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Mathematical modelling as a tool to study population dynamics between sulfate reducing and methanogenic bacteria

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Abstract

The existing mathematical models of sulphate fed anaerobic reactors are reviewed. Special attention was put on pecularities of the description of sulphide inhibition and competition between sulphate reduction and methanogenesis in such systems. The paper also presents an integrated mathematical model of the functioning of a sulphate fed granular sludge reactor taking into account concentration gradients on substrates, intermediates, products and bacteria inside the reactor as well as multiple-reaction stoichiometry and kinetics. The developed model includes the following blocks: a) hydrodynamic block describing liquid flow as well as transport and distribution of the components along the reactor height; b) kinetic block including growth, metabolism, inhibition and competition of acidogenic, acetogenic, methanogenic and sulphate reducing bacteria in the system; c) physico-chemical block for calculation of pH in each compartment of the liquid phase; d) transfer block describing a mass transfer of gaseous components from the liquid to the gas phase. The integrated model was calibrated and validated using laboratory studies on the functioning of sulphidogenic granular sludge reactors, i.e. their start-up and the maximisation of sulphide yield in these reactors. The modelling of the reactor operation is supplemented with hypothetical computer simulations to illustrate the influence of engineering parameters on the operation performance and sulphate conversion of sulphidogenic reactors.

Abbreviations: AB – acetogenic bacteria; AcRR – acetate removal rate; b – bacterial decay rate constant; Bu – butyrate; COD – chemical oxygen demand; Cs – cross-section of the reactor; CSTR – continuous stirred tank reactor; D – axial dispersion coefficient; F – function; FB – fermentative bacteria; H – height of working zone in the reactor; He – Henry constant; HRT – hydraulic retention time; I – inhibitor; $k_L a$ – mass transfer coefficient; K – Monod saturation constant for sulphate (g/l); $K_{a(b)}$ – dissociation constant; K_I – inhibition constant by undissociated hydrogen sulphide; K_S – Monod saturation constant for organic substrates; M – mass transfer rate to the gas phase; MB – methanogenic bacteria; ORR – organic removal rate; p – partial pressure of substrate in gaseous form; Pr – propionate; Q – gas volumetric flow rate from the reactor; r – net biological production/consumption rate; S – substrate concentration in liquid phase; SLR – sludge loading rate; SRB – sulphate-reducing bacteria; t – time; UASB – upflow anaerobic sludge blanket; V_G – volume of reactor gas phase; V_m – specific molar volume of gas; VFA – volatile fatty acids; VSS – volatile suspended solids; W – superficial (vertical) velocity; W_{up} – upflow liquid velocity; X – bacterial concentration; Y – bacterial yield; z – distance along the reactor height from input; μ – specific growth rate; μ_m – maximum specific growth rate. Subscripts: f – free (undissociated); i – substrate i; in – inlet; j – bacterial trophic group j; n – SRB n

Introduction

Modern reactor designs based on biomass retention – such as the upflow anaerobic filter (Young & McCarty 1969), the UASB reactor (Lettinga et al. 1980), the downflow stationary fixed film reactor (Van den Berg & Kennedy 1981), the anaerobic attached film expanded bed reactor (Schwitzenbaum & Jewell 1978), and the fluidized bed reactor (Binot et al. 1983) – extended the applicability of anaerobic technology to the treatment of a variety of waste water streams (Lettinga 1995). Nowadays, numerous successful full scale implementations have been achieved, in part due to substantial advances in the understanding of the fundamentals of anaerobic digestion. Despite this intensive research, anaerobic digestion remains largely a black box process. The lack of insight in the exact biodegradation patterns hampers a comprehensive mathematical modelling, which is needed to underpin and optimise process control.

Modelling provides an important tool for the comprehensive study of microbial ecology and gives expression of conceptual ideas to account for major events of interest occurring within a system. Moreover, it allows evaluation of key hypotheses. Comparing the simulated and the observed response draws attention to deficiencies in the conceptual structure. Modelling can reveal information not apparent from pilot-scale studies. It also allows potentially feasible solutions to be explored without the pilot-scale or other studies, thereby helping in selection of the more promising ones for testing. Modelling is an unchangeable tool for identifying the parameters that significantly influence the system response and giving guidance for the establishment of design criteria. It also assists in identifying possible causes for system malfunction or failure and in devising remedial measures.

Though comprehensive mathematical modelling of anaerobic reactors is a rather complicated task, because the entire process includes complex dynamics of biological, chemical, and physical subsystems with many interrelations between them (Figure 1), substantial advances were made in this area beginning from the pioneering work of Andrews (1968). A review of dynamic models of the anaerobic digestion process was presented by Desjardins and Lessard (1992). The proposed models of the anaerobic treatment processes were mainly developed for the production of methane with an insufficient attention on sulphate reduction. Only few models of sulphate fed anaerobic reactors were elaborated recently (Gupta et al. 1994; Vavilin et al. 1994; Kalyuzhnyi & Fedorovich 1997, 1998).

This paper will firstly review the existing mathematical models of sulphate fed anaerobic reactors. Special attention will focus on the description of sulphide inhibition and competition between sulphate reduction and methanogenesis in such systems. Then an integrated mathematical model of the functioning of sulphate fed granular sludge reactors will be presented taking into account concentration gradients of substrates, intermediates, products and bacteria inside the reactor as well as multiple-reaction stoichiometry and kinetics. The resultant model is then calibrated and validated to existing laboratory studies of this process: i) the start-up of granular sludge reactors and their development (Alphenaar et al. 1994) and ii) maximisation of sulphide yield in these reactors (Omil et al. 1996, 1997). Finally, the modelling of the reactor operation is supplemented with hypothetical computer simulations to illustrate the influence of engineering parameters (hydraulic retention time, upward velocity, quality of seed sludge, sludge retention, recycle number, hydrogen sulphide inhibition, etc.) on the performance of sulphate fed anaerobic reactors.

Preliminary remarks about sulfate fed bioreactors

In sulphate fed anaerobic reactors, both sulphate reduction and methanogenesis can be the final step in the degradation process, because SRB are capable of using many of the intermediates formed during methanogenesis (Figure 2). In general, substrate competition in such systems is possible on two levels: competition between SRB and AB for VFA and ethanol; and competition between SRB and MB for acetate and hydrogen. Sulphate reduction with sugars and amino acids plays an unimportant role (Widdel 1988). Thermodynamic and Monod-kinetic data of SRB, AB and MB for growth on VFA and hydrogen indicate that SRB should be able to out-compete AB and MB (Oude Elferink et al. 1994). This prediction has been confirmed experimentally for hydrogen (Alphenaar et al. 1993; Mulder 1984; Van Houten et al. 1994) and for VFA (Alphenaar et al. 1993; Omil et al. 1996, 1997; Visser et al. 1993). For utilisation of acetate in anaerobic reactors the situation is different. Various researchers have observed that during the breakdown of sulphate-containing waste water SRB can indeed

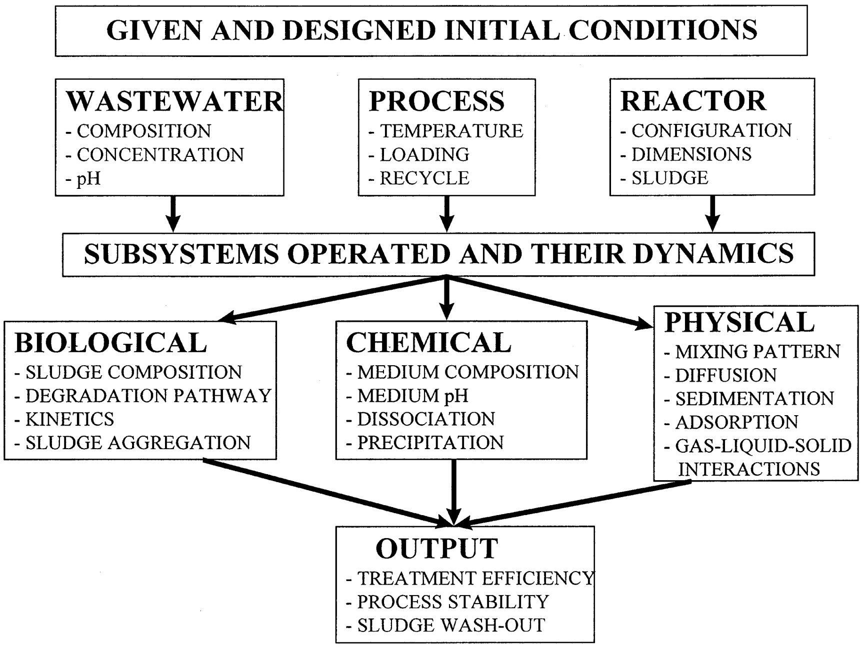

Figure 1. Complex dynamics of anaerobic reactors: subsystems present and their interrelations.

successfully compete with MB for acetate (Alphenaar et al. 1993; Visser 1995) whereas other results indicate that the latter is preferentially degraded to methane (Hoeks et al. 1984; Mulder 1984; O'Flaherty & Colleran 1995; Rinzema & Lettinga 1988). To explain the differences found, besides pure bacterial kinetics, other factors influencing the outcome of competition between SRB and MB should be taken into account. These factors include the COD:SO_4^{2-} ratio, type of seed sludge, sludge retention, hydrogen sulphide inhibition, pH and nutrient limitation (Lens et al. 1998).

The main product of sulphate reduction – sulphide – is a strong toxicant for the majority of anaerobic bacteria including AB, MB and SRB. Toxicity by sulphide is related with the undissociated form which can permeate the cell membrane (Rinzema 1988). The pK_a-value of the dissociation equilibrium of H_2S is about 7 at mesophilic conditions. Consequently, small pH variations can cause significant changes in the degree of inhibition. Except for the results of Isa et al. (1986) who found only 50% inhibition at concentrations exceeding 1000 mg free H_2S/l, total inhibition of growth is generally obtained at concentrations below 550 mg free H_2S/l (Kalyuzhnyi et al. 1997; McCarthy & Oleszkiewicz 1991; Okabe et al. 1992; Reis et al. 1992; Stucki et al. 1993; van Houten et al. 1994). With regard to anaerobic bioreactors, Speece et al. (1986) estimated that for a stable methanogenic process the free H_2S concentration should not exceed 150 mg/l.

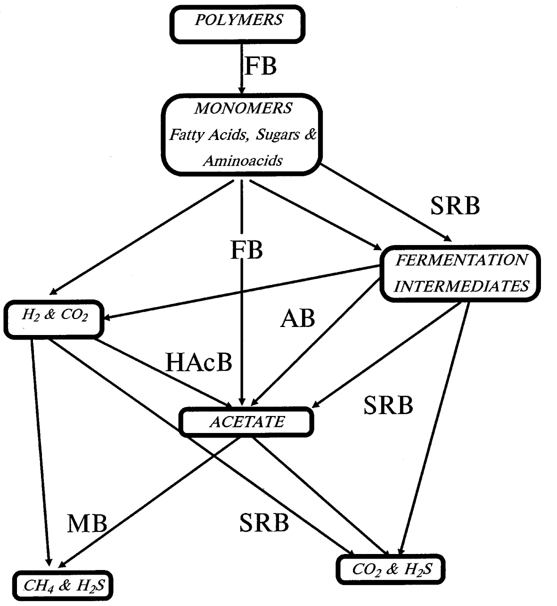

Figure 2. Pathways of competition between acetogenic, methanogenic and sulphate reducing bacteria during anaerobic digestion of organic matter.

Rinzema & Lettinga (1988) used this value as a criterium to predict when anaerobic digestion of sulfate rich wastewaters proceeds successfully. On the basis of a literature survey, they found that for wastewaters with a COD:sulphate ratio > 10, the free H_2S concentration did not exceed the critical value of 150 mg/l and a stable anaerobic degradation was always obtained. On the contrary, a decrease of COD:sulphate ratio below 10 may lead to a substantial drop of the treatment efficiency due to a severe inhibition by elevated free H_2S concentrations.

Existing mathematical models of sulphate fed reactors

The first model of sulphate fed anaerobic reactors was developed by Gupta et al. (1994) for a chemostat. The main achievement of this model is a comprehensive description of the chemical subsystem (Figure 1) where the complex chemistry involved was modelled by incorporating various buffer systems, acid-base and liquid-gas equilibria, ionic interactions and metal precipitation. The following important anaerobic digestion acid-base equilibria were included in the model: the carbonate, the phosphate, the ammonia and the sulphide ones. In addition, metal sulphide and carbonate precipitation was one of the major features of this model. Liquid-gas equilibria (carbon dioxide, hydrogen sulphide, ammonia, methane, nitrogen and water vapour) have been given special consideration in order to accurately predict the gas production rate and composition. On the contrary, the biological subsystem was represented in a simplified way - using the Monod equation for 1 (MB or SRB) or 2 (MB and SRB) bacterial groups without pH modulation and without taking into account a sulphide inhibition:

$$\mu = \mu_m S/(K_S + S) \tag{1}$$

The model was calibrated by experimental data where methanogenic, sulphidogenic and mixed chemostats were fed by three different substrates (acetate, methanol and formate). Iron was added to precipitate the sulphide produced. The model was able to predict both steady-state and transient batch spike experimental data fairly well for homogenic (methanogenic or sulphidogenic) environments. However, the description of mixed chemostats could be considered only on the qualitative level due to the simplified conceptual structure of the biological subsystem in the model of Gupta et al. (1994).

A more complex model of sulphate fed CSTR was proposed by Vavilin et al. (1994). The modelling of the chemical subsystem was similar to Gupta et al. (1994). The representation of the biological subsystem included the Monod relationship (Equation 1) for 2 bacterial groups (acetotrophic MB and SRB) with an inclusion of pH and sulphide inhibition:

$$\mu = \mu_m S \cdot F(pH) \cdot F(H_2S_f)/(K_S + S) \tag{2}$$

The inhibition terms were used in the form of the so called 2x2 constants (Vavilin et al. 1995):

$$F(I, K_2, K_{100}) = 1/(1 + (I/K_2)^{ln 99/ln(K_{100}/K_2)}) \tag{3}$$

where I - pH or H_2S_f;

K_2 – concentration of I at which the growth rate is decreased twice;

K_{100} – concentration of I at which the growth rate is decreased 100 times.

The Vavilin's model was calibrated on the experiments of Parkin et al. (1990) where anaerobic chemostats were operated at variation of COD (acetate)/S ratios from 60:1 to 2:1. The simulations showed that when the COD/S ratio was less than 10:1 both sulphate reduction and methanogenesis shut down, which agreed well with the experimental observations. The model revealed that free H_2S and pH inhibition were the main factors for system failure, and the former acted as a trigger, stimulating the positive feed-back loop between an increase in acetate and sulphate concentrations and a decrease in the pH level through microbial activity. The interesting finding of the model is an oscillating coexistence of MB and SRB with a period of 5-20 days under conditions close to the system failure. This emphasises the high complexity of sulphate fed anaerobic systems. The oscillating phenomenon was further investigated using a reduced model (Fomichev & Vavilin 1997). It was discovered that self-oscillations disappeared at strong venting rates with an inert gas as well as at increased buffer capacity. It was also shown that by decreasing the influent pH one could shift the self-oscillations region to higher sulphate loads. However, the competition between sulphate reduction and methanogenesis was not addressed by Vavilin et al. (1994).

The competition between sulphate reduction and methanogenesis for acetate was studied by Omil et al. (1998) using a simple mathematical model based on the Monod kinetic parameters of acetate utilising SRB and MB without taking into account their sulphide and pH inhibition. The simulations confirmed the long-term nature of the competition between these acetotrophs. It was shown that a high reactor pH (>8), a short solid retention time (<150 days), and the presence of a substantial SRB population in the inoculum could considerably reduce the time required for acetate-utilising SRB to outcompete MB.

All above mentioned models of sulphate fed CSTR were elaborated for reactors with a single substrate (acetate). Multiple substrate competition between sulphate reduction and methanogenesis has received a substantial attention in the most comprehensive (at present time) model of sulphate fed ideally mixed anaerobic reactors developed by Kalyuzhnyi and Fedorovich (1998). There were no significant differences in their approach to describe the chemical subsystem in comparison with the models proposed by Gupta et al. (1994) and Vavilin et al. (1994). In contrast, the conceptual structure of the biological subsystem included 7 bacterial groups (FB, AB, 2 MB and 3 SRB) responsible for the microbial transformation of the multisubstrate influent consisting of sucrose, VFA and sulphate. The main features of the kinetic description can be summarised as the following:

1. The growth of each bacterial group 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 was of zero order in its concentration because carbon dioxide is usually present in significant concentrations in anaerobic reactors. A dual substrate form of the 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 bell-shape pH function normalised to give a value of 1.0 as the centre value (Kalyuzhnyi 1997).
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 is expressed as:

   $$\mu_j = \mu_{m,j} S_i (1 - H_2S_f / K_{I,j}) F(pH) / (K_{S,j} + S_i) \quad (4)$$

   and for SRB bacteria:

   $$\mu_j = \mu_{m,j} S_i [SO_4^{2-}] (1 - H_2S_f / K_{I,j}) F(pH) / ((K_{S,j} + S_i)(K_n + SO_4^{2-})) \quad (5)$$

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.

The developed structured model was calibrated and verified on the experimental study of Alphenaar et al. (1993) where the competition between sulphate reduction and methanogenesis in CSTR-type anaerobic reactors were investigated. The model was able to describe satisfactorily both the steady-state characteristics of reactor performance and the increase of ratio of total COD converted by SRB relative to that converted by MB (main criterion) under the different HRT imposed to the system. The model also predicted that MB and AB failed to compete for hydrogen and propionate, but could effectively compete for acetate which agrees with experimental observations (Alphenaar et al. 1993; Hoeks et al. 1984; Mulder 1984; Omil et al. 1996; Rinzema & Lettinga 1988; van Houten et al. 1994). Since too many factors can influence the outcome of the competition between SRB and MB and not all of these influences can be thoroughly investigated experimentally, this model was used to assess their impact on the main criterion (Kalyuzhnyi & Fedorovich 1998). The modelling data indicated the following for sulphate fed CSTR: a decrease of the HRT led to a minimal decrease of the main criterion in short-term experiments (up to 2.5 months) and a moderate decrease for longer runs. A decrease of the $SO_4{}^{2-}$:COD ratio has no influence under a $SO_4{}^{2-}$:COD ratio > 1 but a further decrease of this ratio led to a decrease of the main criterion. The SRB/MB ratio in the seed sludge has a critical influence on the main criterion during the start-up period (first 2–3 months), but further continuation of the run led to a progressive elimination of this influence. A decrease in retention efficiency of SRB indicated a tendency for a substantial decrease of the main criterion. Sulphide resistance of SRB is very important for such systems, especially for acetate conversion. Variation of influent pH had practically no influence (in a reasonable range of the buffer capacity) on the main criterion.

The role of mass transfer limitation of sulphate within biomass aggregates in the competition between sulphate reduction and methanogenesis was theoretically evaluated in the model of Overmeire et al. (1994). The steady-state microprofiles of sulphate inside a spherical granule were calculated using a reference set of diffusional and kinetic parameters for SRB obtained from literature. The effect of the parameters on mass transport limitation was tested by varying each reference value of the parameters with a factor of 3. The authors concluded from their analysis that sulphate limitation within granules prevailed at sulphate concentrations in the bulk liquid below 0.2 g/l as well as in large aggregates (radius $>$ 0.75 mm) and it could be a factor governing the competition between SRB and MB. The model calculations, however, did not allow to predict the ultimate outcome of this competition because the model did not take into account mass transfer limitation of COD substrates though the importance of diffusional limitations for these substrates within biomass aggregates has been clearly demonstrated (Arcand et al. 1994; Guiot et al. 1992; Lens et al. 1993). The incorporation of all mass transfer limitations as well as the layered structure of granules should be a next step in the development of this type of mathematical models of sulphate fed anaerobic reactors.

Dispersed plug-flow model

All above reviewed models were developed for ideally mixed reactors with no concentration gradients on substrates, intermediates, products and bacteria inside the reactor. These assumptions are not valid for fixed film reactors, e.g. conventional UASB reactors, where the distribution of these components along the reactor height is far from uniform. Some models taking into account this non-uniformity have been published for methanogenic reactors (Bolle et al. 1986; Sam-Soon et al. 1991; Schwarz et al. 1996; Wu & Hickey 1997). The first attempt to develop such a model for sulphate fed anaerobic reactors was undertaken by Kalyuzhnyi & Fedorovich (1997). In the present paper, this approach is generalised, resulting in the development of the dispersed plug-flow model of sulphate fed UASB reactors.

Model description

Stoichiometry

The present model simulates the anaerobic conversion of soluble organic wastewater containing sulphate concentrations comparable to the chemical oxygen demand (COD) concentrations. Since sugars and volatile fatty acids are typical components of the organic part of these wastes, sucrose, butyrate, propionate and acetate were chosen 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 (on molar basis):

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{X_1} 4CH_3COOH + 8H_2 + 4CO_2 \quad (6)$$

$$C_3H_7COOH + 2H_2O \xrightarrow{X_2} 2CH_3COOH + 2H_2 \quad (7)$$

$$C_3H_7COOH + 1/2H_2SO_4 \xrightarrow{X_3} 2CH_3COOH + 1/2H_2S \quad (8)$$

$$C_2H_5COOH + 2H_2O \xrightarrow{X_4} CH_3COOH + 3H_2 + CO_2 \quad (9)$$

$$\begin{aligned} &C_2H_5COOH + 0.75H_2SO_4 \xrightarrow{X_5} \\ &CH_3COOH + 0.75H_2S + CO_2 + H_2O \end{aligned} \quad (10)$$

$$CH_3COOH \xrightarrow{X_6} CH_4 + CO_2 \quad (11)$$

$$CH_3COOH + H_2SO_4 \xrightarrow{X_7} H_2S + 2CO_2 + 2H_2O \quad (12)$$

$$4H_2 + CO_2 \xrightarrow{X_8} CH_4 + 2H_2O \quad (13)$$

$$4H_2 + H_2SO_4 \xrightarrow{X_9} H_2S + 4H_2O \quad (14)$$

Thus, according to the stoichiometric scheme (Equations 6–14) considered, the conversion process is carried out by 9 trophic groups of bacteria: the group X_1 contains all fermentative bacteria (FB); X_2, all butyrate-degrading acetogenic bacteria (Bu-AB); X_3, all butyrate-degrading sulphate-reducing bacteria (Bu-SRB); X_4, all propionate-degrading acetogenic bacteria (Pr-AB); X_5, all propionate-degrading sulphate-reducing bacteria (Pr-SRB); X_6, all acetotrophic methanogenic bacteria (Ac-MB); X_7, all acetotrophic sulphate-reducing bacteria (Ac-SRB); X_8, all hydrogenotrophic methanogenic bacteria (H_2-MB); and X_9, all hydrogenotrophic sulphate-reducing bacteria (H_2-SRB).

Kinetics

The principles of the kinetic description were adapted from the CSTR model (Kalyuzhnyi & Fedorovich 1998). Consideration of the dynamics of aggregation and dispersion of biomass from granulating (flocculating) particles is beyond the scope of the current model.

Liquid Phase Equilibrium Chemistry

For calculation of pH values and concentrations of undissociated species along the reactor height, the approach described previously (Kalyuzhnyi 1997) was used. In short, the pH values were calculated from the ionic balance equation, which included all the ionised species in the liquid phase. The solution of the algebraic equation of high degree on H^+ was done by standard computer iteration (Newton's method) with selection of the roots according to the physical sense.

Hydrodynamics

In the present model, the physical and microbiological processes inside the reactor are considered to be dependent only on the vertical axis of the reactor (distance z from input, z varies from 0 to H) and time t, i.e. all the process characteristics in fixed cross-section Cs_z are uniform. In general, the space distribution of any component N of the liquid phase can be written by the following equation with partial derivatives (Kalyuzhnyi & Fedorovich 1997):

$$\begin{aligned}&\tfrac{\delta}{\delta t}N(z,t)=\tfrac{\delta}{\delta z}[D(z,t)\cdot\tfrac{\delta}{\delta z}N(z,t)]-\\&\tfrac{\delta}{\delta z}[W(z,t)\cdot N(z,t)]+r(z,t)-M(z,t)\end{aligned}\tag{15}$$

The first term in the right part of Equation (15) characterises the degree of mixing by gas-induced dispersion. The second term of the Equation (15) determines a convective part of component transfer in vertical direction. 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 for Equation (15) follow from the relationship between the internal mass transfer given by Fick's law and external mass transfer given by Newton's law (Millne 1955):

$$D(0,t)\cdot\frac{\delta}{\delta z}N(0,t)=W(0,t)\cdot[N(0,t)-N_{in}]\tag{16}$$

$$D(H,t)\cdot\frac{\delta}{\delta z}N(H,t)=0\tag{17}$$

Material balances

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

$$dp_i/dt=((\int_o^H M_i(z)\cdot Cs\cdot dz)\cdot V_m\cdot\sum\rho_i-Q\cdot p_i)/V_G\tag{18}$$

where

$$M_i(z)=k_La(z)\cdot(S_{i,z}-p_i/He_i);\tag{19}$$

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

$$Q=\sum_i(\int_o^H M_i(z)\cdot Cs\cdot dz)\cdot V_m\tag{20}$$

Liquid phase. A general material balance for soluble substrates can be written on the basis of the equation (15) as:

$$\begin{aligned}&\tfrac{\delta}{\delta t}S(z,t)=\tfrac{\delta}{\delta z}[D_i(z,t)\cdot\tfrac{\delta}{\delta z}S(z,t)]-\\&\tfrac{\delta}{\delta z}[W_i(z,t)\cdot S_i(z,t)]+r_i(z,t)-M_i(z,t)\end{aligned}\tag{21}$$

The following assumptions were made: m_i for sucrose, butyrate, propionate, acetate and sulphate are equal to zero. W_i for soluble substrates is equal to W_{up}. D_i is also the same for all substrates.

The general mass balance equation used to describe the behaviour of each bacterial group j in the reactor is presented below:

$$\begin{aligned}&\tfrac{\delta}{\delta t}X_j(z,t)=\tfrac{\delta}{\delta z}[D_j(z,t)\cdot\tfrac{\delta}{\delta z}X_j(z,t)]-\\&\tfrac{\delta}{\delta z}[W_j(z,t)\cdot X_j(z,t)]+(\mu_j-b_j)\cdot X_j(z,t)\end{aligned}\tag{22}$$

For simplicity, D_j and W_j were accepted to be the same for all bacterial groups. W_j was postulated to be equal to zero in the bed zone with lineal increase from 0 to W_{up} along the blanket zone height. Another simplification of the model was related to the dependency of k_La and D on the superficial gas flow (Darton 1985;

Table 1. Details of experimental studies used in model calibration

Parameter	Case	
	Alphenaar (1994)	Omil et al. (1996; 1997)
Reactor type	UASB	UASB
Reactor volume, l	1.1	5.5
Recirculation factor	0 (case 1), 10 (case 2)	7-42
Hydraulic retention time, hours	7.5 (case 1),6.9 (case 2)	0.16-0.26
Upward velocity, m/hours	0.05 (case 1), 0.65 (case 2)	1-6
Temperature, ° C	30	30
Duration of experiments, days	160	325
Seed sludge	80% methanogenic + 20% sulphate adapted	sulphate adapted
Mineral medium content, g/l	NH_4Cl - 1.044; KCl - 0.27; KH_2PO_4 - 0.169; $MgCl_2 \cdot 6H_2O$ - 0.15; $NaHCO_3$ - 1.25	
pH control	No (influent pH - 6.8)	Yes (pH 8.0 or 7.0)
Influent sulphate , g/l	5	1.1-4.6
Sludge loading rate, g COD/g VSS.day	0.25-1.06	0.39-1.01
Influent COD, g/l	2.5	0.5-2.5
COD content	Acetate:Propionate:Sucrose - 5:4:1	Acetate:Propionate:Butyrate - 1:1:1, 5:3:2, 1:2:2

Narnoli & Mehrotra 1997). Both constants were accepted in this variant of the model to be constant along the reactor height and throughout the process because the inferior biogas production (less CH_4 production) in sulphate fed reactors. A variant of the model taking into account the above mentioned dependencies is currently under development.

Experimental systems considered for model calibration and validation

The integrated model described above was calibrated and validated to laboratory studies of the functioning of sulphate fed granular sludge reactors:

- Their start-up and development with almost non-sulphate adapted sludge (Alphenaar 1994)
- Maximisation of sulphide yield in these reactors (Omil et al. 1996, 1997).

The salient features of the experimental protocol are given in Table 1 with further details provided in the original works.

Computational methods

Simulations were performed on an IBM-compatible personal computer (processor Pentium-200) by numeric integration of the differential equations 15–22, using a computer program based on a linearised technique (Millne 1955). With each step of numeric integration, pH values were calculated using an iteration technique (Korn & Korn 1968). The computer program was written by the authors in Fortran-90 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 & Havin 1977). A number of preliminary simulations were undertaken to determine the most appropriate set of kinetic model parameters. Table 2 gives the values of the parameters chosen to fit the data of Alphenaar (1994) and Omil et al. (1996, 1997).

Simulation of start-up and development of sulphate fed granular sludge reactors

Some results of the calibration of the model to Alphenaar’s data are presented in the Figure 3. This figure shows that for the case without recycle, predic-

Table 2. Kinetic parameters used in the model

Trophic group*	μ_m (day^{-1})	K_s (g COD/l)	K (g/l)	K_I (g S/l)	Y (g VSS/g COD)	b (day^{-1})
Start-up (Alphenaar 1994)						
X_1	4.0	0.028	-	0.55	0.034	0.09
X_4	0.16	0.247	-	0.190	0.016	0.014
X_5	0.583	0.295	0.0074	0.185	0.027	0.0185
X_6	0.264	0.12	-	0.185	0.0215	0.02
X_7	0.612	0.024	0.0192	0.164	0.033	0.0275
X_8	1.0	0.00012	-	0.165	0.015	0.04
X_9	2.8	0.00007	0.0192	0.55	0.05	0.06
Maximisation of sulphide production (Omil et al. 1996)						
X_3	0.22	0.009	0.01	0.4	0.03	0.035
X_5	0.29	0.015	0.019	0.22	0.03	0.035
X_6	0.2	0.095	-	0.127	0.036	0.036
X_7	0.151	0.025	0.0192	0.6	0.036	0.044

*Trophic groups not mentioned in the Table 2 are not relevant for the processes to be modelled: butyrate was absent in the experiments of Alphenaar (1994); sucrose and hydrogen were absent in the experiments of Omil et al. (1996). In addition, acetogenic activities on propionate and butyrate in the absence of sulphate were negligible throughout the experiments of Omil et al. (1996).

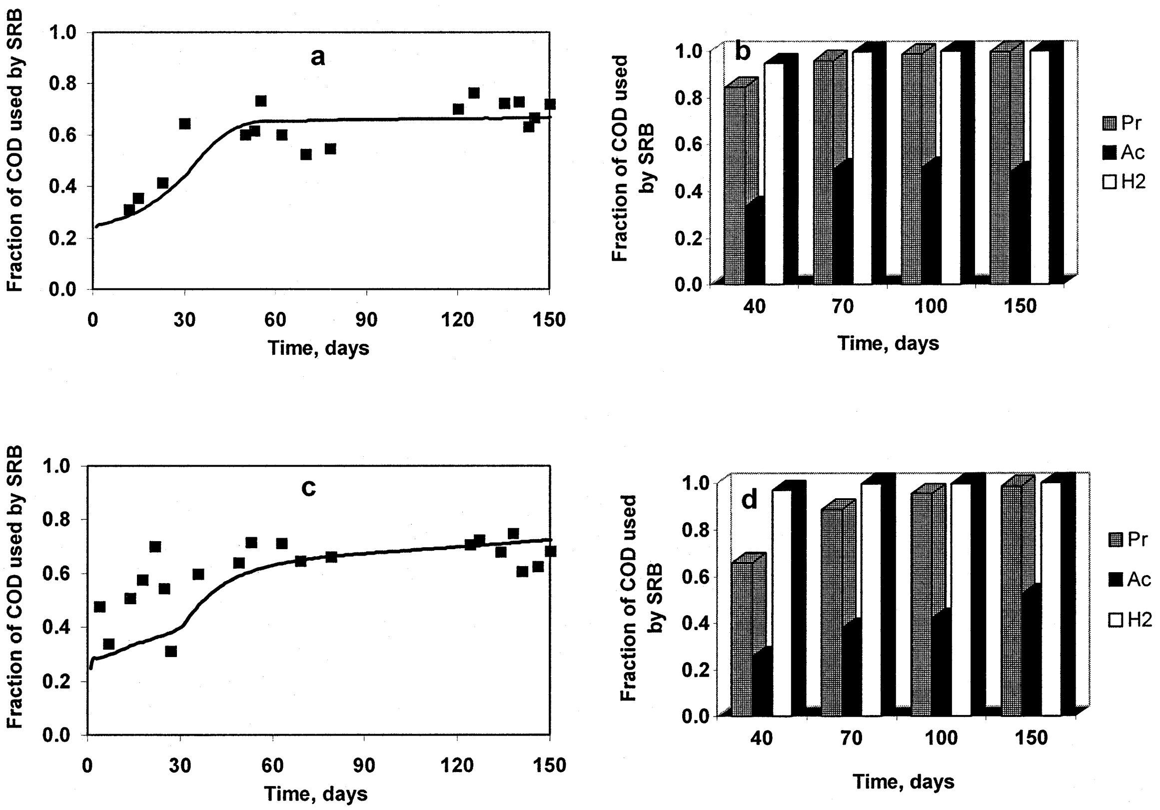

Figure 3. Dispersed plug-flow model versus experiment. Fraction of COD used by SRB in the absence (a) or presence (c) of recycle and modelling results of the fraction of electron donor used by SRB in the absence (b) or presence (d) of recycle: points – experimental data of Alphenaar (1994); lines – model.

Table 3. Summary of modelling scenarios about influence of different factors on the outcome of the competition between SRB and MB on the basis of Alphenaar's experiments

Factor	Fraction of Ac-COD used by SRB
Recirculation factor increase	weak increase
HRT increase	weak increase during the start-up period
	moderate increase in long-term experiments
SO_4^{2-}:COD ratio	sharp decrease when SO_4^{2-}:COD <1.0
	no influence when SO_4^{2-}:COD>1.5
SRB/MB increase in the seed sludge	sharp increase during the start-up period
	weak increase in long-term experiments
SRB sludge quality (sulphide resistance) increase	sharp increase
Influent pH increase	weak increase

tions agree well the reported increase in the fraction of total COD used by SRB during the experiment (Figure 3a). For all that, the three main electron donors (hydrogen, propionate and acetate) for SRB in this system have a different impact relative to this fraction. At the end of the experiment, almost all hydrogen and propionate, but only half of the acetate is converted by SRB (Figure 3b), which corresponds well with the experimental data (Alphenaar 1994). A satisfactory agreement between the model and experiment has also been obtained for the case with recycle (Figure 3c). Similar tendencies for utilisation of electron donors by SRB were also observed for this case (Figure 3d). However, the fraction of total COD used by SRB was slightly higher (Figure 3c) than for the case without recycle (Figure 3a) at the end of the experiment due to the lower concentration of the inhibitory undissociated hydrogen sulphide in the reactor.

Since the competition between SRB and MB proceeded, in general, mainly for acetate, even when non-sulphate adapted sludge was used, special attention in the hypothetical modelling scenarios was focused on the influence of different factors on the outcome of this competition during the start-up and development of sulphate fed granular sludge reactors on the basis of Alphenaar's experiments. A brief summary of these modelling experiments for the case without recycle is presented in Table 3. It should be noted that the tendencies revealed by using a dispersed plug-flow model are, in general, in agreement with the conclusions made from the analysis of the CSTR model (Kalyuzhnyi & Fedorovich 1998). It emphasises the key role of the biological subsystem in the anaerobic processes resulting in the competition between sulphate reduction and methanogenesis.

Simulation of maximisation of sulphide yield using sulphate adapted sludge

The results of the calibration of the dispersed plug-flow model to data on the maximisation of sulphide yield using sulphate adapted sludge are presented in Figure 4. This figure shows that predictions fairly agree with the following reported observations:

a) at a W_{up} of 2 m/h and pH 8 (till day 108, Figure 4a) more than 90% of the COD was used by SRB;
b) with increasing W_{up}-values till 6 m/h (days 169–182), the fraction of COD used by SRB began to decrease (Figure 4a), the acetate effluent concentration increased (Figure 4b), and the VSS in the reactor substantially decreased (Figure 4c);
c) elevation of the influent acetate concentrations by decreasing W_{up}, i.e. lower recirculation (days 183–225), or by use of an influent volatile fatty acid mixture with a higher acetate content (days 226–240), resulted in a further decrease till around 60% of the COD used by SRB (Figure 4a);
d) elevated levels of propionate and butyrate in the influent (days 241–274) favoured the sulphate reducing process (Figure 4a);
e) a decrease of pH from 8 to 7 (days 275-325) resulted in a severe inhibition of methanogenesis while SRB were less affected (Figure 4a) though acetate in the influent increased (Figure 4b).

Thus, the dispersed plug-flow model was able to describe adequately a sufficiently big pool of experimen-

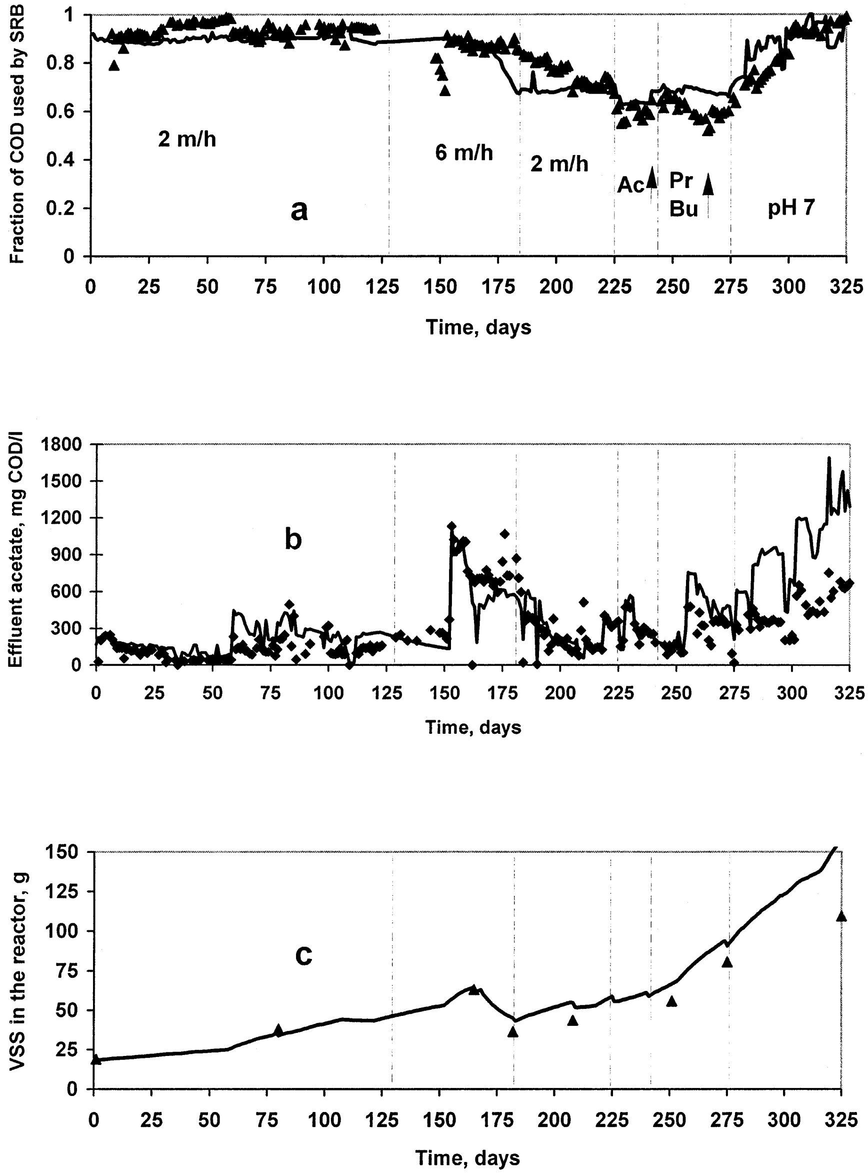

Figure 4. Dispersed plug-flow model versus experiment: points – experimental data of Omil et al. (1996, 1997); lines – model.

tal material dealing with the maximisation of sulphide yield, though some deficiencies in its conceptual structure are revealed. First of all, the model overestimates the effluent acetate concentration during the period of pH decrease from 8 to 7 (days 275–325, Figure 4b). This discrepancy can be attributed to a simplified description of free hydrogen sulphide inhibition in the model (see Equations 4–5). It is likely that this inhibition proceeds in reality by means of a more complex mechanism than the simple first order kinetics postulated in the model on the basis of its wide popularity in anaerobic digestion literature. So, detailed experimental investigations of inhibition kinetics by sulphide are required, especially for SRB and MB. The other weak point of the model follows from the fact that it overestimates the quantity of VSS in the reactor in the late stage of the run. Additional analysis of the model showed a necessity of more comprehensive description of mass transfer of VSS along the reactor height in different regimes of reactor operation to balance the accumulation and wash-out of biomass. This and other (mentioned in paragraph *Material balances*) improvements of the dispersed plug-flow model are currently under investigation.

Conclusions

The existing mathematical models of sulphate fed anaerobic reactors are reviewed. Though they were developed mainly for CSTR reactors having a limited dissemination now, such models are a useful tool to study population dynamics (e.g., mutualism and competition between SRB and MB, existence of trigger and feed-back loop mechanisms) as well as operational performance and stability of sulphate fed anaerobic reactors.

The new integrated mathematical model of the functioning of the sulphate fed granular sludge reactor taking into account concentration gradients on substrates, intermediates, products and bacteria inside the reactor as well as multiple-reaction stoichiometry and kinetics was developed and validated. According to our knowledge, this is the first successfull attempt in the creation of models of a new generation which can be called as dispersed plug-flow models of UASB reactors. The developed integrated model adequately describes the experimental data on the functioning of sulphate fed granular sludge reactors both during their start-up with almost non-sulphate adapted seed sludge (Alphenaar 1994) and on the stage when mature granular sulphidogenic sludge has been already formed (Omil et al. 1996, 1997). The model can be used for maximisation of sulphide yield and optimisation of process control in sulphate fed reactors.

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