_{up}) = Function(V_{up}) \tag{17}$$

The term X_9 is introduced as the so-called inactive biomass, which also needs to be taken into account for the total chemical oxygen demand (COD) balance of the system. X_9 comprises the biomass of bacterial groups, which are present in aggregated biomass (e.g., denitrifying bacteria) but are not

Table 1
Experimental Operating Regimes of Sludge Bed Reactor

Days	OLR_{min} – OLR_{max} (g COD/[L · d])	V_{up} (m/h)	pH
1–58	1.9–3.5	2	8.0
59–108	3.8–6.15	2	8.0
108–122	2.0–5.5	4	8.0
123–168	3.8–15.4	2	8.0
169–182	6.4–9.0	6	8.0
183–208	1.3–6.7	2	8.0
209–274	3.76–12.0	1	8.0
275–325	3.8–17	1	7.0

considered in our stoichiometric scheme. Biomass arising from bacterial decay is also included in X_9.

The gas-phase components include the concentrations and partial pressures in the head space. Since ADM1 is developed for complete mixing conditions, only partial pressures were needed. These components were calculated directly using formulas 5.5–5.10 of section 5.2 of ADM1 *(1)*.

Experimental System Considered

Results of the experimental study carried out by Omil et al. *(16,17)* that considered different operating regimes of granular sludge bed reactor with effluent recycle treating synthetic sulfate-containing wastewater are used here to validate the extended ADM1 model. Operating regimes are summarized in Table 1. Briefly, the granular sludge bed reactor operated in various regimes that differed by average organic loading rate (OLR) values, feed content, and recycling intensity. The variations in the recycling intensity resulted in different upward liquid velocities inside the reactor. All periods in the experiment maintained the pH value inside the reactor at 8.0 except the last one, during which the inhibition effect of hydrogen sulfide was studied at pH 7.0.

Criteria for Evaluation of Reactor Performance

The considered experimental system was created to investigate the processes of sulfate removal from wastewater by means of anaerobic granular sludge, which was exposed to a sulfate-rich influent for a prolonged period of time. Following the main aim of the experimental work, the four types of criteria describing the removal efficiency of acetate, butyrate, propionate, and sulfate will be represented as output information. This enables the input and output value of the extended ADM1 model to be plotted in one curve. Note that since acetate can be produced from various types of reactions, the acetate removal efficiency, which is given by Eq. 19, can be less than zero:

$$RE_{Pr} = (1 - \frac{C_{Pr}^{IN}}{C_{Pr}^{OUT}}) \cdot 100 \qquad \text{(for propionate)} \qquad (18)$$

$$RE_{Ac} = (1 - \frac{C_{Ac}^{IN}}{C_{Ac}^{OUT}}) \cdot 100 \qquad \text{(for acetate)} \qquad (19)$$

$$RE_{Bu} = (1 - \frac{C_{Bu}^{IN}}{C_{Bu}^{OUT}}) \cdot 100 \qquad \text{(for butyrate)} \qquad (20)$$

$$RE_{SO_4} = (1 - \frac{C_{SO_4}^{IN}}{C_{SO_4}^{OUT}}) \cdot 100 \qquad \text{(for sulfate)} \qquad (21)$$

Computational Methods

Simulations were performed on an IBM-compatible personal computer (processor Pentium-233) by numeric integration of the differential equations resulting from the structure of the ADM1 model, with an automatic selection of the time step by a computer program based on a Runge-Kutta (fourth-order) technique. The computer program was written as a Windows application in Fortran-90 using Fortran Power Station FPS-4.0 in a generalized form, in which a variable number of steps, organisms, components, substrates, and inoculum data could be specified through an input file. The program created an output data file in a format suitable for graphic processing.

Model Parameters and Initial Conditions

The parametric values, which have been introduced in the program via the input file, can be divided into initial conditions and adjustable parameters. The adjustable parameters contain the numerical values of the kinetic parameters, which specify Eq. 9 for each process. These values were chosen by fitting to the experimental data *(16,17)* in a range consistent with the set of parameters recommended by ADM1 report for non-sulfidogenic microorganisms *(1)* and with the experimental determination/estimation for sulfidogenic bacteria parameters reported in the literature *(6,15,18–24)*. Taking into account the large number of parameters to be fitted reveals that such an approach has difficulties dealing with a multiplicity of sets of parameter values that may give a similar quality of description of the modeled experiment. However, an extensive pool of experimental data obtained in various operational regimes (Table 1) based on the detailed monitoring of more than 10 variables as well as additional batch studies on sludge activities by others *(16,17)* substantially reduced

the freedom in choosing parametric values and thus significantly justify such a fitting approach.

The group of initial conditions contains the initial substrate concentrations, which were taken to be equal to the reactor inlet concentrations. The range of initial concentrations of bacterial groups was estimated on the basis of the information from batch experiments used to determine the specific activity with butyrate, propionate, and acetate as the substrates *(16)*.

Table 1 contains information about the minimal and maximal experimental values of OLR in all the considered regimes. In the simulation procedure, the experimental OLR values as a function of time from original works *(16,17)* were used as the input parameters.

Results and Discussion

The simulation results, together with experimental data, are presented in Figs. 1–5. The parameters used in the simulation process are presented in Tables 2 and 3. Figures 1–5 show the dynamics of the main process components and removal efficiencies in time. As can be seen, the main tendencies of the experiment are approached by the model. Moreover, having used the minimal set of model parameters, it appeared to be possible to describe the long-term experiment, which contained various types of transition regimes. Nevertheless, within two periods, d 168–208 and d 275–325, one can find several deviations of the model from the experiment.

Comparison of the results given in Figs. 1 and 2 reveals that during d 168–208, the model was not as sensitive to the changes of external conditions as in previous periods. This was most probably owing to temporary overloading of the system. However, as can be seen from Figs. 1–5, after several HRT this perturbation was overcome. Note that the model also reflects this fact, but with lesser amplitudes.

An interesting feature of the experiment used for model calibration is the significant increase in the methane production rate after approx 150 d of operation (Fig. 5A). This was related to a stepwise increase in the concentration of the methanogens in the sludge *(16,17)*. The model took this into account via slightly higher *ER* values for methanogenic species X_7 and X_8 compared to other bacterial groups in the system. This resulted in satisfactory agreement of model predictions with the experiment with respect to methane output throughout almost the entire study (Fig. 5A).

A clear deviation of the model results from experimental values was observed in the last period (d 275–325). This may be explained by the low upward velocity and the decrease in the pH value of the liquid phase from 8.0 to 7.0. These two factors increased the inhibition effect of H_2S. Note that in the present work, the inhibition effect of the neutral form of H_2S in the bulk liquid was assumed. In UASB reactors, however, the major part of biotransformations takes place inside the granulated biomass. An insufficient mass transfer of H_2S between the granulated biomass and surrounding medium can occur, and the decreased V_{up} may have caused additional inhibitory effects.

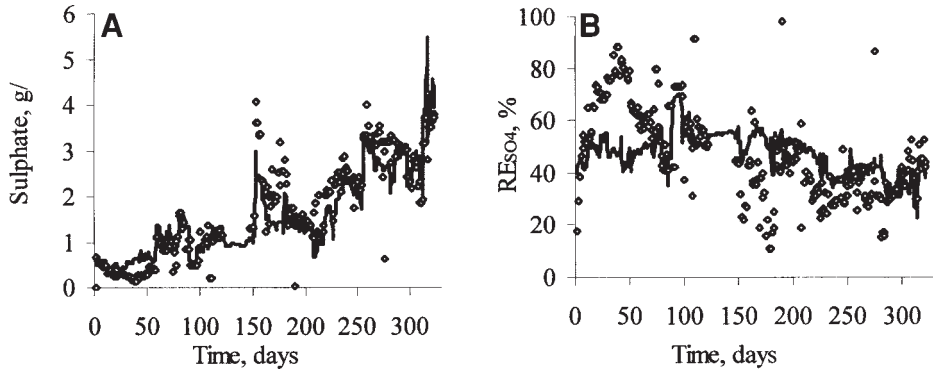

Fig. 1. Model vs experiment for sulfate: **(A)** effluent concentration; **(B)** removal efficiency. (◇) Experiment; (——) model.

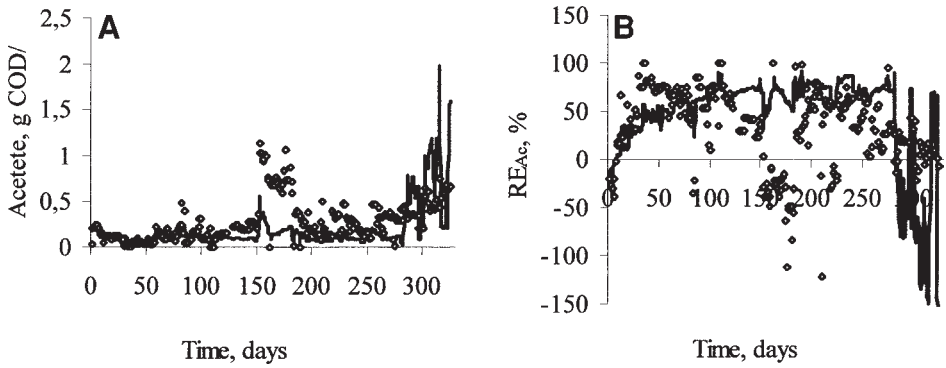

Fig. 2. Model vs experiment for acetate: **(A)** effluent concentration; **(B)** removal efficiency. (◇) Experiment; (——) model.

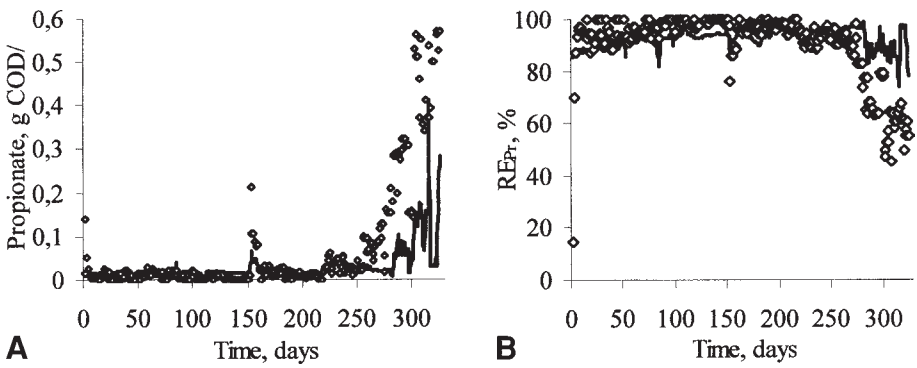

Fig. 3. Model vs experiment for propionate: **(A)** effluent concentration; **(B)** removal efficiency. (◇) Experiment; (——) model.

Taking into account the discussed enhancement of the inhibitory effect of H_2S, one can explain the discrepancy between the model and experiment regarding methane production during the last period (Fig. 5A).

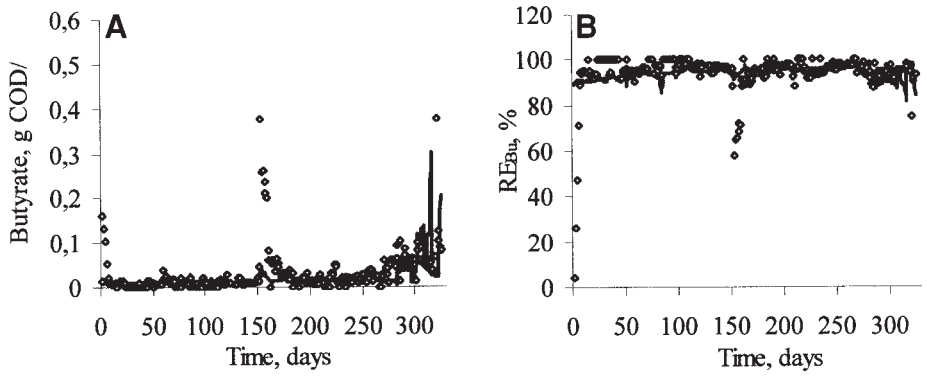

Fig. 4. Model vs experiment for butyrate: **(A)** effluent concentration; **(B)** removal efficiency. (◇) Experiment; (——) model.

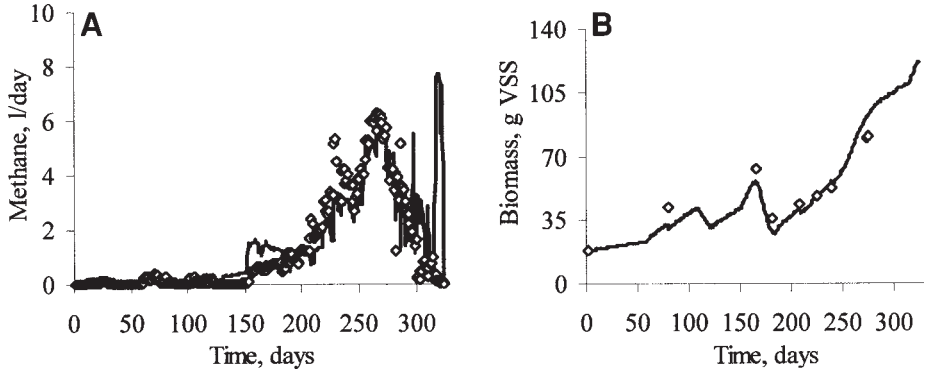

Fig. 5. Model vs experiment for **(A)** methane production and **(B)** biomass accumulation in reactor. (◇) Experiment; (——) model.

Note that some fluctuations in model variables at the final stage of simulations (such as chaos) were caused by frequent variation in actual OLR during the experimental study *(16)*. These fluctuating experimental OLR values were used as input parameters during simulations. Finally, in spite of some discrepancies in the behavior of the main components, the agreement between the experiment and the model for biomass dynamics was good throughout the study (Fig. 5B).

According to the approach introduced earlier (Eqs. 14–17), the logarithmic dependence of all *ER* values from V_{up} was introduced in the model because the biomass retention inside the sludge bed reactor was high, even under high V_{up} values in the considered experiment (Fig. 5B):

$$ER_i(V_{up}) = K^i_{ER}\,[1 - K_V \cdot \mathrm{Log}_{10}(V_{up}/2)] \qquad (22)$$

The K_v value here was found by fitting to be equal to 0.028.

In conclusion, for engineering purposes in which sulfate removal efficiencies are of primary interest, the proposed extension of ADM1 is generally valid, as evidenced from Figs. 1–5.

Table 2
Parameters of Sulfidogenic Bacterial Groups Used in Model[a]

Bacterial group	$k_{max,i}$ (g S-COD/[g VSS-COD·d])	K_S (g COD/L)	K_{SO_4} (mol/L)	K_I (mol/L)	Y_i (g VSS-COD/g S-COD)	b_i (1/d)	K^i_{ER}
X_5	13.7	0.10	2.1×10^{-4}	8.13×10^{-3}	0.0329	0.01	0.998
X_6	12.6	0.11	2.0×10^{-4}	8.13×10^{-3}	0.0329	0.01	0.998
X_7	7.1	0.22	1.0×10^{-4}	7.81×10^{-3}	0.0342	0.015	0.998
X_8	26.7	0.0001	1.04×10^{-4}	7.8×10^{-3}	0.0366	0.01	0.998

[a]COD, chemical oxygen demand; S-COD, substrate-chemical oxygen demand; VSS-COD, volatile suspended solids-chemical oxygen demand.

Table 3
Parameters of Other Bacterial Groups Used in Model[a]

Bacterial group	$k_{max,i}$ (g S-COD/[g VSS-COD·d])	K_S (g COD/L)	K_I (mol/L)	Y_i (g VSS-COD/g S-COD)	b_i (1/d)	K^i_{ER}
X_1	12.00	0.10	7.53×10^{-3}	0.0366	0.01	0.998
X_2	10.33	0.10	7.53×10^{-3}	0.0366	0.01	0.998
X_3	9.62	0.21	7.19×10^{-3}	0.0317	0.015	0.9995
X_4	24.24	0.0001	6.25×10^{-3}	0.0403	0.01	0.9995
X_9					0	0.998

[a]COD, chemical oxygen demand; S-COD, substrate-chemical oxygen demand; VSS-COD, volatile suspended solids-chemical oxygen demand.

Nomenclature

b = bacterial decay rate constant (d^{-1})
ER = efficiency of retention of bacterial group in reactor
K_{ER} = ER under V_{up} = 2 m/h (dimensionless)
K_I = inhibition constant by undissociated hydrogen sulfide (mol/L)
k_La = mass transfer coefficient (d^{-1})
k_{max} = maximum substrate rate uptake (1/d)
K_S = Monod saturation constant (g COD/L for organic substrates and hydrogen or mol/L for sulfate)
K_V = ER dependency from V_{up} (dimensionless)
M = mass transfer rate to gas phase (g COD[mol]/[L · d])
p = partial pressure of substrate in gaseous form (atm)
pK_1, pK_2 = parameters of pH inhibition functions
q = liquid flow rate (L/d)
RE_A = removal efficiency of component A (dimensionless)
S = substrate concentration in liquid phase (g COD/L for organic components and hydrogen or mol/L for sulfate, sulfide, and soluble CO_2 and its ionized form)
V_G = volume of reactor gas phase (L)
V_R = volume of reactor liquid phase (L)
V_{up} = upward liquid velocity (m/h)
X = bacterial concentration (g COD/L)
Y = bacterial yield (g COD/g COD consumed)
V_{ij} = rate coefficients for component i on process j
ρ_i = conversion rate (g S-COD [g VSS-COD or mol]/[L · d])

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