User-Friendly Mathematical Model for the Design of Sulfate Reducing H_2/CO_2 Fed Bioreactors

G. Esposito[1]; P. Lens[2]; and F. Pirozzi[3]

Abstract: This paper presents three steady-state mathematical models for the design of H_2/CO_2 fed gas-lift reactors aimed at biological sulfate reduction to remove sulfate from wastewater. Models 1A and 1B are based on heterotrophic sulfate reducing bacteria (HSRB), while Model 2 is based on autotrophic sulfate reducing bacteria (ASRB) as the dominant group of sulfate reducers in the gas-lift reactor. Once the influent wastewater characteristics are known and the desired sulfate removal efficiency is fixed, all models give explicit mathematical relationships to determine the bioreactor volume and the effluent concentrations of substrates and products. The derived explicit relationships make application of the models very easy, fast, and no iterative procedures are required. Model simulations show that the size of the H_2/CO_2 fed gas-lift reactors aimed at biological sulfate removal from wastewater highly depends on the number and type of trophic groups growing in the bioreactor. In particular, if the biological sulfate reduction is performed in a bioreactor where ASRB prevail, the required bioreactor volume is much smaller than that needed with HSRB. This is because ASRB can out-compete methanogenic archaea (MA) for H_2 (assuming sulfate concentrations are not limiting), whereas HSRB do not necessarily out-compete MA due to their dependence on homoacetogenic bacteria (HB) for organic carbon. The reactor sizes to reach the same sulfate removal efficiency by HSRB and ASRB are only comparable when methanogenesis is inhibited. Moreover, model results indicate that acetate supply to the reactor influent does not affect the HSRB biomass required in the reactor, but favors the dominance of MA on HB as a consequence of a lower HB requirement for acetate supply.

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Introduction

Dissimilatory sulfate reduction is the basis of the biological treatment of sulfate-rich waste streams, e.g., inorganic wastewaters such as acid rock drainage or flue gas scrubbing waters (Lens et al. 1998, 2002). Sulfide generated by sulfate reduction can be used to chemically precipitate heavy metals as sulfides or partially oxidized to elemental sulfur in a sulfide oxidation reactor for sulfur recovery (Liamleam and Annachhatre 2007). Since the above-mentioned wastewaters contain little or no organic compounds, biological sulfate reduction can only take place when an external electron donor and carbon source are supplied. The gas-lift reactor design using H_2 and CO_2 as, respectively, electron donor and carbon source are highly attractive for obtaining high sulfate reduction rates (van Houten et al. 1994; Lens et al. 1998; Esposito et al. 2003b).

Biological sulfate reduction in anaerobic H_2/CO_2 fed gas-lift reactors has been investigated extensively using lab-scale bioreactors during the last decade (van Houten et al. 1994; Weijma et al. 2002; Esposito et al. 2003b). In particular, the competition for hydrogen between the different trophic groups present in these reactors has been examined (Fig. 1), as H_2 consumption by non-sulfate reducing bacteria (nonSRB), i.e., methanogenic archaea (MA) and homoacetogenic bacteria (HB), is a loss of electron donor and, thus, an undesired cost factor. Besides, two distinct groups of SRB prevail: autotrophic sulfate reducing bacteria (ASRB) able to provide in their own carbon (C)-source out of CO_2 and heterotrophic sulfate reducing bacteria (HSRB) that rely on an organic C-source. This is mostly acetate produced by HB, but it can also be supplied externally by the plant operator. The biochemical mechanisms which regulate the competition between these trophic groups growing in gas-lift reactors are nevertheless still mostly unknown and both HSRB or ASRB have been shown to become dominant during long-term bioreactor operation (Weijma et al. 2002; Esposito et al. 2003b). Thus, further research is needed to assess the effect of different process conditions on this competition and to define control criteria to favor the dominance of one species over the other.

Mathematical models aimed at simulating the biochemical processes prevailing in the bioreactors should be coupled to experimental studies in order to: (1) address the laboratory experimental procedures; (2) enhance the design and operation of the treatment systems (Henze et al. 2000); and (3) optimize the reactor process control criteria. However, although mathematical modeling of sulfate reducing anaerobic bioreactors has been pro-

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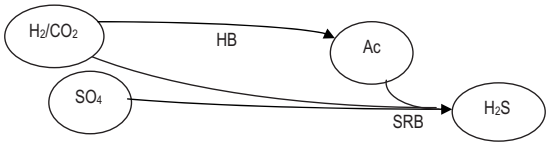

Fig. 1. Schematic representation of bioconversion pathways described by Model 1A

posed to a large extent in the literature (Gupta et al. 1994; Vavilin et al. 1994; Overmeire et al. 1994; Kalyuzhnyi and Fedorovich 1997, 1998; Kalyuzhnyi et al. 1998; Omil et al. 1998; Noguera et al. 1999; Spanjers et al. 2002; Fedorovich et al. 2003), no models are, to the best of our knowledge, available for the design and performance prediction of sulfate reducing H_2/CO_2 fed gas-lift reactors.

In this paper, three mathematical steady-state models for the design of gas-lift reactors aimed at sulfate removal from wastewater are proposed. Models 1A and 1B are based on the hypothesis that HSRB dominate the biochemical system, while Model 2 is developed for reactor systems with ASRB as the dominant microbial group. The main objective of the present study is to provide a user-friendly mathematical tool able to give the optimal size of sulfate reducing gas-lift reactors as a function of the influent wastewater characteristics and the required treatment performance under different operational conditions, e.g., H_2/CO_2 load, external organic carbon addition, or biomass concentration in the reactor. A further aim is to apply this mathematical tool to investigate the effect of the heterotrophic or autotrophic (Brysch et al. 1987; Herrera et al. 1997) trophic status of the SRB on the bioreactor size required to achieve sulfate removal at a desired level.

Mathematical Models

Model 1A

Model 1A is based on mass balance equations for substrates, products, and bacterial groups and includes the chemical reactions of substrate conversion [Eqs. (1) and (2), and Fig. 1] and the kinetics of microbial growth and decay [Eqs. (4)–(6)]. In particular, the model takes two groups of bacteria (HB and HSRB), three substrates (H_2, sulfate, SO_4^{2-} abbreviated as SO_4, and acetate, Ac) and two products (Ac and sulfide, H_2S) into account. Note that acetate is a product of HB [Eq. (1)] and a carbon source for HSRB. MA are not included in model 1A

$$4H_2 + 2CO_2 \rightarrow {}_{HB} \rightarrow CH_3COOH + 2H_2O \quad (1)$$

$$4H_2 + H_2SO_4 \rightarrow {}_{HSRB} \rightarrow H_2S + 4H_2O \quad (2)$$

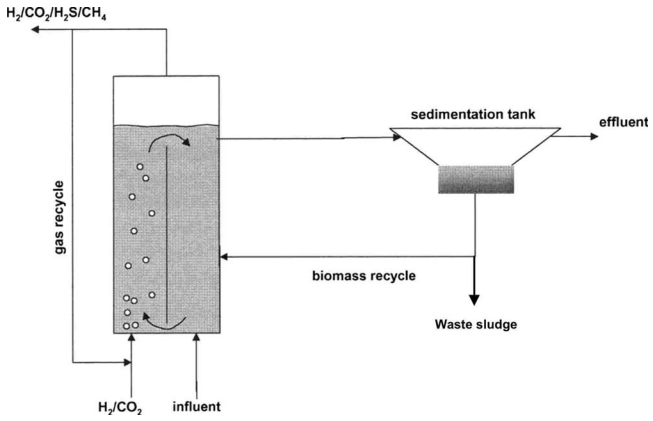

Fig. 2. Flowsheet of the sulfate reducing gas-lift system

The following assumptions have been made to develop this model: (1) the biological reactor is a completely stirred tank reactor (CSTR); (2) it contains only hydrogenotrophic HSRB using hydrogen as electron donor and acetate as carbon source; and (3) the following processes are not considered: pH effect; effect of sulfide toxicity on the bacteria; gas-liquid mass transfer; CO_2 consumption, and chemical oxygen demand (COD) production from biomass decay. The assumption of CSTR hydrodynamic conditions was made since a gas recycle assures ideal mixing in gas-lift reactors (Fig. 2). Furthermore, due to gas recycle, the H_2/CO_2 transfer from gas to liquid does not limit the process (Esposito et al. 2003b). The sulfide toxicity was not taken into account due to a lack of quantitative data in the literature, which are often contradictory. The pH effect was neglected as gas-lift reactors are well buffered at neutral pH. The biological utilization of CO_2 was not included in the model as no CO_2 limitation occurs at the usual CO_2 loading rates applied during the operation of gas-lift reactors (van Houten et al. 1994; Weijma et al. 2002; Esposito et al. 2003b). Acetotrophic HSRB able to use acetate as an electron donor are not included, as hydrogenotrophic SRB are dominant in H_2/CO_2 fed gas-lift reactors (van Houten et al. 1994; Weijma et al. 2002; Esposito et al. 2003b).

The bioconversion rates were described by Monod-type kinetics [Eqs. (3) and (4)]. These relationships include hydrogen threshold concentrations, S_{H_2tHB} and S_{H_2tSRB}, which account for the inability of HB and SRB, respectively, to grow below these threshold concentrations (Spanjers et al. 2002; Ribes et al. 2004). A sulfate threshold (S_{SO_4tSRB}) and CO_2 threshold (S_{CO_2tHB}) concentration are included as well. Eqs. (3*a*) and (4) describe the growth rates of HB and SRB, respectively, while biomass decay is described by a first order equation [Eq. (5)]. CO_2 serves as the electron acceptor for the HB and is, thus, an important component of the model. However, as CO_2 is assumed to be present in excess, Eq. (3*a*) results in the simplified Eq. (3*b*). The acetate saturation term in Eq. (4) accounts for limitation of HSRB growth due to limited availability of acetate as a carbon source

$$\mu_{HB} = \begin{cases} 0 & \text{if } S_{H_2} < S_{H_2tHB} \text{ or } S_{CO_2} < S_{CO_2tHB} \\ \hat{\mu}_{HB} \cdot \dfrac{S_{H_2} - S_{H_2tHB}}{K_{HB,H_2} + S_{H_2} - S_{H_2tHB}} \cdot \dfrac{S_{CO_2} - S_{CO_2tHB}}{K_{HB,CO_2} + S_{CO_2} - S_{CO_2tHB}} & \text{if } S_{H_2} \geq S_{H_2tHB} \text{ and } S_{CO_2} \geq S_{CO_2tHB} \end{cases} \quad (3a)$$

$$\mu_{HB} = \begin{cases} 0 & \text{if } S_{H_2} < S_{H_2tHB} \\ \hat{\mu}_{HB} \cdot \dfrac{S_{H_2} - S_{H_2tHB}}{K_{HB,H_2} + S_{H_2} - S_{H_2tHB}} & \text{if } S_{H_2} \geq S_{H_2tHB} \end{cases} \tag{3b}$$

$$\mu_{SRB} = \begin{cases} 0 & \text{if } S_{H_2} < S_{H_2tSRB} \text{ or } S_{SO_4} < S_{SO_4tSRB} \\ \hat{\mu}_{SRB} \cdot \dfrac{S_{H_2} - S_{H_2 2tSRB}}{K_{SRB,H_2} + S_{H_2} - S_{H_2tSRB}} \cdot \dfrac{S_{SO_4} - S_{SO_4tSRB}}{K_{SRB,SO_4} + S_{SO_4} - S_{SO_4tSRB}} \cdot \dfrac{S_{Ac}}{K_{SRB,Ac} + S_{Ac}} & \text{if } S_{H_2} \geq S_{H_2tSRB} \text{ and } S_{SO_4} \geq S_{SO_4tSRB} \end{cases} \tag{4}$$

$$D_j = -b_j X_j \tag{5}$$

The following mass balance equations [Eqs. (6)–(11)] are considered for substrates, products, and bacterial groups:

$$\frac{Q}{V} \cdot (S_{H_20} - S_{H_2}) - \frac{1}{Y_{HB,H_2}} \cdot \mu_{HB} \cdot X_{HB} - \frac{1}{Y_{SRB,H_2}} \cdot \mu_{SRB} \cdot X_{SRB} = 0 \tag{6}$$

$$\frac{Q}{V} \cdot (S_{SO_40} - S_{SO_4}) - 1{,}5 \cdot \frac{1 - Y_{SRB,H_2}}{Y_{SRB,H_2}} \cdot \mu_{SRB} \cdot X_{SRB} = 0 \tag{7}$$

$$\frac{Q}{V} \cdot (S_{Ac0} - S_{Ac}) + \frac{1 - Y_{HB,H_2}}{Y_{HB,H_2}} \cdot \mu_{HB} \cdot X_{HB} - \frac{1}{i_{SRB,Ac}} \cdot \mu_{SRB} \cdot X_{SRB} = 0 \tag{8}$$

$$-\frac{Q}{V} S_{H_2S} + \frac{1 - Y_{SRB,H_2}}{Y_{SRB,H_2}} \cdot \mu_{SRB} \cdot X_{SRB} = 0 \tag{9}$$

$$(\mu_{HB} - b_{HB}) + \frac{Q}{V} \cdot [R \cdot (\alpha - 1) - 1] = 0 \tag{10}$$

$$(\mu_{SRB} - b_{SRB}) + \frac{Q}{V} \cdot [R \cdot (\alpha - 1) - 1] = 0 \tag{11}$$

All substrates in the above equations are expressed as COD, except S_{SO4} Thus, the coefficient 1.5 in equation (7) represents 1.5 g SO_4^{2-}/gCOD.

A further equation [Eq. (12)] is obtained by assigning the total biomass concentration X_{TOT} in the biological reactor. X_{TOT} is maintained at a target concentration by controlling the sludge recycle flow rate and the waste sludge flow rate (Fig. 2). The ratio $\alpha = (X_{TOT})_r / (X_{TOT})$ can be assigned on the basis of the expected thickening efficiency of the settling tank. The latter influences the biological process in the gas-lift reactor as the biomass recycle from the settler to the reactor is used as the biomass retention method (Fig. 2). For Model 1A it is assumed that the total biomass concentration (X_{TOT}) is the sum of the SRB (X_{SRB}) and HB (X_{HB}) biomass concentrations

$$X_{TOT} = X_{SRB} + X_{HB} \tag{12}$$

When the desired effluent sulfate concentration is fixed, Eqs. (6)–(12) are an algebraic seven-equation system with seven unknowns: S_{H2}, S_{Ac}, V, X_{HB}, X_{SRB}, R, and S_{H2S}. The resolution of this system gives six explicit relationships [Eqs. (13)–(18)], which express all model unknowns as a function of S_{H2}. The latter can be calculated by solving Eq. (6). In fact, when all unknowns in Eq. (6) are expressed using the relationships [Eqs. (13)–(18)], Eq. (6) results in a nonlinear equation with only S_{H2} unknown

$$S_{Ac} = K_{SRB,Ac} \cdot \frac{\hat{\mu}_{HB} \cdot \dfrac{S_{H_2} - S_{H_2tHB}}{K_{HB,H_2} + S_{H_2} - S_{H_2tHB}} - b_{HB} + b_{SRB}}{\left(\hat{\mu}_{SRB} \cdot \dfrac{S_{H_2} - S_{H_2tSRB}}{K_{SRB,H_2} + S_{H_2} - S_{H_2tSRB}} \cdot \dfrac{S_{SO_4} - S_{SO_4tSRB}}{K_{SRB,SO_4} + S_{SO_4} - S_{SO_4tSRB}} \right) - \hat{\mu}_{HB} \cdot \dfrac{S_{H_2} - S_{H_2tHB}}{K_{HB,H_2} + S_{H_2} - S_{H_2tHB}} + b_{HB} - b_{SRB}} \tag{13}$$

$$X_{SRB} = -\frac{\dfrac{1 - Y_{HB,H_2}}{Y_{HB,H_2}} \cdot \mu_{HB}}{1.5 \cdot \dfrac{1 - Y_{SRB,H_2}}{Y_{SRB,H_2}} \cdot \dfrac{S_{Ac0} - S_{Ac}}{S_{SO_40} - S_{SO_4}} \cdot \mu_{SRB} - \dfrac{1 - Y_{HB,H_2}}{Y_{HB,H_2}} \cdot \mu_{HB} - \dfrac{1}{i_{SRB,Ac}} \cdot \mu_{SRB}} \cdot X_{TOT} \tag{14}$$

$$V = \frac{Q \cdot (S_{SO_4 0} - S_{SO_4})}{1.5 \cdot \frac{1 - Y_{SRB,H_2}}{Y_{SRB,H_2}} \cdot \mu_{SRB} \cdot X_{SRB}} \quad (15)$$

$$X_{HB} = X_{TOT} - X_{SRB} \quad (16)$$

$$R = \frac{1}{\alpha - 1} \cdot \left[1 - \frac{V}{Q} \cdot (\mu_{HB} - b_{HB}) \right] \quad (17)$$

$$S_{H_2S} = \frac{V}{Q} \cdot \frac{1 - Y_{SRB,H_2}}{Y_{SRB,H_2}} \cdot \mu_{SRB} \cdot X_{SRB} \quad (18)$$

Model 1B

Model 1B considers the same assumptions as Model 1A, but is based on the hypothesis that, besides HSRB and HB, MA may also grow on H_2/CO_2 with methane (CH_4) as the end product, whereas acetoclastic methanogens do not grow in the reactor (van Houten et al. 1994; Weijma et al. 2002; Esposito et al. 2003b).

Therefore, the model takes three groups of bacteria (HSRB, HB, and MA) into account, which utilize three substrates and intermediates (H_2, SO_4 and Ac) and produce two products (CH_4 and H_2S), according to the bioconversion reactions described by Eqs. (1), (2), and (19)

$$4H_2 + 2CO_2 \rightarrow_{MA} CH_4 + 2H_2O \quad (19)$$

The same kinetic expressions of SRB and HB as in Model 1A [Eqs. (3)–(5) are used, whereas Eq. (20) describes the growth rate of MA

$$\mu_{MA} = \begin{cases} 0 & \text{if } S_{H_2} < S_{H_2tMA} \\ \hat{\mu}_{MA} \cdot \dfrac{S_{H_2} - S_{H_2tMA}}{K_{MA,H_2} + S_{H_2} - S_{H_2tMA}} & \text{if } S_{H_2} \geq S_{H_2tMA} \end{cases} \quad (20)$$

In the mass balance equations for model 1B, Eqs. (6) and (12) are replaced by Eqs. (21) and (22), respectively, and the mass balances for CH_4 and MA are included [Eqs. (23) and (24), respectively). Eqs. (7)–(11) are identical as in model 1A

$$\frac{Q}{V} \cdot (S_{H_2 0} - S_{H_2}) - \frac{1}{Y_{HB,H_2}} \cdot \mu_{HB} \cdot X_{HB} - \frac{1}{Y_{SRB,H_2}} \cdot \mu_{SRB} \cdot X_{SRB} - \frac{1}{Y_{MA,H_2}} \cdot \mu_{MA} \cdot X_{MA} = 0 \quad (21)$$

$$X_{TOT} = X_{HB} + X_{SRB} + X_{MA} \quad (22)$$

$$-\frac{Q}{V} \cdot S_{CH_4} + \frac{1 - Y_{MA,H_2}}{Y_{MA,H_2}} \cdot \mu_{MA} \cdot X_{MA} = 0 \quad (23)$$

$$(\mu_{MA} - b_{MA}) + \frac{Q}{V} \cdot [R \cdot (\alpha - 1) - 1] = 0 \quad (24)$$

When the desired effluent sulfate concentration is fixed, Eqs. (7)–(11) and (21)–(24) are an algebraic nine-equation system with nine unknowns: S_{H2}, S_{Ac}, V, X_{HB}, X_{SRB}, X_{MA}, R, S_{H2S} and S_{CH4}. The resolution of this system results in the following nine relationships that express in explicit terms all model unknowns:

$$S_{H_2} = \frac{-b - \sqrt{b^2 - 4ac}}{2a} \quad (25)$$

where

$$a = \hat{\mu}_{HB} - b_{HB} - \hat{\mu}_{MA} + b_{MA} \quad (26)$$

$$b = \hat{\mu}_{HB} \cdot (K_{MA,H_2} - S_{H_2tMA} - S_{H_2tHB}) - \hat{\mu}_{MA} \cdot (K_{HB,H_2} - S_{H_2tMA} - S_{H_2tHB}) + (b_{MA} - b_{HB}) \cdot (K_{MA,H_2} + K_{HB,H_2} - S_{H_2tMA} - S_{H_2tHB}) \quad (27)$$

$$c = \hat{\mu}_{HB} \cdot S_{H_2tHB} \cdot (S_{H_2tMA} - K_{MA,H_2}) - \hat{\mu}_{MA} \cdot S_{H_2tMA} \cdot (S_{H_2tHB} - K_{HB,H_2}) + (b_{MA} - b_{HB}) \cdot (K_{MA,H_2} \cdot K_{HB,H_2} - K_{HB,H_2} \cdot S_{H_2tMA} - K_{MA,H_2} \cdot S_{H_2tHB} + S_{H_2tMA} \cdot S_{H_2tHB}) \quad (28)$$

$$S_{Ac} = K_{SRB,Ac} \cdot \frac{\mu_{MA}}{\left(\hat{\mu}_{SRB} \cdot \frac{S_{H_2} - S_{H_2tSRB}}{K_{SRB,H_2} + S_{H_2} - S_{H_2tSRB}} \cdot \frac{S_{SO_4} - S_{SO_4tSRB}}{K_{SRB,SO_4} + S_{SO_4} - S_{SO_4tSRB}} \right) - \mu_{MA}} \quad (29)$$

$$X_{SRB} = \frac{\frac{\mu_{MA} \cdot X_{TOT}}{Y_{MA,H_2}}}{\left\{ \left(\frac{1.5 \cdot \frac{1 - Y_{SRB,H_2}}{Y_{SRB,H_2}} \cdot \mu_{SRB}}{(S_{SO_4} - S_{SO_4})} \right) \cdot \left[(S_{H_2 0} - S_{H_2}) + \frac{(S_{Ac0} - S_{Ac})}{1 - Y_{HB,H_2}} \cdot \left(1 - \frac{\mu_{MA}}{\mu_{HB}} \cdot \frac{Y_{HB,H_2}}{Y_{MA,H_2}} \right) \right] - \frac{\mu_{SRB}}{i_{SRB,Ac} \cdot (1 - Y_{HB,H_2})} + \left[-\frac{\mu_{SRB}}{Y_{SRB,H_2}} + \frac{\mu_{MA}}{Y_{MA,H_2}} + \frac{\mu_{MA} \cdot \mu_{SRB} \cdot Y_{HB,H_2}}{\mu_{HB} \cdot Y_{MA,H_2} \cdot i_{SRB,Ac} \cdot (1 - Y_{HB,H_2})} \right] \right\}} \quad (30)$$

$$V = \frac{Q \cdot (S_{SO_4 0} - S_{SO_4})}{1.5 \cdot \frac{1 - Y_{SRB,H_2}}{Y_{SRB,H_2}} \cdot \mu_{SRB} \cdot X_{SRB}} \quad (31)$$

$$X_{HB} = \frac{\frac{1}{i_{SRB,Ac}} \cdot \mu_{SRB} \cdot X_{SRB} - \frac{Q}{V} \cdot (S_{Ac0} - S_{Ac})}{\frac{1 - Y_{HB,H_2}}{Y_{HB,H_2}} \cdot \mu_{HB}} \quad (32)$$

$$X_{MA} = X_{TOT} - X_{SRB} - X_{HB} \quad (33)$$

$$R = \frac{1}{\alpha - 1} \cdot \left[1 - \frac{V}{Q} (\mu_{MA} - b_{MA}) \right] \quad (34)$$

$$S_{H_2S} = \frac{V}{Q} \cdot \frac{1 - Y_{SRB,H_2}}{Y_{SRB,H_2}} \cdot \mu_{SRB} \cdot X_{SRB} \quad (35)$$

$$S_{CH_4} = \frac{V}{Q} \cdot \frac{1 - Y_{MA,H_2}}{Y_{MA,H_2}} \cdot \mu_{MA} \cdot X_{MA} \quad (36)$$

Model 2

This model is based on the hypothesis that ASRB are the dominant microbial group in the reactor and considers the same assumptions as previous models. ASRB grow on H_2/CO_2 and do not require an organic carbon source. Therefore, Model 2 takes into account one group of bacteria (ASRB), two substrates (H_2 and SO_4^{2-}), and one product (H_2S). Eq. (37) is used to describe the growth rate of ASRB while biomass decay is described by Eq. (5)

$$\mu_{SRB} = \hat{\mu}_{SRB} \cdot \frac{S_{H_2} - S_{H_2 tSRB}}{K_{SRB,H_2} + S_{H_2} - S_{H_2 tSRB}} \cdot \frac{S_{SO_4} - S_{SO_4 tSRB}}{K_{SRB,SO_4} + S_{SO_4} - S_{SO_4 tSRB}} \quad (37)$$

The mass balance equations for SO_4^{2-}, H_2S, and SRB are the same as in the previous models [Eqs. (7), (9), and (11), while Eq. (38) describes the mass balance for H_2

$$\frac{Q}{V} \cdot (S_{H_2 0} - S_{H_2}) - \frac{1}{Y_{SRB,H_2}} \cdot \mu_{SRB} \cdot X_{SRB} = 0 \quad (38)$$

When the desired effluent sulfate concentration is fixed, Eqs. (7), (9), (11), and (38) are an algebraic four-equation system with four unknowns: S_{H2}, V, R, and S_{H2S}. In this case, X_{SRB} is not an unknown as it corresponds to the total biomass concentration in the reactor, which can be maintained at a target concentration as described above. The resolution of the algebraic system results in the following four mathematical relationships, giving all model unknowns in explicit terms:

$$S_{H_2} = S_{H_2 0} - \frac{S_{SO_4 0} - S_{SO_4}}{1.5 \cdot (1 - Y_{SRB,H_2})} \quad (39)$$

$$V = \frac{Q \cdot (S_{SO_4 0} - S_{SO_4})}{1.5 \cdot \frac{1 - Y_{SRB,H_2}}{Y_{SRB,H_2}} \cdot \mu_{SRB} \cdot X_{SRB}} \quad (40)$$

$$R = \frac{1}{\alpha - 1} \cdot \left[1 - \frac{V}{Q} \cdot (\mu_{SRB} - b_{SRB}) \right] \quad (41)$$

$$S_{H_2S} = \frac{V}{Q} \cdot \frac{1 - Y_{SRB,H_2}}{Y_{SRB,H_2}} \cdot \mu_{SRB} \cdot X_{SRB} \quad (42)$$

Results

Models 1 and 2 were used to do a sensitivity analysis of the bioreactor volume required to achieve an assigned sulfate reduction efficiency as a function of the influent flow rate [Fig. 3(a)], the hydrogen loading rate [Fig. 3(b)], and the acetate supply to the reactor [Fig. 3(d)]. All simulations were carried out using typical kinetic and stoichiometric parameters reported in the literature (Table 1). In particular, a set of simulations [Fig. 3(a)] were performed with the following hypothetical data: S_{SO40}=0.681 g/l, S_{H20}=2 gCOD/l (thus, the molar ratio between the hydrogen and sulfate load was 17.6), S_{Ac0}=0 gCOD/l, S_{SO4}=0.002 g/l, X_{TOT}=2.6 gCOD/l, α=3.1, and Q ranges between 200 and 700 m^3/d. A second set of simulations [Fig. 3(b)] was carried out with Q=300 m^3/d, S_{H20} ranges between 2 and 10 gCOD/l, and the same values of the other parameters as used in the previous set.

Effect of Influent Flow Rate and H_2 Loading Rate

When Model 1B was applied, the bioreactor volume increased from 54 to 189 m^3 [Figs. 3(a)] or from 81 to 362 m^3 [Fig. 3(b)], respectively, when increasing the influent flow rate from 200 to 700 m^3/d or the influent hydrogen concentration from 2 to 10 gCOD/l. Much lower bioreactor volumes, ranging between 5 and 22 m^3, were obtained when applying Model 1A and Model 2 [Figs. 3(a and b)]. The increase of the influent hydrogen concentration from 2 to 10 gCOD/l affected the bacterial competition when the three groups of microorganisms were considered to grow in the biological system (Model 1B). In particular, the concentration of the HB and SRB in the gas-lift reactor decreased from 0.18 to 0.04 and from 1.15 to 0.26 gCOD/l, respectively, while the MA concentration increased from 1.27 to 2.30 gCOD/l [Fig. 4(a)]. The MA dominance in the reactor resulted in a higher methane production, while no effect was observed on the acetate and sulfide production [Fig. 4(b)].

Effect of Acetate Supply to the Bioreactor Influent

A further set of simulations [Fig. 3(d) and 5] were performed to assess the effect of acetate addition into the bioreactor. The influent flow rate Q was set to 500 m^3/d and the influent acetate concentration S_{Ac0} ranged between 0 and 0.3 gCOD/l, while all other input data to the models were the same as used for the first set of simulations. Model 1B simulations showed a slight increase of the gas-lift reactor volume from 81 to 87 m^3 with a 0.3 gCOD/l acetate supply [Fig. 3(d)]. The same acetate addition gave a slight decrease of the gas-lift reactor volume from 9.3 to 8.4 m^3 when applying Model 1A, while it did not affect the Model 2 results [Fig. 3(d)]. Both Models 1A and 1B predicted that acetate addition affected the bacterial competition in the reactor: increasing the acetate influent concentration from 0 to 0.3 gCOD/l resulted in a linear decrease of HB from 0.31 to 0.07 and from 0.18 to 0.03 gCOD/l when using Model 1A [Fig. 5(a)]

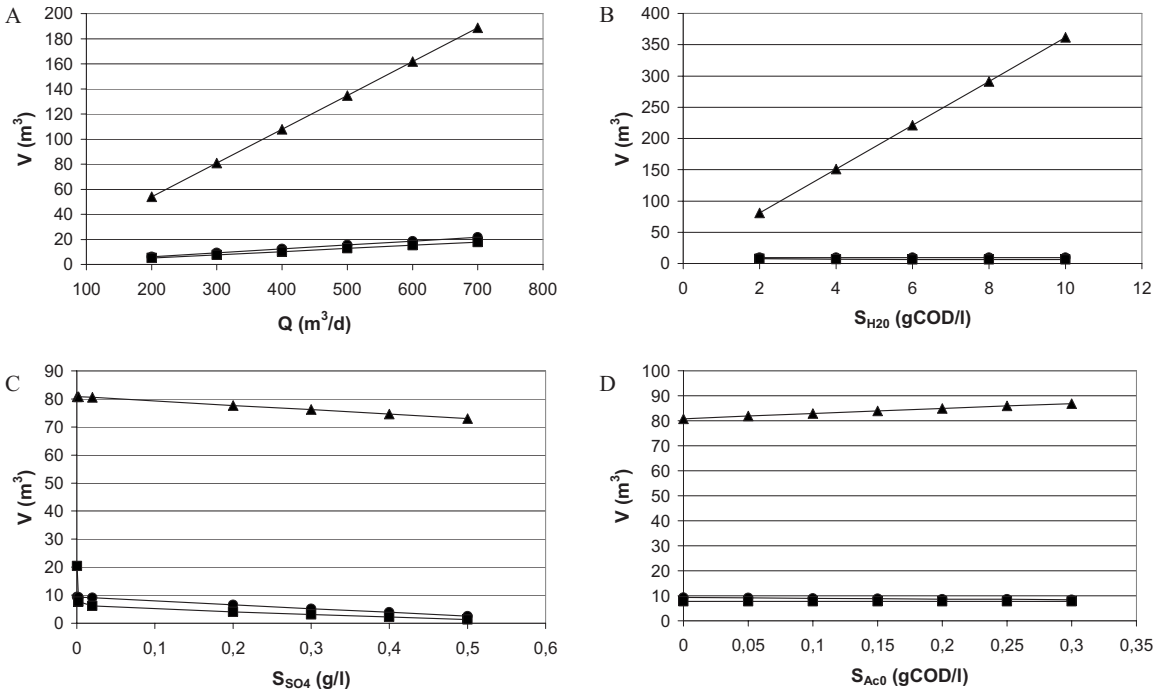

Fig. 3. Effect of the influent flow rate (A); the hydrogen load (B); the desired effluent sulfate (C); and the acetate addition (D) on the bioreactor volume when applying Model 1A (●), 1B (▲), or 2 (■)

and 1B [Fig. 5(b)], respectively. Model 1A simulations indicated a SRB dominance in the reactor [Fig. 5(a)], while methanogenesis was favored over sulfate reduction when Model 1B was applied [Figs. 5(b and c)].

Effect of the Required Sulfate Reduction Efficiency

The effect of the desired sulfate reduction efficiency on the required volume of the biological reactor was investigated running various simulations with different effluent sulfate concentrations (S_{SO_4}). Fig. 3(c) indicates that increasing S_{SO_4} from 0.0002 to 0.5 g/l resulted in a decrease of the bioreactor volume from 9.4 to 2.5, from 81 to 73, and from 20.4 to 1.3 m^3 when running Models 1A, 1B, and 2, respectively. In particular, Model 1A gave constant HB and SRB concentrations in the reactor of 0.31 and 2.29 gCOD/l, respectively, indicating no influence of S_{SO_4} on the bacterial competition. However, S_{SO_4} affected the biomass concentrations in the reactor when Model 1B was applied. In particular, the S_{SO_4} increase from 0.0002 to 0.5 g/l resulted in a predicted decrease of the HB and SRB concentrations in the gas-lift reactor from 0.19 to 0.05 and from 1.15 to 0.34 gCOD/l, respectively, while the MA concentration increased from 1.26 to 2.21 gCOD/l [Fig. 6(a)]. The MA dominance in the reactor resulted in a higher methane and lower sulfide production, while no effect on the acetate formation was observed [Fig. 6(b)].

The ratio R between the sludge recycle flow rate and the influent flow rate was around 0.5 in all simulations performed.

Discussion

The proposed model is a design model, which gives the reactor volume required to achieve the assigned substrate removal effi-

Table 1. Model Kinetic and Stoichiometric Parameters

Bacteria j	$\hat{\mu}$ d^{-1}	b^j d^{-1}	$K_{j,H2}$ $g^{COD/l}$	K_{j,SO_4} g/l	$K_{j,Ac}$ $gCOD/l$	$Y_{j,H2}$ $gCOD/gCOD$	$Y_{j,Ac}$ $gCOD/gCOD$	S_{H2tj} $gCOD/l$	S_{SO4tj} g/l	Reference
HB	0.6		$2.3\cdot10^{-4}$	—	—		—		—	Lokshina and Vavilin (1999)
		0.01		—	—	0.015	—		—	Vavilin et al. (2000)
				—	—		—	$1.0\cdot10^{-6}$	—	Kotsyurbenko et al. (2001)
HSRB	4.9			$4.5\cdot10^{-4}$	$1.5\cdot10^{-2}$					Oude Elferink et al. (1994)
		0.04	$6.0\cdot10^{-5}$			0.09	0.12			Kalyuzhnyi and Fedorovich (1998)
								$2.7\cdot10^{-7}$		Spanjers et al. (2002)
									0	—
ASRB	1.1				—		—			Brysch et al. (1987)
		0.04	$6.0\cdot10^{-5}$	$4.5\cdot10^{-4}$	—	0.09	—	$2.7\cdot10^{-7}$	0	[a]
MA	0.8			—	—	0.044	—		—	Oude Elferink et al. (1994)
		0.04		—	—		—		—	Kalyuzhnyi and Fedorovich (1998)
			$2.5\cdot10^{-4}$	—	—		—	$1.5\cdot10^{-7}$	—	Kotsyurbenko et al. (2001)

[a]Same values as used for HSRB as no different values were found in the literature.

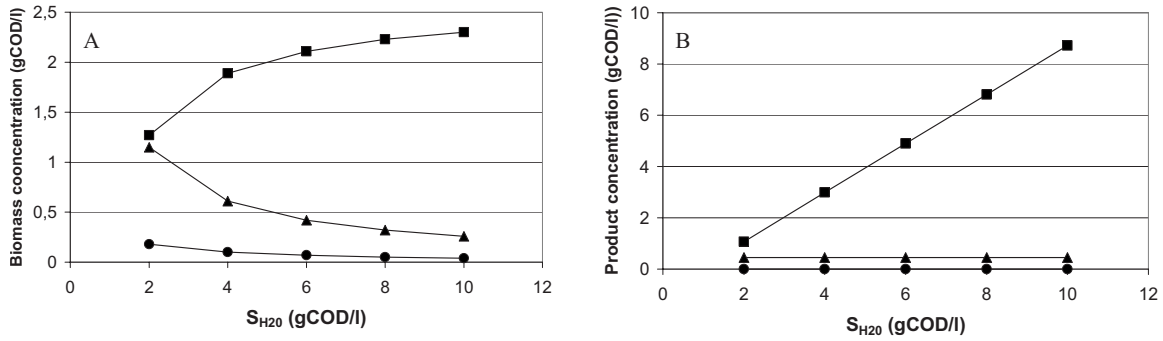

Fig. 4. Effect of the hydrogen load on the competition between HB (●), SRB (▲), and MA (■) in the gas-lift reactor (A); product (● Ac, ▲ H_2S, ■ CH_4) formation (B) when applying Model 1B

ciency as model output. Therefore, it is different than typical literature models that are aimed at simulating the reactor performances. These models are usually complex dynamic models, which give the effluent substrate concentrations as model output and, thus, can be compared and validated with experimental results. However, they require accurate calibration for the specific reactor studied, a task that is often difficult to achieve (Argaman 1995). The present model is most applicable in the preliminary phases of a system design for sizing purposes and comparison of process alternatives, making the absolute accuracy of all process parameters less critical (Argaman 1995; Esposito et al. 2003a). It should be noted that the estimation of the kinetic parameters of the model was beyond the scope of this study and, thus, literature values of the kinetic parameters have been used for the simulations (Table 1), although extremely large ranges of values are reported in the literature for these parameters.

This paper shows that the size of H_2/CO_2 fed gas-lift reactors aimed at sulfate removal from wastewater highly depends on the number and type of trophic groups present in the sludge (Fig. 3). This is due to the need of keeping a coexistence of different groups of bacteria in the reactor in the case of Model 1A or Model 1B. According to the Model 1A hypothesis, when no organic carbon source is supplied to the reactor, HSRB grow only if acetate is produced, i.e., only when HB are present. Under these conditions, according to the model 1B hypothesis, MA also grow in the reactor. However, the microbial equilibrium is only possible when the following conditions are met, for Models 1A and 1B, respectively:

$$(\mu_{HB} - b_{HB}) = (\mu_{SRB} - b_{SRB}) \tag{43}$$

$$(\mu_{HB} - b_{HB}) = (\mu_{SRB} - b_{SRB}) = (\mu_{MA} - b_{MA}) \tag{44}$$

Eqs. (43) and (44), which derive from mass balance Eqs. (10), (11), and (24), express a necessary condition for the microbial equilibrium, i.e., the differences between the specific growth and decay rates of different bacterial groups in the reactor have to be equal, otherwise, the slower growing bacteria would be washed out. However, in the case of Model 1B, according to the growth kinetics of HB and MA [Eqs. (3*b*) and (20)], the microbial equilibrium [Eq. (44)] is only achieved at a very low hydrogen concentration in the reactor. Therefore, the bioreactor volume needs to be big enough to assure the required hydrogen consumption. This is not necessary if the growth of MA is inhibited (Model 1A hypothesis) or ASRB prevail in the reactor (Model 2 hypothesis).

The availability of three different steady-state design models, as proposed in this study, should cover all practical cases of

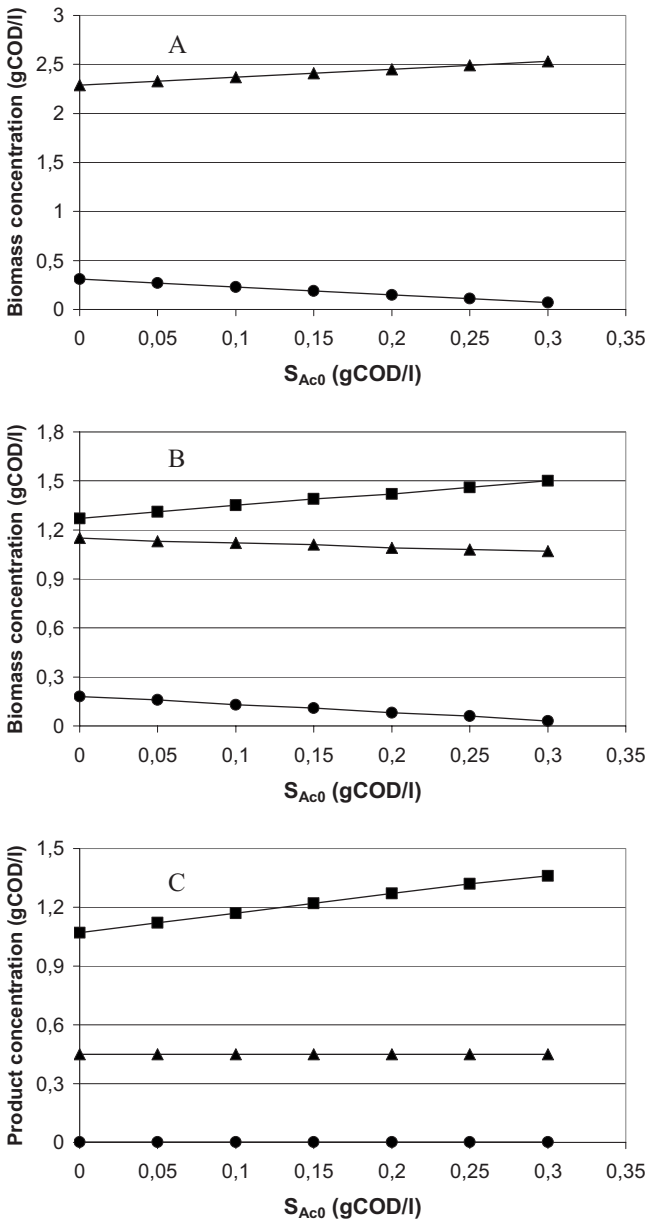

Fig. 5. Effect of acetate addition on the competition between HB (●), SRB (▲), and MA (■) in the gas-lift reactor when applying Model 1A (A); 1B (B); and product (● Ac, ▲ H_2S, ■ CH_4) formation when applying Model 1B (C)

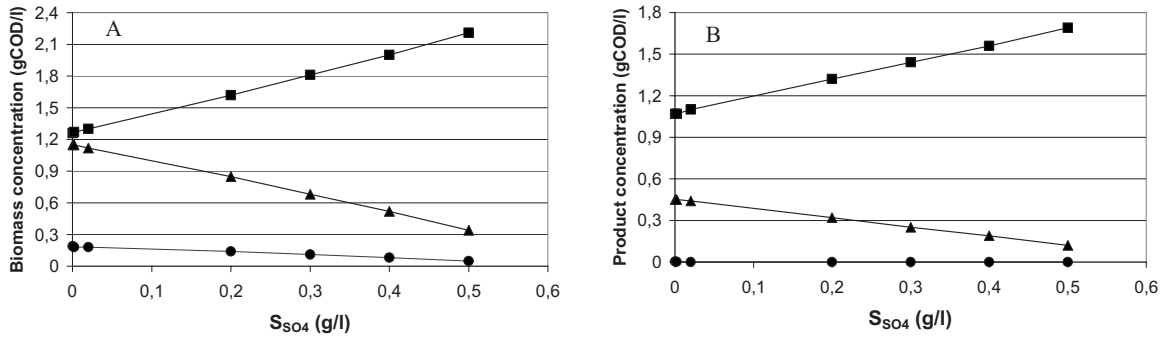

Fig. 6. Effect of the desired effluent sulfate concentration on the competition between HB (●), SRB (▲), and MA (■) in the gas-lift reactor (A) and product (● Ac, ▲ H_2S, ■ CH_4) formation (B), when applying Model 1B

H_2/CO_2 fed gas-lift reactors aimed at sulfate removal from wastewater. If SRB are heterotrophic, Model 1B is preferred to Model 1A for the reactor design. Model 1A can be used only if methanogenesis is absent, but a complete MA inhibition cannot be achieved in practice (Esposito et al. 2003b). Therefore, if the biological sulfate reduction is performed by ASRB (Model 2), the required bioreactor volume is much smaller than that needed if HSRB prevail (Model 1B). This emphasizes the need of laboratory experiments aimed at investigating the nature of the dominant SRB growing in H_2/CO_2 fed gas-lift reactors and identifying the proper operational conditions to favor the growth of ASRB.

Fig. 3(b) shows that an increase of the influent hydrogen concentration does not affect the reactor volume when Model 1A or Model 2 are applied. On the contrary, when Model 1B was applied, the increased S_{H20} resulted in a sharp increase of the required reactor volume to achieve the assigned sulfate removal efficiency [Fig. 3(b)]. This outcome is due to the above cited need of a very low hydrogen concentration in the reactor when applying Model 1B. In fact, a higher hydrogen loading rate to the reactor means a higher amount of hydrogen to be consumed and, thus, the need for a higher reactor volume. This also explains the results of the first set of simulations [Fig. 3(a)], which show that larger bioreactor volumes are required to face higher influent flow rates. The increase of the influent hydrogen concentration from 2 to 10 gCOD/l affected the bacterial competition as well, favoring the methanogenesis [Fig. 4(a)]. Indeed, the required HB and SRB biomass to achieve the desired sulfate reduction efficiency did not change and the decrease of their concentrations [Fig. 4(a)] was just related to the increase of the bioreactor volume. On the contrary, increasing the influent flow rate, i.e., both the hydrogen and sulfate loading rates, when keeping their ratio constant implied an increase of the reactor volume while the HB, SRB, and MA concentrations remained constant.

When SRB are heterotrophic (Models 1A and 1B), acetate addition in the reactor entails a lower requirement of HB acetate production, thus, a lower HB concentration in the reactor [Figs. 5(a and b)]. This is, in contrast, not effective when ASRB grow in the reactor (Model 2). Acetate addition seemed to result in a decrease of HSRB [Fig. 5(b)]. However, the decrease of the HSRB concentration [Fig. 5(b)] is compensated by the increase of the reactor volume [Fig. 3(d)], i.e., the HSRB biomass does not change at all. This is due to the fact that the HSRB biomass required to reach a fixed sulfate removal efficiency does not depend on the acetate source. It is the same if acetate is produced by HB or if it is externally supplied. This also explains the increase of the MA concentration, as the total biomass concentration in the reactor is not a variable but a priori fixed in the present design approach. Therefore, the increase of the MA concentration is a consequence of the decrease of both the HSRB and HB concentrations.

The presented simulations were carried out with acetate additions ranging between 0 and 0.3 gCOD/l. It should be observed that Models 1A and 1B could not be applied for acetate influent concentrations higher than this range as the HB presence would be redundant, which contrasts with the basic hypothesis of Models 1A and 1B (i.e., the need of acetate production by HB for HSRB). However, acetate addition is not common in full-scale gas-lift reactors.

Conclusions

- Three steady-state design models are proposed that cover all practical cases of H_2/CO_2 fed gas-lift reactors aimed at sulfate removal from wastewater. Once the effluent sulfate concentration and bioreactor total biomass concentration are fixed and the influent wastewater characteristics are assigned, all models give explicit mathematical relationships to determine the bioreactor volume and the effluent concentrations of substrates and products. The models also give explicit relationships to calculate the biomass recycle flow and the bacterial concentrations in the reactor.
- Sulfate removal to target effluent sulfate concentrations requires lower bioreactor volumes in ASRB-dominated than in HSRB-dominated gas-lift reactors.
- The hydrogen loading rate hardly affects the reactor size required to reach an assigned sulfate removal efficiency when HSRB prevail over ASRB and methanogenesis is inhibited (Model 1A) or ASRB are dominant (Model 2). On the contrary, when HSRB prevail over ASRB and methanogenesis is not inhibited (Model 1B), an increase of the hydrogen loading rate implies the requirement of a larger reactor volume to achieve the desired level of sulfate reduction.
- When HSRB are dominant, the acetate supply to the reactor influent affects the competition between SRB, HB, and MA, entailing a lower requirement of HB acetate production and, thus, a smaller HB population present in the reactor.

Notation

The following symbols are used in this paper:

b_j = specific decay rate of biomass j(T^{-1});
D_j = decay rate of biomass j($M\,L^{-3}\,T^{-1}$);

$i_{SRB,Ac}$ = SRB biomass produced for unit mass of acetate degraded, dimensionless;
$K_{j,i}$ = half-saturation coefficient referred to biomass j and substrate i ($M L^{-3}$);
Q = influent flow rate ($L^3 T^{-1}$);
R = ratio between the sludge recycle flow rate and the influent flow rate, dimensionless;
S_i = substrate i concentration ($M L^{-3}$);
$S_{i,0}$ = influent concentration of substrate i ($M L^{-3}$);
$S_{i,t,j}$ = threshold concentration of substrate i for the growth of biomass j ($M L^{-3}$);
V = liquid phase volume in the gas-lift reactor (L^3);
X_j = biomass j concentration in the reactor effluent flow ($M L^{-3}$);
X_{TOT} = total biomass concentration in the reactor effluent flow ($M L^{-3}$);
$(X_{TOT})_r$ = total biomass concentration in the recycle flow ($M L^{-3}$);
$Y_{j,i}$ = yield for biomass j, referred to substrate i, dimensionless;
α = thickening ratio in the sedimentation tank (i.e., the ratio between $(X_{TOT})_r$ and X_{TOT}), dimensionless;
μ_j = specific growth rate of biomass j (T^{-1}); and
$\hat{\mu}_j$ = maximum specific growth rate of biomass j (T^{-1}).

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