INTEGRATED MATHEMATICAL MODEL OF UASB REACTOR FOR COMPETITION BETWEEN SULPHATE REDUCTION AND METHANOGENESIS

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ABSTRACT

The existing mathematical models of anaerobic treatment processes were mainly developed for ideally mixed reactors with no concentration gradients on substrates, intermediates, products and bacteria inside the reactor. But for conventional UASB reactors with low upward velocity, the distribution of these components along the reactor height is very far from uniform. This paper presents an integrated mathematical model of the functioning of UASB reactor taking into account this non-uniformity as well as multiple-reaction stoichiometry and kinetics. In general, our integrated model includes the following blocks: a) kinetic block, including the growth and metabolism of acidogenic, acetogenic, methanogenic and sulphate-reducing bacteria; b) physico-chemical block, for the calculation of pH in each compartment of the liquid phase; c) hydrodynamic block, describing liquid flow as well as the transport and distribution of the components along the reactor height; d) transfer block, describing a mass transfer of gaseous components from the liquid to gas phase. This model was calibrated to some experimental studies of the functioning of UASB reactors made by in 1994. Hypothetical computer simulations are presented to illustrate the influence of different factors (recycle number, hydraulic retention time, quality of seed sludge, SO_4^{2-}:COD ratio etc.) on the operation performance of UASB reactor. © 1997 IAWQ. Published by Elsevier Science Ltd
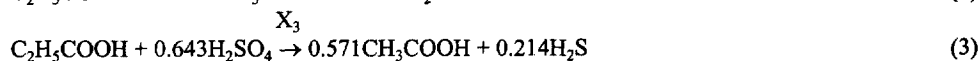
INTRODUCTION

The main goals of mathematical modelling in the field of biological wastewater treatment are the generalisation of knowledge and experience, the verification of conceptual ideas, the prediction of behaviour of complicated treatment biosystems and control of the processes. Anaerobic digestion is a very interesting object for modelling because of its extreme mechanistic complexity. The existing mathematical models of anaerobic wastewater treatment were mainly developed for ideally mixed reactors with no concentration gradients on substrates, intermediates, products and bacteria inside the reactor. But, for example, for conventional UASB reactors with low upward velocity, the distribution of

these components along the reactor height is very far from uniform. This paper will first develop an integrated mathematical model of the functioning of UASB reactors taking into account this non-uniformity as well as multiple-reaction stoichiometry and kinetics. The resultant model is then calibrated to existing laboratory studies of this process. Finally, several scenarios are presented to determine the influence of different factors (recycle number, hydraulic retention time (HRT), quality of seed sludge, SO_4^{2-}:COD ratio etc.) on performance of UASB reactors.

MODEL DESCRIPTION

Stoichiometry

The present model simulates the anaerobic treatment of soluble organic wastewater containing sulphate concentrations comparable with COD concentrations. Since sugars and volatile fatty acids are typical components of the organic part of these wastes, we chose sucrose, propionate and acetate as influent substrates in the variant of our model discussed below. The general simplified reaction sequence by which the chosen influent substrates are transformed by the different groups of anaerobic bacteria can be presented as (organic contaminants are expressed in g COD/l, sulphates - in g/l, sulphides - in g S/l; components with zero COD are omitted; for sulphate reduction: consumption of 1 g COD corresponds the consumption of 1.5 g sulphate and evolution of 0.5 g sulphide (as S)):

$$C_{12}H_{22}O_{11} \xrightarrow{X_1} 0.667CH_3COOH + 0.333H_2 \tag{1}$$

$$C_2H_5COOH \xrightarrow{X_2} 0.571CH_3COOH + 0.429H_2 \tag{2}$$

$$C_2H_5COOH + 0.643H_2SO_4 \xrightarrow{X_3} 0.571CH_3COOH + 0.214H_2S \tag{3}$$

$$CH_3COOH \xrightarrow{X_4} CH_4 \tag{4}$$

$$CH_3COOH + 1.5H_2SO_4 \xrightarrow{X_5} 0.5H_2S \tag{5}$$

$$H_2 \xrightarrow{X_6} CH_4 \tag{6}$$

$$H_2 + H_2SO_4 \xrightarrow{X_7} 0.5H_2S \tag{7}$$

Thus, according to the stoichiometric scheme (1-7) accepted by us, the conversion process is carried out by 7 groups of microorganisms: the group X_1 contains all fermentative bacteria (FB); X_2, all propionate-degrading acetogenic bacteria (AB); X_3, all acetogenic sulphate-reducing bacteria (SRB); X_4, all acetotrophic methanogenic bacteria (MB); X_5, all acetotrophic SRB; X_6, all hydrogenotrophic MB; and X_7, all hydrogenotrophic SRB. Since carbon dioxide has zero COD, its stoichiometric relationships in the model are expressed in mol/l.

Kinetics

The kinetics are based on the following assumptions and considerations (Kalyuzhnyi, 1996).
1. The growth of biomass proceeds according to Monod kinetics with simultaneous inhibition by undissociated H_2S. Instead of using true Monod kinetics, it is assumed that reaction kinetics for carbon dioxide is of zero order for concentration because carbon dioxide is usually present in significant concentrations in anaerobic reactors. A dual substrate form of Monod equation is postulated for SRB to account for their growth limitations under treatment of sulphate-deficient wastewaters.

2. The effect of pH on the growth rates is described by a Michaelis pH function F(pH) normalised to give a value of 1.0 as the centre value (Kalyuzhnyi, 1996).

3. Undissociated H_2S inhibition proceeds according to first order inhibition kinetics for all bacteria. Thus, a specific growth rate equation for FB, AB and MB has a form:

$$\mu_j = \mu_{m,j} \times S_i \times (1-H_2S_f/K_{I,j}) \times F(pH)/(K_{S,j}+S_i);$$ (8)

for SRB bacteria:

$$\mu_j = \mu_{m,j} \cdot S_i \cdot [SO_4^{2-}] \cdot (1-H_2S_f/K_{I,j}) \cdot F(pH)/((K_{S,j}+S_i) \cdot (K_n+SO_4^{2-})),$$ (9)

where

K_n - Monod saturation constant for sulphate (g/l);
K_I - inhibition constant for undissociated hydrogen sulphide (g S/l);
K_S - Monod saturation constant for organic substrate and hydrogen (g COD/l);
S_i - substrate concentration in liquid phase (g COD/l);
μ_m - maximum specific growth rate (d^{-1});
f - undissociated;
i - substrate i;
j - bacteria j;
n - SRB n

4. All product formations are directly coupled to biomass production due to the dissimilatory nature of sulphate reduction and methanogenesis.

5. Bacterial decay is described by first-order kinetics.

6. Substrate consumption for maintenance is incorporated in the overall biomass yield.

7. Sulphate consumption for biomass growth is negligible.

8. All reactions are effectively rate controlled, i.e. the effects of diffusional limitations of biomass aggregates are constant and incorporated into the kinetic term.

Liquid Phase Equilibrium Chemistry

For calculation of pH values and concentrations of undissociated species along the reactor height, the approach described previously (Kalyuzhnyi, 1996) was used. In short, the pH values were calculated from the ionic balance equation, which included all the ionised species in the liquid phase.

Hydrodynamics

The present model simulates the hydrodynamic characteristics of a UASB reactor with height H and cross-section Cs. The physical and microbiological processes inside the reactor are considered to be dependent only on longitudinal axis of reactor (distance z from input) and time t, i.e. all the process characteristics in fixed crosssection Cs_z are the uniform. In general, the space distribution of any component N of liquid phase can be written by the following equation with partial derivatives:

$$\frac{\partial}{\partial t} N(z,t) = D \frac{\partial^2}{\partial z^2} N(z,t) - V \frac{\partial}{\partial z} N(z,t) + r(z,t) - Tr(z,t)$$ (10)

The first term in the right part of equation (10) characterises the degree of mixing, i.e., the longitudinal mass distribution when the input distribution has a delta-functional form. The value of D represents the width of this longitudinal distribution and can be estimated by existing lithium technique. The second term of equation (10) determines a convective part of mass transfer and contains the value V, which can be considered as upflow liquid velocity. The third and fourth terms are the net biological production/consumption rate and transfer rate from liquid to gas phase for the component N, respectively. The boundary conditions follow from the relationship between the internal mass transfer given by Fourrier law and external mass transfer given by Newton law.

Material balances

Gas phase. The partial pressure of i-substrate (methane, hydrogen, carbon dioxide and hydrogen sulphide) in the gas volume is calculated by a component balance around the gas phase:

$$dp_i/dt = (\int M_i(z) \times Cs \times dz) \times V_m \times p_t - G \times p_i)/V_G \tag{11}$$

where

$M_i(z)$ - mass transfer rate of i-substrate to the gas phase from the compartment z:

$$M_i(z) = k_L a(z) \cdot (S_{i,f} - p_i/He_i); \tag{12}$$

V_m - specific molar volume of gas under given temperature;

p_t - total pressure in the reactor headspace ($p_t = \Sigma p_i$, p_t was accepted to be equal to 1 atm);

V_G - volume of reactor gas phase;

$k_L a(z)$ - mass transfer coefficient for the compartment z;

He_i - Henry coefficient for i-substrate.

A total balance gives the gas volumetric flow rate from the reactor:

$$G = \sum_i (\int M_i(z) \cdot Cs \cdot dz) \cdot V_m \tag{13}$$

Liquid phase. A general material balance for soluble substrates can be written on the basis of the equation (10) as:

$$\frac{\partial}{\partial t} S_i(z,t) = D_i \frac{\partial^2}{\partial z^2} S_i(z,t) - V_i \frac{\partial}{\partial z} S_i(z,t) + r_i - M_i \tag{14}$$

M_i for sucrose, propionate, acetate and sulphate are equal zero. The general mass balance equation used to describe the behaviour of each bacteria group in the reactor is presented below:

$$\frac{\partial}{\partial t} X_j(z,t) = D_j \frac{\partial^2}{\partial z^2} X_j(z,t) - V_j(z) \frac{\partial}{\partial z} X_j(z,t) + \mu_j X_j - b_j X_j \tag{15}$$

where

b - bacterial decay rate coefficient.

Hence, the consideration of the dynamics of aggregation and dispersion of biomass from support media or granulating (flocculating) particles is beyond the scope of the current model.

CRITERIA FOR EVALUATION OF OUTCOME OF COMPETITION BETWEEN SRB AND MB OR AB

The ratio of COD converted by SRB relative to that converted by MB was used as the main criterion for the evaluation of outcome of competition between SRB and MB:

$$CRIT = COD_{SRB}/COD_{MB} = 2/3 \times ([SO_4^{2-}]_{in} - [SO_4^{2-}]_{ef})/HRT/r_{CH4}. \tag{16}$$

Also three specific criteria were introduced to evaluate an outcome of competition between SRB and MB or AB for specific substrates:

$$CRIT_{Pr} = Pr\text{-}COD_{SRB}/Pr\text{-}COD_{AB} = 2 \times r_{H2S\text{-}Pr}/r_{H2\text{-}Pr} \text{ (for propionate)} \tag{17}$$

$$CRIT_{Ac} = Ac\text{-}COD_{SRB}/Ac\text{-}COD_{MB} = 2 \times r_{H2S\text{-}Ac}/r_{CH4\text{-}Ac} \text{ (for acetate)} \tag{18}$$

$$CRIT_{H2} = H_2\text{-}COD_{SRB}/H_2\text{-}COD_{MB} = 2 \times r_{H2S\text{-}H2}/r_{CH4\text{-}H2} \text{ (for hydrogen)} \tag{19}$$

EXPERIMENTAL SYSTEMS CONSIDERED

The results of Alphenaar's experimental study (1994) which considered the competition between sulphate reduction and methanogenesis in UASB reactors treating synthetic sulphate-containing wastewater, are used here to calibrate the integrated model above. The salient features of experimental protocol are given in Table 1 with further details provided in the original work.

COMPUTATIONAL METHODS

Simulations were performed on an IBM-compatible personal computer (processor Pentium-133) by

Table 1. Details of experimental study of Alphenaar (1994) used in model calibration

Parameter	Case	
	1	2
Reactor type	UASB	UASB
Reactor volume, l	1.1	1.1
Recirculation factor	0	10
Hydraulic retention time, days	0.3125	0.2875
Upward velocity, m/day	1.2	15.6
Temperature, °C	30	30
Seed sludge	80% granular + 20% sulphate adapted	
Mineral medium content, g/l	NH_4Cl - 1.044; KCl - 0.27; KH_2PO_4 - 0.169; $MgCl_2.6H_2O$ - 0.15; $NaHCO_3$ - 1.25; influent pH -6.8	
Influent sulphate , g/l	5	5
Sludge loading rate, g COD/g VSS* day:		
start-up (days 0-50)	gradual increase from 0.25 to approx. 1	
steady-state (aver., days 50-150)	1.06	0.98
Influent COD, g/l	2.5	2.5
COD content	Acetate:Propionate:Sucrose - 5:4:1 (as COD)	

numeric integration of the differential equations (11-15), using a computer program based on a linearised technique (Millne, 1953). With each step of numeric integration, pH values were calculated using an iteration technique (Korn & Korn, 1968). The computer program was written by these authors in Fortran-77 in a generalised form, where a variable number of steps, organisms, components, substrate 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

The physico-chemical model parameters were directly taken from the literature (Rabinovich and Havin, 1977). A number of preliminary simulations were undertaken to determine the most appropriate set of bacterial, hydrodynamic, and mass-transfer model parameters. After all, the values of these parameters have been chosen in a range consistent with the experimental study of Alphenaar (1994).

RESULTS AND DISCUSSION

The results of the calibration of the model are presented in the Table 2 and Figs. 1a-2a. It is seen that for the case without recycle, predictions agree well with reported integrated parameters like SLR, ORR, AcRR and Y (Table 2) as well as with reported increase in the ratio of total COD converted by SRB relative to that converted by MB (main criterion) during the experiment (Fig. 1a). For all that, three main electron donors (hydrogen, propionate and acetate) for SRB have a different impact relative to this ratio. At the end of the experiment, almost 100% of hydrogen and propionate and only 55% of acetate are converted by SRB (Fig. 1b), which corresponds well the experimental data (Alphenaar, 1994). Thus, the model predicts that MB and AB almost completely lose the competition for hydrogen and propionate, but not for acetate.

A satisfactory agreement between the model and experiment has also been obtained for the case with recycle (Table 2, Fig. 2a). Similar tendencies of the percentage of electron donors used by SRB were also

Table 2. Model versus experiment (average values over days 50-150)

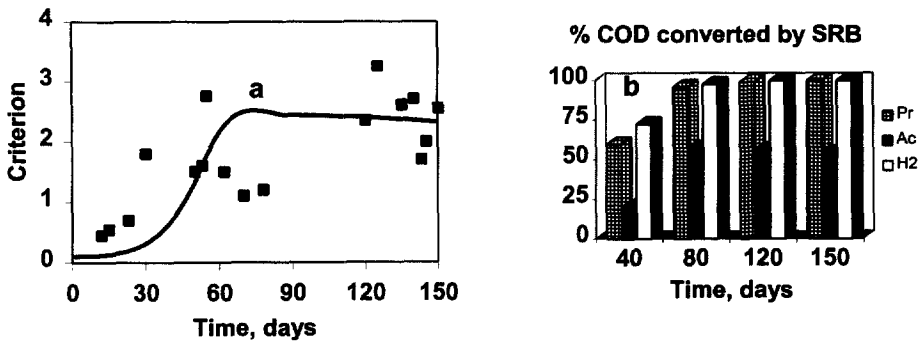| Parameters	Case 1 (without recycle)		Case 2 (with recycle)	
	Experiment	Model	Experiment	Model
Y_{tot}, g VSS/g COD	0.041	0.042	0.041	0.043
Sludge loading rate (SLR), g COD/g VSS*day	1.06	1.08	0.98	0.97
Organic removal rate (ORR), g COD/g VSS*day	0.79	0.81	0.73	0.7
Acetate removal rate (AcRR), g COD/g VSS*day	0.66	0.68	0.61	0.6

Fig. 1. Model versus experiment, case without recycle.
    a. Main criterion (eq. 16): points - experimental data of Alphenaar (1994); lines - model.
    b. Modelling results about percentage of electron donors used by SRB.
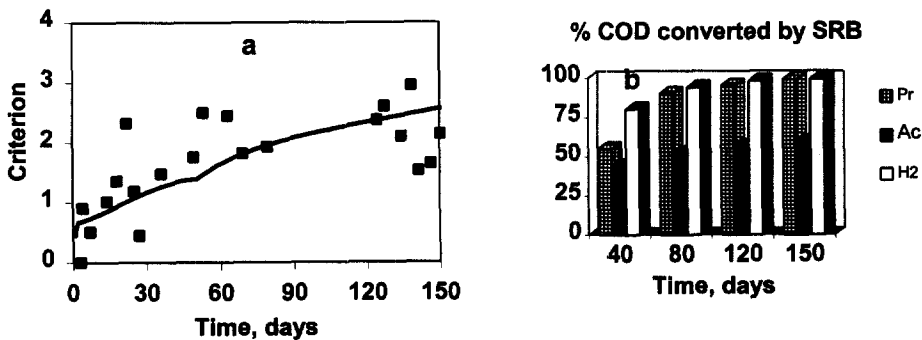

Fig. 2. Model versus experiment, case with recycle.
    a. Main criterion (eq. 16): points - experimental data of Alphenaar (1994); lines - model.
    b. Modelling results about percentage of electron donors used by SRB.

observed for this case (Fig. 2b); however, the value of the main criterion was slightly higher (Fig. 2a) than for the case without recycle (Fig. 1a) at the end of experiment due to the lower concentration of inhibitor (undissociated hydrogen sulphide) in the reactor (Fig. 3).
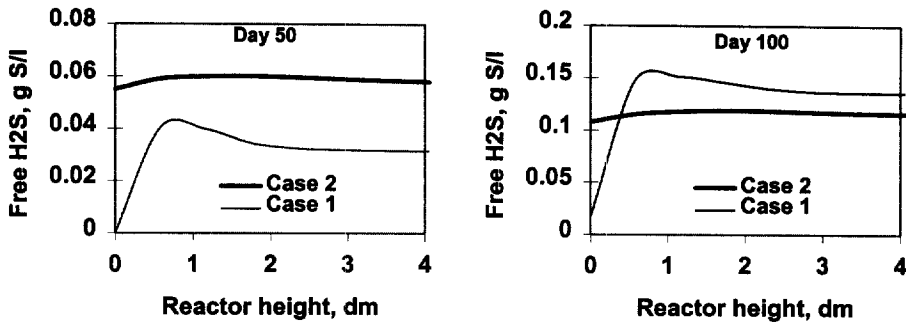

Fig. 3. Profiles of concentration of undissociated H_2S along the reactor height for the cases without (1) and with (2) recycle according to the model.

Since the competition between SRB and MB proceeded, in general, mainly for acetate, special attention in the hypothetical modelling scenarios was focused on the influence of different factors on the outcome of this competition. A brief description of these modelling experiments follows below.

The modelling results under a variation of HRT showed that the six-times increase of HRT from the basic variant (case 1) hardly influenced the main criterion and percentage of Ac-COD used by SRB in the short-term experiments (up to 2 months). A further continuation of the experiments (i.e. long-term experiments) led to a substantial increase in both the parameters mentioned above. This was due to decreased wash-out of relatively slow growing acetotrophic SRB under longer HRT.

An important factor which is not always taken into account when analysing the outcome of competition for acetate between SRB and MB is SO_4^{2-}:COD ratio. The corresponding modelling results showed that the decrease in this ratio below the proportion 1.5:1 led to a sharp decrease in both the main criterion and the percentage of Ac-COD used by SRB. This was because under conditions of a deficiency of sulphate, the Ac-COD is consumed by fast growing acetogenic and hydrogenotrophic SRB rather than by slow growing acetotrophic SRB. Hence, sulphate deficiency leads to a scarce utilisation of acetate as an electron donor for SRB, and acetate is mainly used by MB.

The next important factor for the investigated system is the initial proportion of SRB/MB in the seed sludge. From the modelling results, it follows that an increase in this proportion led to a substantial increase in both the main criterion and percentage of Ac-COD used by SRB, especially in the beginning of the experiment. In the long-term experiments, the differences are not so pronounced. Thus, if the seed sludge is precultivated under sulphate-limiting conditions, it may take a long time before SRB can become predominant. Therefore, the duration of the experiment can be a factor.

Since not much actual information about inhibition kinetics is available, one can assume that sulphide toxicity is different for AB, MB and SRB, and this factor can potentially play a determining role in the outcome of long-term competition between methanogenesis and sulphate reduction. It should be noted in this connection that sulphide resistance depends on the state (disperse or granular/biofilm) of the sludge. So, the granular sludge demonstrates an elevated sulphide resistance in comparison with the disperse one with respect to methanogenic activity (Alphenaar, 1994). It is evident that bacteria growing in a biofilm

(e.g. granular sludge) might be more protected against undissociated H_2S, due to the existence of a pH and sulphide gradient in the granule/biofilm. Modelling results under variation of sludge quality (or sulphide resistance) of SRB showed that a decrease (or increase) of granulation extent of SRB in comparison with MB led to a sharp decrease (or increase) in both the main criterion and percentage of Ac-COD used by SRB. Thus, if the seed sludge contains MB mainly in granular form and SRB mainly in disperse form, it can be a factor for the predominance of methanogenesis over sulphate reduction. Some oscillations of the main criterion were observed due to self-oscillating coexistence of MB and SRB under conditions of their strong inhibition by undissociated H_2S as was recently shown by Vavilin et al. (1994). Modelling results under variation of influent pH demonstrated a weak influence of this factor (up to moderate buffer capacity of influent) on the main criterion because intensively forming carbon dioxide and hydrogen sulphide create a sufficient level of buffer capacity of the reactor medium. A summary of modelling data about influence of different factors on outcome of competition between SRB and MB is presented in Table 3.

Table 3. Summary of modelling scenarios about influence of different factors
on outcome of competition between SRB and MB

Factor	COD_{SRB}/COD_{MB}
Recirculation factor increase	weak increase
HRT increase	weak increase in short-term experiments moderate increase in long-term experiments
SO_4^{2-}:COD ratio	sharp decrease under low SO_4^{2-}:COD ratio no influence under SO_4^{2-}:COD>1.5
SRB/MB increase in the seed sludge	sharp increase in short-term experiments moderate increase in long-term experiments
SRB sludge quality (sulphide resistance) increase	sharp increase
Influent pH increase	weak increase

CONCLUSIONS

Thus, the integrated mathematical model of UASB reactor developed by us adequately describes the experimental data and can be used for further investigation of competition between sulphate reduction and methanogenesis in anaerobic reactors.

ACKNOWLEDGEMENT

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