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Industrial Electrical Engineering and Automation

Mathematical Models for Sulphate Reduction Processes

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– A BRIEF OVERVIEW

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INTRODUCTION

This is a brief overview of two mathematical models describing sulfate reduction processes in anaerobic systems. Both models are developed in order to describe the anaerobic digestion process of industrial waste streams that are rich in sulfate, such as those coming from pulp and paper manufacturing, mineral processing, petrochemical industries, mining activities, etc.

Under anaerobic conditions, sulfate is converted to hydrogen sulfide (H_2S), the latter being both poisonous and corrosive. This process is mediated by sulfate reducing bacteria (SRB), which requires electron donor and a carbon source for cell growth. Usually, both roles are filled by a single compound (e.g. short chain fatty acids) but some species of SRB can also utilize hydrogen as an electron donor and CO_2 as carbon source. Not all possible electron donor substrates have been considered as a result of simplification of these models but this in no way limits their usefulness.

The first model is presented in Knobel and Lewis (2002), while the second model is presented in Fedorovich et al. (2003). In the following sections, each model is discussed separately followed by a summarized comparison. Finally, a short description of the sulfate reduction model used in the extension of the Benchmark Simulation Model No. 2 (Gernaey et al., 2014) is presented.

1. A mathematical model of a high sulfate wastewater anaerobic treatment system (Knobel and Lewis, 2002)

This model was developed in order to describe the anaerobic treatment process occurring in digesters treating sulfate-rich wastewaters. It also includes mass transfer of hydrogen sulfide from the liquid to the gas phase. The model is able to simulate sulfate reduction using different substrates: hydrogen, acetate, propionate, butyrate, lactate, and corresponding sulfate reducers (SRB): *hSRB*, *aSRB*, *pSRB*, *bSRB*, *lSRB*, respectively.

Inhibition due to sulfide production is also described in addition to pH inhibition. More information is presented in Section 3.

2. Extension of Anaerobic Digestion Model No. 1 with processes of sulfate reduction (Fedorovich et al., 2003)

This model was developed to upgrade the Anaerobic Digestion Model No. 1 (ADM1) with processes for sulfate reduction. SRBs utilize several intermediates during breakdown of organic matter, resulting in competition for these substrates by different micoorganisms, for example: SRBs vs acidogens (for sugars and amino acids), SRBs vs acetogens (for VFAs and ethanol), SRBs vs methanogens (for acetate and hydrogen). The competition first described above (i.e. SRBs vs acidogens) is won by acidogens, which is why it is not incorporated into ADM1 for this extension. However, the other two are actual competitions and are thus accounted for in this model extension. The model is able to simulate sulfate reduction using different substrates: hydrogen, acetate, propionate, butyrate, and corresponding sulfate reducers (SRB): *hSRB*, *aSRB*, *pSRB*, *bSRB*, respectively.

Kinetic expressions are also modified to account for H_2S inhibition and pH inhibition. More information is presented in Section 3. Nevertheless, gas transfer of hydrogen sulfide is not well-defined in this model.

3. Summarized comparison between the two sulfate reduction models

3.1. Stoichiometry of sulfate-reducing processes

A major difference between the two models is the set of substrates utilized by the SRBs, which consequently clarifies the difference in the number of groups of SRBs included in each model. **Table 1** presents a summary of the stoichiometry of the sulfate reduction processes in each model.

Table 1. Stoichiometry of sulfate reduction reactions included in the two models.

Electron Donor	Knobel and Lewis (2002)	Fedorovich et al. (2003)
H_2	$4H_2 + H_2SO_4 \rightarrow H_2S + 4H_2O$	$4H_2 + H_2SO_4 \rightarrow H_2S + 4H_2O$
Acetate	$CH_3COOH + H_2SO_4 \rightarrow 2CO_2 + H_2S + 2H_2O$	$CH_3COOH + H_2SO_4 \rightarrow 2CO_2 + H_2S + 2H_2O$
Butyrate	$2C_3H_7COOH + H_2SO_4 \rightarrow 4CH_3COOH + H_2S$	$2C_3H_7COOH + H_2SO_4 \rightarrow 4CH_3COOH + H_2S$
Propionate	$4C_2H_5COOH + 3H_2SO_4 \rightarrow 4CO_2 + 3H_2S + 4H_2O$ $(4C_2H_5COOH + 3H_2SO_4 \rightarrow 4CH_3COOH + 4CO_2 + 3H_2S + 4H_2O)$	$4C_2H_5COOH + 3H_2SO_4 \rightarrow 4CH_3COOH + 4CO_2 + 3H_2S + 4H_2O$
Lactate	$2CH_3CHOHCOOH + H_2SO_4 \rightarrow 2CH_3COOH + H_2S + 2H_2O$ $(2CH_3CHOHCOOH + H_2SO_4 \rightarrow 2CH_3COOH + H_2S + 2CO_2 + 2H_2O)$	

As observed, the stoichiometry for sulfate reduction using either H_2, acetate or butyrate is equivalent for both models. In addition, the difference between the two models when considering the utilization of propionate for sulfate reduction can be attributed to a typographical error (the corrected stoichiometry is written between parentheses). Lastly, the model from Knobel and Lewis (2002) considers lactate as an additional substrate. Sulfate reduction using lactate results in the production of acetate, sulfide, water, and carbon dioxide. The latter was not written in the stoichiometry presented by Knobel and Lewis (2002) as listed in **Table 1** (probably due to a typographical error) and the corrected stoichiometry is written between parentheses.

3.2. Kinetics

The Monod equation to describe the biomass growth rate, where sulfate and an electron donor are considered as substrates, is:

$$\rho = \mathrm{k}_{\mathrm{max}} \cdot \frac{S}{\mathrm{K_S} + S} \cdot \frac{S_{\mathrm{SO_4}}}{\mathrm{K}_{\mathrm{SO_4}} + S_{\mathrm{SO_4}}} \cdot X \qquad \textbf{Eq. 1}$$

where:

ρ	Kinetic rate
$\mathrm{k}_{\mathrm{max}}$	Maximum specific uptake rate
S	Concentration of dissolved substrate
$\mathrm{K_S}$	Monod half-saturation constant
$S_{\mathrm{SO_4}}$	Concentration of sulfate

K_{SO_4}	Monod half-saturation constant for sulfate
X	Concentration of SRB

3.3. Inhibition terms

The rate equation in **Eq. 1** is further amended by multiplying with inhibition factors for pH (I_{pH}) and H_2S (I_{H_2S}).

$$\rho = k_{max} \cdot \frac{S}{K_S + S} \cdot \frac{S_{SO_4}}{K_{SO_4} + S_{SO_4}} \cdot X \cdot \mathbf{I_{H_2S}} \cdot \mathbf{I_{pH}} \qquad \textbf{Eq. 2}$$

Each model has different approximations for the inhibition kinetics, as shown in Tables 2 and 3.

Table 2. Kinetic term for H_2S inhibition (I_{H_2S}) in the two models.

Knobel and Lewis (2002)	**Fedorovich et al. (2003)**
$I_{H_2S} = \frac{1}{1 + \frac{S_{H_2S}}{K_I}}$	$I_{H_2S} = 1 - \frac{S_{H_2S}}{K_I}$ (if $S_{H_2S} > K_I$, $I_{H_2S} = 0$)

where:

I_{H_2S}	H_2S inhibition term
S_{H_2S}	Concentration of H_2S
K_I	50 % inhibitory concentration

Knobel and Lewis (2002) assumes a non-competitive inhibition term to describe H_2S inhibition. On the other hand, according to Fedorovich et al. (2003), little reliable information is known on H_2S inhibition and thus, the simple equation in **Table 2** is assumed to be a reasonable approximation.

Table 3. Kinetic term for pH inhibition (I_{pH}) in the two models.

Knobel and Lewis (2002)	**Fedorovich et al. (2003)**
$I_{pH} = \frac{1}{1 + e^{-\alpha_{LL}(pH - pH_{LL})}} \cdot \frac{1}{1 + e^{-\alpha_{UL}(pH - pH_{UL})}}$	$I_{pH} = \frac{1 + 2 \cdot 10^{0.5(pH_{LL} - pH_{UL})}}{1 + 10^{(pH - pH_{UL})} + 10^{(pH_{LL} - pH)}}$

where:

I_{pH}	pH inhibition term
pH, pH_{LL}, pH_{UL}	Measured pH, lower pH limit, upper pH limit
α_{LL}, α_{UL}	Positive values which affect steepness of the curve (i.e. higher α means faster onset of inhibition)

I_{pH} can take any value between 0 and 1. Fedorovich et al. (2003) uses the same pH inhibition as in ADM1 (Batstone et al., 2002), wherein both high and low pH inhibitions occur.

4. DISCUSSION

The sulfur reduction processes added to the ADM1 (Flores-Alsina et al., 2016) within the Benchmark Simulation Model No. 2 (Gernaey et al., 2014) platform are based on both the papers of Knobel and Lewis (2002) and Fedorovich et al. (2003) with some adaptations:

- There are two options for sulfate reduction: (1) sole use of H_2 as electron donor, or (2) the utilization of H_2 and the volatile fatty acids (acetate, butyrate, propionate, and in addition, valerate) as electron donors.
- Mass transfer of hydrogen sulfide into the gas phase is included.
- pH inhibition is given by the function:

  $$\mathrm{I_{pH}} = \frac{\mathrm{K_{pH}^{n}}}{S_{\mathrm{H^+}}^{\mathrm{n}} + \mathrm{K_{pH}^{n}}}$$

  with $\mathrm{K_{pH}} = 10^{-\frac{\mathrm{pH_{LL}} + \mathrm{pH_{UL}}}{2}}$ and $\mathrm{n} = \frac{3}{\mathrm{pH_{UL}} + \mathrm{pH_{LL}}}$
- H_2S inhibition is given by the function:

  $$\mathrm{I_{H_2S}} = \frac{1}{1 + \frac{S_{\mathrm{H_2S}}}{\mathrm{K_I}}}$$

5. REFERENCES

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