Model-based optimization of microaeration of biogas desulfurization in UASB reactors

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1. Introduction

Wastewater from industrial processes such as the production of paper, textile, pharmaceuticals and explosives may contain high concentrations of sulfate. While sulfate emissions are not a direct threat to the environment, during anaerobic treatment of these wastewaters sulfate is reduced to sulfide, including gaseous hydrogen sulfide (H2S). Sulfide causes the inhibition of anaerobic digestion, because of its toxicity to methanogens [1]. Moreover, high concentrations of H2S in the biogas cause the corrosion of concrete and steel and are toxic to humans. Therefore, sulfide has to be removed from the biogas.

Microaeration, the dosing of limited amount of air or oxygen into the anaerobic reactor allowing sulfide oxidizing bacteria (SOB) to oxidize sulfide to harmless elemental sulfur, has been demonstrated as an efficient desulfurization method [2–5]. However, the basic mechanisms involved in microaerobic sulfide oxidation are not sufficiently understood and control strategies for microaeration are not yet very much developed [6]. Mathematical modeling of microaeration is expected to increase our knowledge on microaerobic processes and improve our ability to control the process.

The Anaerobic Digestion Model No. 1 (ADM1) [7] has been generally accepted and widely applied for mathematical modeling of anaerobic wastewater treatment, but it does not include sulfate reduction processes. The competition between sulfate-reducing bacteria (SRB) and methanogens for acetate in UASB reactors was modeled by Kalyuzhnyi and Fedorovich [8] and by Kalyuzhnyi et al. [9] for a dispersed plug flow UASB reactor. Ristow et al. [10] Modeled the anaerobic digestion process including sulfate reduction in a Recycling Sludge Bed Reactor (RSBR) treating acid mine drainage. Knoblo and Lewis [11] developed a model for the treatment of molasses and acid mine drainage in a packed bed, UASB, and gas-lift reactors under steady state and dynamic conditions. Also, Poinapen and Ekama [12] developed a model including sulfate reduction processes and validated it with experimental results. The most comprehensive approach to modeling sulfate reduction in anaerobic digestion is the ADM1 extension reported by Fedorovich et al. [13], who described the competition between SRB on the one hand and acetogenic bacteria and methanogenic archaea on the other hand for butyrate, propionate, acetate and hydrogen. All these studies addressed the competition among acetogenic bac-
teria, methanogenic archaea, and SRB and the resulting sulfate removal, focusing on model calibration and/or assessing the influence of operational parameters and influent concentrations. Less work has been done concerning the prediction and validation of \( H_2S \) transfer to the gas phase, even though it constitutes an important aspect in the anaerobic treatment of high-sulfate wastewater. Barrera et al. [14] included \( H_2S \) transfer to the gas phase while modeling anaerobic digestion including sulfate reduction of cane-molasses vinasse, a very high strength and sulfate-rich wastewater. Carrera-Chapela et al. [15] set up a model to describe \( H_2S \) formation and transfer during anaerobic digestion of sewage sludge, which was calibrated and validated with experimental data from two pilot-scale reactors.

While a number of (above mentioned) studies has been devoted to the incorporation of sulfate reduction in anaerobic digestion models, chemical and/or biological oxidation of sulfate through microaerobic during anaerobic wastewater treatment has not yet been modeled [16,6]. Bothju et al. [17] developed a model describing oxygen effects in anaerobic digestion, focusing on anaerobic oxidation of soluble carbon, the improvement of organic matter solubility and the inhibition of obligatory anaerobic organisms. Models describing biochemical oxidation of sulfate to elemental sulfur have only been set up for dedicated processes in biofilters or biotrickling filters [18–21].

In this contribution, the ADM1 model was extended with sulfate reduction and sulfate oxidation to elemental sulfur. The main purpose was to study the effect of oxygen under microaerobic conditions. The resulting model, termed ADM1-S/O, was validated on available experimental data for a strictly anaerobic UASB reactor and an Up-flow Microaerobic Sludge Blanket (UMSB) reactor previously published by Krayzelova et al. [4].

2. Modeling microaerobiosis in UASB reactors

2.1. Biological conversion processes – ADM1-S/O

The ADM1 was extended with four additional processes of sulfate reduction [22,13] and one additional process of sulfide oxidation [23] (Tables 1 and 2): conversion of butyrate and sulfate to acetate and hydrogen sulfide by \( X_{BSRB} \) (process 9a); conversion of propionate and sulfate to acetate and hydrogen sulfide by \( X_{pSBR} \) (process 10a); conversion of acetate and sulfate to carbon dioxide and hydrogen sulfide by \( X_{BSRB} \) (process 11a); conversion of hydrogen and sulfuric acid to hydrogen sulfide by \( X_{JSRB} \) (process 12a); and oxidation of hydrogen sulfide and oxygen to elemental sulfur by \( X_{SOB} \) (process 12b).

For each process, the stoichiometric coefficients were calculated by closing the COD, carbon, nitrogen and sulfur balances (Table 1). The kinetic expressions (Table 2) describe substrate limitation of both the electron donor (organic substrate or \( H_2 \) for SRB and \( H_2S \) for SOB) and the electron acceptor (\( SO_4^{2−} \) for SRB and \( O_2 \) for SOB) through a Monod-type function, as in Fedorovich et al. [13].

Inhibition by undissociated \( H_2S \) (\( IH_2S \)) was described for acetogens, methanogens, and all SRBs following [24]:

\[
IH_2S = \left( 1 - \frac{S_{IH_2S}}{K_{IH_2S}} \right)^n \text{ for } S_{IH_2S} < K_{IH_2S} \]  
(1a)

\[
IH_2S = 10^{-6} \text{ for } S_{IH_2S} \geq K_{IH_2S} \]  
(1b)

where \( S_{IH_2S} \) is the concentration of hydrogen sulfide, \( K_{IH_2S} \) is the hydrogen sulfide inhibition constant, which is set to 0.0161 M [25], and \( n \) is an empirical constant, equal to 0.401 [25]. If \( S_{IH_2S} \geq K_{IH_2S} \), complete inhibition due to hydrogen sulfide occurs, a small value was used to avoid numerical problems.

Oxygen inhibition on acidogens, acetogens [17], hydrogenotrophic methanogens and acetotrophic methanogens (Ueki et al., 1997) was added compared to Fedorovich et al. [13]. It was described through non-competitive inhibition kinetics [17]:

\[
\begin{align*}
I_{O_2} &= \frac{K_{O_2} + S_{O_2}}{K_{O_2} + S_{O_2}} \text{ for } S_{O_2} \geq K_{O_2} \\
I_{O_2} &= 1 \text{ for } S_{O_2} < K_{O_2}
\end{align*}
\]  
(2a)

(2b)

where \( S_{O_2} \) is the concentration of oxygen and \( K_{O_2} \) is the oxygen inhibition constant, which is set to 0.25 mM for granular sludge [26]. However, since the concentration of oxygen in the reactor is lower than the inhibition concentration, it had no effect on the results as such.

The overall ADM1-S/O model and the list of all parameter values applied in ADM1-S/O are in the Supplementary material, section S.1. Note that the hydrolysis rates of carbohydrates, lipids and proteins were assumed unaffected by the small amounts of oxygen present. While enhanced hydrolysis in the presence of oxygen was observed by some authors [27,28], others found no evidence of it [44]. According to Bothju and Bakke [27], oxygen utilization would result in an additional hydrolysis of about 0.4 mg carbon per mg \( O_2 \). The average oxygen concentration of 1.92 \( 10^{-5} \) mg \( O_2 \) L\(^{-1}\) in this study (model validation case) thus corresponds with an additional amount of hydrolysed carbon of 0.768 \( 10^{-5} \) mg CL\(^{-1}\) or less than 0.001% of the total carbon amount in the reactor. The effect of \( O_2 \) on the hydrolysis rate was therefore neglected.

2.1.1. Liquid and gas phase mass balances

Liquid phase mass balances were set up for all state variables, including sulfide (\( S_{SO_4^{2−}} \)) and sulfide (\( S_{H_2S} \)) in addition to the ADM1 state variables (see Supplementary material, Tables S1 and S2). The liquid mass balance of a component \( i \) is given by Eq. (3):

\[
\frac{dS_{liq,i}}{dt} = V_I - Q_{in,i} + Q_{out,l,i} + k_{l,i} \cdot \left( S_{liq,i} - S_{liq,i,ss} \right) \cdot V_I + \sum_{j=1}^{n} \left( A_{ij} \cdot \rho_{j} \cdot V_j \right)
\]  
(3)

where \( V_I \) is the volume of the liquid phase [m\(^3\)], \( Q_{in,i} \) and \( Q_{out,i} \) are the influent and effluent flows, respectively, [m\(^3\) d\(^{-1}\)], \( S_{liq,i} \) and \( S_{liq,i,ss} \) are the concentrations of component \( i \) in the liquid phase and in the influent [kmol m\(^{-3}\) or kg COD m\(^{-3}\)]. \( k_{l,i} \) represents the equilibrium constant of component \( i \) in the liquid phase corresponding with the prevailing gas phase concentration [kmol m\(^{-3}\) or kg COD m\(^{-3}\)]. \( A_{ij} \) is the interphase mass transfer coefficient [d\(^{-1}\)], \( \rho_{j} \) denotes the rate of process \( j \) [d\(^{-1}\)].

Expression (3) expresses that accumulation of a component \( i \) (left-hand side) is due to advective transport (in- and outflows), interphase transfer and biological conversions (respectives terms on right-hand side).

Interphase transfer was considered for \( CH_4, CO_2, H_2S, H_2, O_2 \), and \( N_2 \). For these components (\( i \)), a gas phase mass balance was set up as represented by Eq. (4):

\[
\frac{dS_{gas,i,gen}}{dt} = V_g \cdot Q_{in,gen,i,gen} - Q_{out,gen,i,gen} + k_{gen,i} \cdot \left( S_{liq,i} - S_{liq,i,ss} \right) \cdot V_I
\]  
(4)

where \( V_g \) denotes the volume of the gas phase [m\(^3\)], \( Q_{in,gen,i,gen} \) and \( Q_{out,gen,i,gen} \) are the influent and effluent flows of gas, respectively, [m\(^3\) d\(^{-1}\)], \( S_{liq,i} \) is the influent gas concentration of component \( i \) [kmol m\(^{-3}\)] or [kg COD m\(^{-3}\)] and \( k_{gen,i} \) is the concentration of component \( i \) in the gas phase [kmol m\(^{-3}\)] or [kg COD m\(^{-3}\)].

It was assumed that no reactions take place in the gas phase. Details on the implementation of gas-liquid transfer are given in the Supplementary material, Section S.4.

The \( pH \) was calculated at each time step from the electro-neutrality equation (charge balance method, see Supplementary material, section S.3 Calculation of \( pH \)). Components involved
Table 1: Stoichiometric matrix $A_j$ and composition matrix for the sulfate reduction and sulfide oxidation processes considered in ADM1-S/O.

| Processes j | Components i | $S_{Yb}$ | $S_{pro}$ | $S_{ac}$ | $S_{mol}$ | $S_{rH}$ | $S_{o2}$ | $S_{m}$ | $S_{HCO3}$ | $S_{CO2}$ | $S_{IN}$ | $X_c$ | $X_{SRB}$ | $X_{pro}$ | $X_{ac}$ | $X_{SOB}$ | $X_{SRB}$ |
|-------------|--------------|----------|----------|---------|----------|---------|---------|---------|------------|----------|---------|------|----------|----------|---------|----------|--------|----------|
| 9a          | Uptake of Butyrate by SRB | –1       |          |         |          |         |         |         | –1         |          |         |      |          |          |         |          |        |          |
| 10a         | Uptake of Propionate by SRB | –1       |          |         |          |         |         |         | –1         |          |         |      |          |          |         |          |        |          |
| 11a         | Uptake of Acetate by SRB | –1       |          |         |          |         |         |         | –1         |          |         |      |          |          |         |          |        |          |
| 12a         | Uptake of Hydrogen by SRB | –1       |          |         |          |         |         |         | –1         |          |         |      |          |          |         |          |        |          |
| 12b         | Uptake of H$_2$S by X$_{SOB}$ | –1       |          |         |          |         |         |         | –1         |          |         |      |          |          |         |          |        |          |
| 16a         | Decay of X$_{SRB}$ |          |          |         |          |         |         |         |            |          |         |      |          |          |         |          |        |          |
| 17a         | Decay of X$_{SRB}$ |          |          |         |          |         |         |         |            |          |         |      |          |          |         |          |        |          |
| 18a         | Decay of X$_{SRB}$ |          |          |         |          |         |         |         |            |          |         |      |          |          |         |          |        |          |
| 19a         | Decay of X$_{SRB}$ |          |          |         |          |         |         |         |            |          |         |      |          |          |         |          |        |          |
| 19b         | Decay of X$_{SRB}$ |          |          |         |          |         |         |         |            |          |         |      |          |          |         |          |        |          |
| A1          | H$_2$S acid-base reaction | –1       | 1        |         |          |         |         |         |            |          |         |      |          |          |         |          |        |          |
| A2          | CO$_2$ acid-base reaction | –1       |          |         |          |         |         |         |            |          |         |      |          |          |         |          |        |          |

Composition matrix:

- 1 g COD per unit mole N per unit mole C per unit

$S_{Yb}$ Total Butyrate (kg COD/m$^3$)
$S_{pro}$ Total Propionate (kg COD/m$^3$)
$S_{ac}$ Total Acetate (kg COD/m$^3$)
$S_{mol}$ Total Mol (kg COD/m$^3$)
$S_{rH}$ Total Oxygen (kmol S/m$^3$)
$S_{o2}$ Total Hydrogen Sulphide (kmol S/m$^3$)
$S_{m}$ Total Hydrogen Sulphide (kmol S/m$^3$)
$S_{HCO3}$ Total Bicarbonate (kmol CO$_3^-$)
$S_{CO2}$ Total Carbon Dioxide (kmol CO$_2$)
$S_{IN}$ Total Inorganic Nitrogen (kmol N/m$^3$)
$X_c$ Total Elemental Sulfur (kmol S/m$^3$)
$X_{SOB}$ Total Butyrate (kg COD/m$^3$)
$X_{SRB}$ Total Propionate (kg COD/m$^3$)
$X_{pro}$ Total SRB Butyrate (kg COD/m$^3$)
$X_{ac}$ Total SRB Propionate (kg COD/m$^3$)
$X_{SRB}$ Total SRB Acid (kg COD/m$^3$)
$X_{SOB}$ Total SRB SRB (kg COD/m$^3$)

Note: $Y_{SRB}$, $Y_{IN}$, and $N_{biom}$ represent stoichiometric coefficients for SRB, Nitrifiers, and Biomass, respectively.
Table 2

Kinetic expressions for the sulfate reduction and sulfide oxidation processes considered in ADM1-SO.

<table>
<thead>
<tr>
<th>( \mathcal{A}_i )</th>
<th>Components</th>
<th>Process rate ( (p_i, \text{kg COD m}^{-3} \text{ d}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>9a</td>
<td>Uptake of Butyrate by bsSRB</td>
<td>( \rho_{9a} = k_{9a,bsSRB} \cdot X_{bsSRB} \cdot X_{\text{pH,biom}} \cdot h_{\text{bs}} )</td>
</tr>
<tr>
<td>10a</td>
<td>Uptake of Propionate by psSRB</td>
<td>( \rho_{10a} = k_{10a,psSRB} \cdot X_{psSRB} \cdot X_{\text{pH,biom}} \cdot h_{\text{ps}} )</td>
</tr>
<tr>
<td>11a</td>
<td>Uptake of Acetate by sSRB</td>
<td>( \rho_{11a} = k_{11a,sSRB} \cdot X_{sSRB} \cdot X_{\text{pH,biom}} \cdot h_{\text{s}} )</td>
</tr>
<tr>
<td>12a</td>
<td>Uptake of Hydrogen by HSRB</td>
<td>( \rho_{12a} = k_{12a,HSRB} \cdot X_{HSRB} \cdot X_{\text{pH,biom}} \cdot h_{\text{H}} )</td>
</tr>
<tr>
<td>12b</td>
<td>Uptake of H2S by XOH</td>
<td>( \rho_{12b} = k_{12b,XOH} \cdot X_{XOH} \cdot X_{\text{pH,biom}} \cdot h_{\text{X}} )</td>
</tr>
<tr>
<td>16a</td>
<td>Decay of XSRB</td>
<td>( \rho_{16a} = k_{16a,XSRB} \cdot X_{XSRB} \cdot X_{\text{pH,biom}} \cdot h_{\text{X}} )</td>
</tr>
<tr>
<td>17a</td>
<td>Decay of YSRB</td>
<td>( \rho_{17a} = k_{17a,YSRB} \cdot X_{YSRB} \cdot X_{\text{pH,biom}} \cdot h_{\text{Y}} )</td>
</tr>
<tr>
<td>18a</td>
<td>Decay of XSRB</td>
<td>( \rho_{18a} = k_{18a,XSRB} \cdot X_{XSRB} \cdot X_{\text{pH,biom}} \cdot h_{\text{X}} )</td>
</tr>
<tr>
<td>19a</td>
<td>Decay of YSRB</td>
<td>( \rho_{19a} = k_{19a,YSRB} \cdot X_{YSRB} \cdot X_{\text{pH,biom}} \cdot h_{\text{Y}} )</td>
</tr>
<tr>
<td>19b</td>
<td>Decay of XOH</td>
<td>( \rho_{19b} = k_{19b,XOH} \cdot X_{XOH} \cdot X_{\text{pH,biom}} \cdot h_{\text{X}} )</td>
</tr>
<tr>
<td>A1</td>
<td>( \text{H}_2\text{S} ) acid-base reaction</td>
<td>( \rho_{A1} = k_{A1,\text{H}<em>2\text{S}} \cdot \left( X</em>{\text{H}<em>2\text{S}} \cdot X</em>{\text{pH,biom}} \cdot h_{\text{H}_2\text{S}} \right) )</td>
</tr>
<tr>
<td>A2</td>
<td>( \text{CO}_2 ) acid-base reaction</td>
<td>( \rho_{A2} = k_{A2,\text{CO}<em>2} \cdot \left( X</em>{\text{CO}<em>2} \cdot X</em>{\text{pH,biom}} \cdot h_{\text{CO}_2} \right) )</td>
</tr>
</tbody>
</table>

In a chemical equilibrium and present only in the liquid phase, i.e. acetate \((S,\text{Tac})\), propionate \((S,\text{Tpro})\), butyrate \((S,\text{Tbu})\), valerate \((S,\text{Tva})\) and inorganic nitrogen \((S,\text{TN})\) were assumed to reach their chemical equilibrium instantaneously. These components were characterized by their total concentrations as state variables; the concentrations of the individual equilibrium forms \((S,\text{Ac}, \ S,\text{Tpro}, \ S,\text{bu}, \ S,\text{va}, \ S,\text{nh3})\) were subsequently calculated from the total concentrations and the prevailing pH (see Supplementary materials, section S.3). For components involved in a chemical equilibrium and taking part in gas-liquid transfer, i.e. inorganic carbon \((S,\text{hco3-I})\) and sulfide \((S,\text{hS})\), gas liquid mass balances were set up for the unionized species \((S,\text{CO2}, S,\text{HS2})\) involved in gas-liquid transfer, while the ionized forms were calculated from dynamic equations describing the chemical equilibria. Considering the typical pH operating range \((7-7.5)\), only the dissociation reactions between \(H_2S\) and \(HS^-\) \((pK = 6.9)\) and between \(CO_2\) and \(HCO_3^-\) \((pK = 6.4)\) were taken into account, neglecting the \(HS^-\)↔\(S^2^-\) \((pK = 11.96)\) and \(HCO_3^-\)↔\(CO_3^{2-}\) \((pK = 10.25)\) equilibria, since they were far from the normal pH operating range. A detailed description is given as Supplementary material, section S.3.

The total gas pressure in headspace \((P_{\text{headspace}})\) is calculated as the sum of all partial pressures [bar], which are related to the gas phase concentrations through the ideal gas law:

\[
P_{\text{headspace}} = P_T \cdot H_2 + P_T \cdot CH_4 + P_T \cdot CO_2 + P_T \cdot H_2S + P_T \cdot H_2 + P_T \cdot O_2
\]

\[
= S_{\text{gas},H_2} \cdot RT + S_{\text{gas},CH_4} \cdot RT + S_{\text{gas},CO_2} \cdot RT + S_{\text{gas},H_2S} \cdot RT + S_{\text{gas},H_2} \cdot RT + S_{\text{gas},O_2} \cdot RT
\]

(5)

The biogas flow rate, \(Q_{\text{gas}}\) [m³ d⁻¹] was calculated from the overpressure in the headspace, according to Batstone et al. [7]:

\[
Q_{\text{gas}} = k_p \cdot (P_{\text{headspace}} - P_{\text{atm}})
\]

(6)

where \(P_{\text{atm}}\) is an atmospheric pressure [bar] and parameter \(k_p\) is the pipe resistance coefficient [m³ d⁻¹ bar⁻¹], which was adjusted to 1.6 to achieve a reasonable overpressure (around 10 bar) in the headspace.

2.2. Reactor configuration – simulation set-up

The model was validated on the experimental data described by Krayzelova et al. [4], comparing the behavior of two UASB reactors, a strictly anaerobic UASB and a microaerobic one (termed UMSB). Both reactors consisted of a liquid phase \((2.7 L)\) and a gas phase \((0.3 L)\) and were assumed to be completely mixed. The reactor cross section area, \(A_r\), was 0.02 m². The operation temperature was kept constant at 35 °C. The liquid phase recirculation rate was 8.1 h⁻¹. The amount of VSS in biomass equaled to 50 kg VSS m⁻³, corresponding to 70 kg COD m⁻³, using a typical conversion factor of 1.4 g COD g⁻¹ VSS. The reactors were fed with synthetic wastewater mimicking brewery wastewater at a flow rate of 0.0082 m³ d⁻¹, containing average COD and sulfate concentrations of 3.23 g COD L⁻¹ and 0.072 g SO₄²⁻ L⁻¹, respectively (a concentrated synthetic wastewater was prepared and then diluted). The reactors were operated for 373 days. The influent flow of air \((Q_{\text{air}})\) was turned on the 74th day of experiment for UMSB reactor \((0.001 m^3 d^{-1})\).

The reactor model was implemented in Aquasim 2.0 [29], based on the Aquasim implementation of ADM1 for UASB reactors of Batstone et al. [30]. The total liquid phase of the reactor, consisting of the bulk liquid volume and the biofilm matrix, was assumed constant, so a growing biofilm implied a decreasing bulk liquid volume. The biofilm matrix corresponded to experimental data and consisted of 1 L of granular sludge with uniform granules with a diameter of 7 mm. The amount of granules \((n_{\text{gran}} = 5 600)\) was calculated based on the predefined total granule volume, \(V_{\text{gran}} = 1\). Since granular sludge is usually quite dense and contains extremely small pores it was assumed that granule structure had no diffusive solid transport (rigid biofilm matrix) and had no suspended solids within the pores (pore volume contains only liquid phase). External mass transfer limitation was neglected. The biomass porosity, \(\varepsilon_W\), was assumed to be constant at 0.70 and was calculated based on the initial biomass volume fraction \(\varepsilon_{\text{ini}} = 0.3\).

The influent concentrations fed to the model \((\text{Feed}_{\text{in}})\) were set up dynamically according to the experimentally measured influent flow rate, which was fluctuating with the influent pump operation, and taking into account the fixed component fractions in the influent: \(X_{\text{h2o}} = 4.94\%\); \(X_{\text{h2}} = 4.94\%\); \(X_{\text{ac}} = 55.85\%\); \(X_{\text{pro}} = 0.026\%\); \(X_{\text{but}} = 1.97\%\); \(X_{\text{va}} = 2.44\%\); \(X_{\text{co2}} = 2.70\%\); \(X_{\text{h2s}} = 25.20\%\); \(X_{\text{h2s}} = 1.92\%\); \(X_{\text{nh3}} = 0.028\%\). The concentration of cations/anions \((S^{-})\) was calculated based on the charge balance. The influent hydrogen ion \((S_{\text{h}^+})\) reflected an influent pH of 7. The influent flow \((Q_{\text{in}})\) corresponded to dynamic experimental data. For the simulation of microaerobic conditions (UMSB reactor), a small amount of air was supplied to the reactor in ADM1-SO while for the simulation of anaerobic conditions (UASB reactor) aeration was completely turned off.

The initial conditions were defined for biofilm matrix as well as for the bulk liquid volume. All 12 bacterial species were considered to have equal initial concentrations of 5.55 kg COD m⁻³ in the biofilm matrix; the initial biofilm thickness was set at 0.03 mm. The initial bulk liquid concentrations were set at 2.15 kg COD m⁻³ for carbohydrates \((X_{\text{ch}})\); 0.19 kg COD m⁻³ for proteins \((X_{\text{pro}})\).
(X_{pr}) and 0.19 kg COD m^{-3} for lipids (X_{li}); 10^{-6} kg COD m^{-3} for VFAs; 10^{-7} kmol m^{-2} for hydrogen ion (pH = 7) according to the wastewater composition, and 10^{-2} kg COD m^{-3} for all bacterial species.

The granular sludge from UASB and UMSB reactor [4] was analyzed by PCR and DGGE. SOBs were found in the UMSB reactor proving the biologically mediated oxidation of sulfide to elemental sulfur (unpublished results). Nevertheless, the presence of SOBs was the motivation to model the biological sulfur oxidation in the present manuscript.

The model was first validated upon the dynamic experimental data of Krayzelova et al. [4], characterized by a dynamic influent flow, Q_in, an influent S:COD ratio (mol SO_4^{2-} - S kg COD) of approximately 0.0003 and an influent molar O_2:S ratio (for UMSB reactor) of 0.5. The model was then applied for steady state scenario analyses concerning the effect of the influent S:COD ratio and of the aeration intensity (O_2:S ratio), for a constant influent flow rate (Q_in = 0.0082 m^3 d^{-1}) and constant influent COD concentration (Feed_in = 2.32 kg m^{-3}). In a first series of simulations, the influent S:COD ratio was varied by keeping the influent sulfate concentration (5—15.5 mol SO_4^{2-} - S m^{-3}) while the oxygen concentration was fixed at 0.03 mol O_2 m^{-3}. In a second series of simulations, the influent O_2:S ratio was varied by keeping the dissolved oxygen concentration (0.03—2.32 mol O_2 m^{-3}) for a constant S:COD concentration of 1.16 mol SO_4^{2-} - S m^{-3} (corresponding with a S:COD ratio of 0.0003).

3. Results and discussion

3.1. Validation of ADM1-S/O

The simulated biogas flow rate and the H_2S concentration in the biogas were compared to the experimental data for both the UASB reactor (without microaeration) and the UMSB reactor (with microaeration) (Fig. 1). An average biogas flow rate of 8.51 d^{-1} and 9.61 d^{-1} was measured experimentally for the UASB reactor and for the UMSB reactor, respectively. The simulated biogas flow rate showed a good fit (Fig. 1A). 8.51 d^{-1} and 9.51 d^{-1} on average for the UASB and the UMSB reactor, respectively, corresponding with a Root-Mean-Square Error of 1.371 for UASB and 0.993 for UMSB. The experimentally measured methane content in the biogas reached 77% and 75% in UASB and UMSB reactor, respectively, while in the simulation, the fraction of methane reached 77% in both reactors (see Fig. S1 in Supplementary material, section S5). The pH of both reactors was on average 7.3 and 7.1 in the experiments and in the simulations, respectively. The average COD removal measured experimentally was on average 87% in the UASB and 89% in the UMSB reactor, while the simulated value was 90% for both. Some fluctuations were observed during the experiments [4], caused most probably by the irregular pumping of feed and by experimental measurement inaccuracies, which also caused dynamics in the simulated behavior.

The experimentally measured average H_2S concentration in the biogas of the UASB reactor was 8.9 g H_2S m^{-3}, the simulated one amounted to 8.3 g m^{-3}. With microaeration (UMSB reactor), the average H_2S concentration in the biogas was brought down to 2.2 g H_2S m^{-3} measured experimentally and 1.3 g m^{-3} simulated, corresponding to the removal efficiency of 75% for experiments and 84% for simulation. Overall, a very good match was obtained between experimental and simulated H_2S concentration in the biogas, even though some of the fast changes in H_2S concentrations were not fully captured because of the resolution of the available influent data (Fig. 1B).

Table 3 summarizes the sulfur balance over the experimental data and the simulation results. The simulation showed a good fit for the decrease of H_2S from biogas in UASB reactor compare to the UMSB reactor, 73.5% (34% of H_2S in UASB and 9% of H_2S in UMSB) for experiments and 73.9% for simulation (23% of H_2S in UASB and 6% of H_2S in UMSB).

While elemental sulfur in experimental UMSB accounted only for 43%, in the modeled UMSB it reached 71%. The sulfur uptake (accumulation) in the granules was not modeled. The sulfur composition in the granular sludge after a year of operation was the same (8%) for the UASB and UMSB reactors [4]. No significant increase of the sulfur concentration in the granular sludge was observed during the operation in any of the reactors. In other words, elemental sulfur formed in UMSB reactor due to microaeration did not accumulate in granular sludge.

The simulated decrease in dissolved sulfide concentration in the effluent, i.e. 73% (calculated as the decrease of 75% dissolved sulfide in UMSB reactor compare to 20% dissolved sulfide in UASB reactor) was much higher than the experimentally observed one, only 15% (calculated as the decrease of 49% of dissolved sulfide in the model of UMSB reactor compare to 41% of dissolved sulfide in the model of UASB reactor). The most probable reason for the higher sulfide removal in the simulations is the lack of competing reactions for O_2. In the model, oxygen was used only for sulfide removal while in reality, oxygen is consumed by other processes such as the oxidation of organic matter [31,32] thereby decreasing the sulfide removal efficiency in UMSB. A second explanation for the poor agreement between the experimental and predicted values could be the uncertainty regarding the exact location of the sulfide oxidation process. In this study, sulfide oxidation was assumed to take place in the liquid phase, while no reactions took place in the gas phase. Some authors observed oxidation of both gaseous and liquid sulfide [49,46,47,33,32,4], others did not observe the oxidation of dissolved sulfide and assumed the oxidation occurs only in gas phase [34,2] or at the gas-liquid interphase [35]. If hydrogen sulfide removal would occur only in the gas phase, its simulated removal efficiency could be lower and thus closer to the experimental values. However, if the reactions in both the liquid and the gas phase would be assumed in the model, the hydrogen sulfide removal as well as the difference with the experimental results would be even higher.

A third possible explanation for the higher sulfide removal efficiencies in the model compared to the experimental results could be the reverse reduction of elemental sulfur back to sulfide which was not modeled. Since oxygen is limited in the UMSB reactor, the conditions are still “anaerobic” and SRB might be able to take the elemental sulfur and reduced it to sulfide again.

<table>
<thead>
<tr>
<th></th>
<th>UASB</th>
<th>UMSB</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>experiment</td>
<td>simulation</td>
</tr>
<tr>
<td>Sulfate in the influent [%]</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Sulfate in the effluent [%]</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Sulfide in the effluent [%]</td>
<td>49</td>
<td>75</td>
</tr>
<tr>
<td>Hydrogen sulfide in biogas [%]</td>
<td>34</td>
<td>23</td>
</tr>
<tr>
<td>Elemental sulfur [%]</td>
<td>7*</td>
<td>0</td>
</tr>
<tr>
<td>Sulfur in granular sludge [%]</td>
<td>8</td>
<td>n.c.</td>
</tr>
<tr>
<td>Gap [35S_g−35S_m]</td>
<td>2</td>
<td>0</td>
</tr>
</tbody>
</table>

n.c. not considered in the model.

* The elemental sulfur in experiments is taken as the sum of elemental sulfur found in the gas and liquid phase.
3.2. Microbiological composition of anaerobic granular sludge

The composition of granular sludge in terms of active biomass fractions for both the UASB and UMSB reactors is given in Table 4. Sulfate reduction was mainly performed by hydrogenotrophic sulfate reducing bacteria, which were able to compete with hydrogenotrophic methanogens. Sulfate reducing bacteria growing on butyrate, propionate and acetate (X_bSRB, X_pSRB and X_aSRB, respectively) only accounted for trace quantities of the active biomass. Although the influent sulfate was almost completely converted, its amount was not high enough for SRB to out-compete other butyrate, propionate and acetate degraders. According to the literature, SRB will out-compete methanogens for the substrates acetate [36,37], butyrate and propionate [38] when excess sulfate is present and/or at COD/SO\textsubscript{4}\textsuperscript{2−} ratios lower than 1.3 g COD/g SO\textsubscript{4}\textsuperscript{2−}. Zhou et al. [45] observed that SRB out-competed methanogens for ethanol even at COD/SO\textsubscript{4}\textsuperscript{2−} ratios around 4.0. In this study, the influent COD/SO\textsubscript{4}\textsuperscript{2−} ratio amounted to 32.2 g COD/g SO\textsubscript{4}\textsuperscript{2−} (~1 mol SO\textsubscript{4}\textsuperscript{2−}/mol COD). But even though SRB growing on butyrate, acetate and propionate do not play a significant role in this study (the growth and decay rates of bSRB, aSRB and pSRB could be turned off in the model without visible effect on the simulations results – not shown) it was preferred to keep the model sufficiently general for application to other influent conditions. In the study of Carrera-Chapela et al. [15] only VFA was used as electron donor (the ratio between 53 and 104 g COD/g SO\textsubscript{4}\textsuperscript{2−}). Barrera et al. [14] used propionic acid, acetic acid and hydrogen as the electron donors (with 10–20 g COD/g SO\textsubscript{4}\textsuperscript{2−} ratio) for the sulfate reduction, leaving only butyric acid behind.

When applying microaeration, SOB (X_SOB) accounted for 0.05% of the active biomass. Overall, the biomass fractions of the major biomass populations were hardly affected by the application of microaeration.

Table 4
Simulated active biomass composition of the granular sludge of UASB and UMSB reactor on day 200.

<table>
<thead>
<tr>
<th>Active biomass</th>
<th>Fraction [%]</th>
<th>UASB reactor</th>
<th>UMSB reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>X_su</td>
<td>30.28</td>
<td>31.20</td>
<td></td>
</tr>
<tr>
<td>X_aa</td>
<td>5.47</td>
<td>5.45</td>
<td></td>
</tr>
<tr>
<td>X_a</td>
<td>0.29</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>X_c</td>
<td>6.48</td>
<td>6.07</td>
<td></td>
</tr>
<tr>
<td>X_bSRB</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>X_pro</td>
<td>7.13</td>
<td>6.88</td>
<td></td>
</tr>
<tr>
<td>X_pSRB</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>X_ac</td>
<td>21.79</td>
<td>21.03</td>
<td></td>
</tr>
<tr>
<td>X_aSRB</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>X_h2</td>
<td>9.90</td>
<td>9.72</td>
<td></td>
</tr>
<tr>
<td>X_hSRB</td>
<td>18.65</td>
<td>19.11</td>
<td></td>
</tr>
<tr>
<td>X_SOB</td>
<td>0.00</td>
<td>0.05</td>
<td></td>
</tr>
</tbody>
</table>

3.3. Scenario analysis

3.3.1. Effect of the influent S:COD ratio

The effect of influent S:COD ratio on the percentage of H\textsubscript{2}S in the biogas of the UASB and UMSB reactors is shown in Fig. 3. For a UASB reactor, the fraction of H\textsubscript{2}S in the biogas increased almost linearly, from 0.02% to 0.26%, with an increasing influent S:COD ratio of 0.2–2.5. The H\textsubscript{2}S concentration reached a constant value of 0.32% for an influent S:COD ratio of 0.003 or higher. This plateau corresponded to hydrogen depletion in reactor. Indeed, only hydrogenotrophic SRB (X_hSRB) played an important role in H\textsubscript{2}S formation; sulfate reducing bacteria growing on butyrate, propionate and acetate were not able to outcompete methanogens growing on these substrates, not even at the highest simulated S:COD ratio of 6.7. When applying microaeration (UMSB reactor) the H\textsubscript{2}S formation in biogas stabilized at lower values and for lower S:COD concentrations: the maximum H\textsubscript{2}S fraction in biogas was 0.14% and 0.002%, applying an influent O\textsubscript{2}:S ratio of 0.25 and 0.5, respectively, for an influent S:COD ratio 0.003–0.007.

Comparing the performance of the UASB and UMSB reactors, the addition of oxygen resulted in a decrease of the maximum H\textsubscript{2}S concentration in biogas by 56% for an influent O\textsubscript{2}:S ratio of 0.25 and a decrease of 99% for an influent O\textsubscript{2}:S ratio of 0.5 at an influent S:COD ratio of 3.3 and higher. Díaz et al. [2] reached 99% removal of H\textsubscript{2}S for an influent S:COD ratio of 0.001 applying an influent O\textsubscript{2}:S ratio 1.27. This agreed very well with our simulation results, which showed a 97% removal efficiency of H\textsubscript{2}S for an influent S:COD ratio of 0.001 and an O\textsubscript{2}:S ratio of 1.25. The simulated amount of oxy-
gen in the biogas was 0.9%, which also matched the experimentally measured value (1%) of Díaz et al. [2].

3.3.2. Effect of the influent O₂:S ratio

The effect of aeration intensity in terms of the influent O₂:S ratio on the biogas quality and on the H₂S removal efficiency is displayed in Fig. 4. For an influent O₂:S ratio of 0.5 the H₂S removal efficiency amounted to 91.2% with 0.24% of O₂ in biogas. When increasing the influent O₂:S ratio, the H₂S removal efficiency increased, up to 96.5% (corresponding with H₂S concentration of 0.4 g m⁻³) for an influent O₂:S ratio of 3. However, the increasing H₂S removal efficiency could only be realized at the expense of a linearly increasing leftover of oxygen in the biogas, up to 4% for an influent O₂:S ratio of 3. An oxygen content below 1% is required for biogas application in fuel cells and below 3% (after carbon dioxide removal and upgrading) for application as vehicle fuel or injection of biogas into the natural gas grid [41]. Since oxygen can create a dangerous and explosive gas mixture with methane [42,48], increasing the amount of oxygen could endanger the whole process. However, in some studies O₂ fractions in biogas of 4% were reported [34,43].

Comparing the simulation results with experimental data, at an influent O₂:S ratio of 0.5, 91.2% H₂S removal was simulated with 0.24% O₂ left in biogas, while in the experiments, only 73% H₂S from biogas was removed with less than 0.02% O₂ in biogas [4]. The higher H₂S removal efficiency simulated than for the experimental data can be explained by the microaeration model considering oxygen to be used for the oxidation of sulfide to elemental sulfur, while in reality other components such as organic matter may be oxidized as well. Comparing simulation with experiments where oxygen was blown into the gas phase (i.e. oxidation of organic matter can be omitted), a very good match was obtained. At an O₂:S ratio of 1.25, 96.2% of H₂S was removed with 1.34% O₂ left in biogas. Díaz et al. [2] injected the air into the headspace at the O₂:S ratio 1.23 (omitting the oxidation of organic matter) and removed 97.5% H₂S from biogas with 1.5% O₂ in biogas. It is clear that aerobic
carbon oxidation needs to be considered in the model when oxygen is blown through the liquid phase.

4. Conclusions

An anaerobic digestion model with sulfur and oxygen (ADM1-S/O) was set up to describe and control sulfate reduction and sulfide oxidation in anaerobic and microaerobic environments:

- The model validation showed a good fit in terms of H₂S emissions and biogas flow. The results of sulfur balance showed the limitations of the present model as it predicted higher H₂S removal (lower H₂S concentrations in the effluent) than observed experimentally. In case microaeration is realized by blowing oxygen into the liquid phase, aerobic carbon oxidation and re-reduction of elemental sulfur back to sulfide need to be considered in the model.
- The simulated composition of active biomass in the microaerobic reactor was not significantly affected by microaerotation. Sulfur oxidizing bacteria only made up a small fraction of the active biomass (0.05% of active biomass for an influent COD:SO₄²⁻ ratio of 32.3 g g⁻¹).
- Hydrogen sulfide in biogas proportionally increased with increasing influent S:COD ratio. Maximum H₂S concentrations of 0.32 and 0.14% were observed in the biogas from UASB and UMB reactor, respectively, for S:COD ratio of 3.3 g g⁻¹ and O₂:S ratio of 0.25.
- The highest H₂S removal efficiency from biogas was obtained for a O₂:S ratio 0.5 kmol O₂ kmol SO₄²⁻–S. Increasing the O₂:S ratio to over 0.5 did not significantly improve H₂S removal.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [http://dx.doi.org/10.1016/j.ijbeij.2017.06.009](http://dx.doi.org/10.1016/j.ijbeij.2017.06.009).

References


