A Comparative Model-Analysis on Sulphide Bio-oxidation with Different Electron Acceptors

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Abstract

Sulphide (H_2S, HS^- and S^{2-}) is an undesired by-product of biogas production processes. This modelling work in Aquasim was carried out to study three parallel processes related to sulphide in AD environments: 1) H_2S liquid-gas mass transfer; 2) Acid-base equilibrium; and 3) Sulphide oxidation with three different electron acceptors; nitrate, oxygen, and a biotic anode with a given potential. Multiplicative Monod (biotic processes) and Nernst-Monod kinetics (bioelectrochemical process) provide the basis for the sulphide bio-oxidation processes. At the current stage, the model can be used to study sulphide bio-oxidation and the effect of relevant parameters, including initial biomass concentration, uptake rates, temperature, and pH. The model can be improved further by implementing anaerobic microbial processes as competing reactions. With the proposed improvements, the model can be a useful tool for calculating the chemical dosage or electrode potential required for sulphide removal. These calculations can be based on both the concentration of H_2S(g) in the headspace (ppm) often available at full-scale plants and the concentration of sulphide (HS^-(liq)) in effluent streams from the plants.

Keywords: Sulphide oxidation, liquid-gas mass transfer, nitrate, oxygen, bioelectrochemistry

1. Introduction

Biogas produced through anaerobic digestion (AD) contains 30-50 % CO_2, 50-70 % CH_4 and trace gases, including H_2S. Depending on the substrate composition, normal H_2S(g)- concentrations are 0-10 000 ppm (Angelidaki *et al.*, 2018). Sulphide is toxic, odorous, and corrosive, even at low concentrations. Different techniques can remove sulphide from liquid and gaseous streams, including physicochemical and biological methods. Biological desulphurisation processes exploit the microbial ability to oxidise sulphide with oxygen or nitrate as electron acceptors. Bioelectrochemical systems (BESs) with a bioanode working as the electron acceptor have been examined as an alternative (Sun *et al.*, 2009). In these systems, microorganisms work as catalysts at the electrodes in oxidation or reduction reactions. A solid anodic surface can function as an electron acceptor for the electrons generated through sulphide oxidation. The electrons are transported to the cathode, where reduction reactions such as CH_4 production from CO_2 occur. This bioelectrochemical technique can provide a chemical-free and environmentally friendly solution for sulphide removal if a renewable energy source is used to supply electricity.

The processes related to sulphide in AD environments are complex and usually involve the following main processes: 1) Sulphate bioreduction to sulphide; 2) Liquid-gas mass transfer of H_2S; 3) Acid-base equilibrium of $H_2S/HS^-/S^{2-}$; and 4) Chemical and biological sulphide oxidation to remove sulphide. Barrera *et al.* (2015) implemented the first three processes as an extension of ADM1. In our modelling work, the main focus was sulphide removal through bio-oxidation (process 4). The primary goal of the model was to develop a simple simulation tool for studying sulphide bio-oxidation with different electron acceptors and estimating H_2S(g) based on liquid-gas mass transfer. The secondary target was estimating the required chemical dosage to reduce the sulphide concentration to a specified target concentration.

The bio-oxidation processes were implemented with three different electron acceptors; nitrate, oxygen (biotic processes) and a bioanode (bioelectrochemical process). At this modelling stage, the aim was to study these oxidation processes and identify the most critical parameters for further model development.

2. Methodology

The model was developed using Aquasim as a simulation tool. The reactor space was defined as a modified mixed compartment. The following assumptions were made: 1) Sulphide was included as a loading rate. The model's primary focus is sulphide bio-oxidation processes. Therefore, sulphate bioreduction to sulphide was not included; 2) The microorganisms are assumed to be chemolithoautotrophs, capable of gaining energy by oxidising inorganic sulphur-containing compounds. One microbial group is included for each of the sulphide oxidising processes instead of specific microbial species; X_{eet} for electroactive microorganisms, X_{sob} for microorganisms with oxygen as the electron acceptor, and X_{snb} for microorganisms with nitrate as the electron acceptor; 3) For all the microbial groups, first-order kinetics for decay were assumed valid, as proposed by Batstone *et al.*, (2002); 4) Due to the slower kinetics compared to biotic oxidation, chemical

oxidation is not included; 5) Biotic oxidation of H_2S is slower compared to oxidation of HS^- (Hvitved-Jacobsen *et al.*, 2013), thereby requiring separate rate kinetics. For simplicity, only oxidation of HS^- was included in the model; 6) It is assumed that the microbial culture is adapted to the substrate. The growth kinetics only depends on the concentrations of the electron donor and acceptor (substrate dependence); 7) Only sulphur and sulphate are included as oxidation products. Other sulphur intermediate products are assumed to have faster kinetics; 8) A Nernstian expression can be used to model the transfer of electrons from the microorganisms to the conductive biofilm on the anode surface. This is applicable because the transfer is assumed to be reversible and rapid, as adapted from a modelling study by Marcus *et al.* (2007). 9) It is assumed that there is no proton accumulation in the reactor.

2.1. The reactor vessel and operational parameters

A virtual full-scale biogas reactor with a total volume of 2000 m^3 was defined in the model (Figure 1). A representative initial biogas composition of 60-70 % CH_4, 30-40 % CO_2, and 100-10000 ppm H_2S was considered. The pH range for AD reactors is often 6.8 to 8.0. In the model, this range is important for estimating H_2S(g) in biogas. To estimate the H_2S-generation with psychrophilic, mesophilic, and thermophilic microorganisms, a representative temperature range of 15-55 ˚C was chosen. The pH and temperature ranges were used in the acid-base equilibrium- and air-water equilibrium calculations (3.1.2). In the Aquasim simulations, a representative temperature of 308 K and pH of 7.2 were used if not stated otherwise. Other relevant parameters used in the model are listed in Table 1.

Table 1: Parameters related to the modelled AD reactor.

Parameter	**Value**
Total reactor size [m^3]	2000
Constant bulk liquid [m^3]	1600
Headspace [m^3]	400
Inflow [m^3 d^{-1}]	75
HRT [d]	21

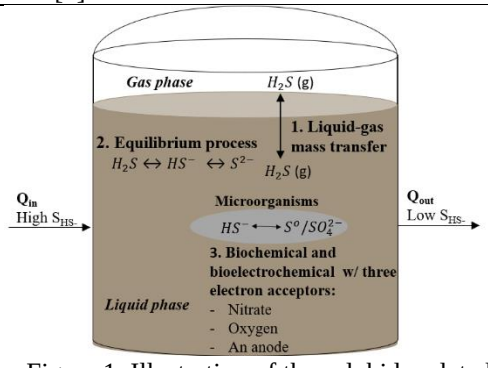

Figure 1: Illustration of the sulphide related processes implemented in the model.

2.2. Liquid-Gas transfer

The H_2S liquid-gas mass transfer was included based on the following expression used by Barrera *et al.* (2015):

$$\rho = k_{La,H_2S} \cdot (S_{H_2S} - K_{H_{H_2S}} \cdot P_{H_2S}) \quad (1)$$

Where k_{La}: gas transfer coefficient, S_{H_2S}: concentration of H_2S, P_{H_2S}: partial pressure of H_2S, and $K_{H_{H2S}}$: temperature-dependent Henry's law constant calculated with the following equation (Eq. 2):

$$K_{H\_H2S} = k_{H^0\_H_2S} \cdot R \cdot T \cdot \exp\left(\frac{\Delta H^0{}_{kH_{H_2S}}}{R \cdot 100} \cdot \left(\frac{1}{298} - \frac{1}{T}\right)\right) \quad (2)$$

Where $k_{H^0\_H_2S}$: Henry's constant at standard conditions and $k_{H^0\_H_2S}$: enthalpy of reaction for H_2S(g) to H_2S(liq).

2.3. Liquid-liquid transfer /acid-base equilibrium

Depending on the pH in the liquid, sulphide can be present as H_2S, HS^-, or S^{2-} (Eq. 3).

$$H_2S\ (liq) \overset{pK_{a1}}{\leftrightarrow} HS^-\ (liq) \overset{pK_{a2}}{\leftrightarrow} S^{2-}\ (liq) \quad (3)$$

The negative logarithm of the first dissociation constant (pK_{a1}) is close to 7, whereas a pK_{a2} from 14 is reported in the literature (Barrera *et al.*, 2015). Therefore, the concentration of S^{2-} is negligible within the pH range relevant for AD. Only the first dissociation step (H_2S/HS^-) was included in the model. The pK_{a1}-value is calculated as a function of temperature, based on Eq. 4 implemented by Broderius *et al.* (1977).

$$pK_a = 3.122 + 1132/T \quad (4)$$

Eq. 5 represents the expression incorporated for sulphide acid-base equilibrium in the model, based on the acid-base equilibrium included in ADM1 by Batstone *et al.* (2002).

$$\rho_{H_2S/HS^-} = K_{a,H_2S} \cdot S_{H_2S} - (S_{HS^-} \cdot (S_{H^+} + K_{a,H_2S})) \quad (5)$$

Where ρ_{H_2S/HS^-}: kinetic rate equation for the acid-base equilibrium, S_{H_2S} : concentration of H_2S, S_{HS^-}: concentration of HS^-, S_{H^+}: concentration of protons, and K_{a,H_2S} : acidity constant of H_2S with temperature correction.

2.4. Sulphide oxidation

The model was developed to predict biological and bioelectrochemical sulphide removal. The microorganisms oxidise sulphide with three different electron acceptors; 1) Nitrate; 2) Oxygen; and 3) A bioanode with a given potential (Fig. 2).

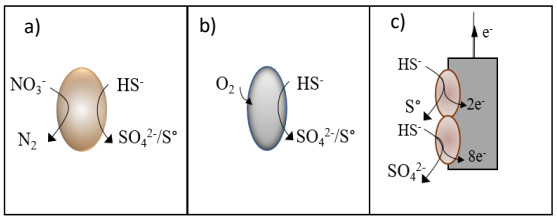

Figure 2: The biotic sulphide oxidation processes implemented in the model, with a) nitrate, b) oxygen, and c) an anode as the electron acceptors.

In this model, the basis of the growth kinetics is the multiplicative Monod established by Bae and Rittman (1996). The kinetics display dependence on both the electron donor and acceptor concentrations. The resulting formula is used to express the uptake rate in this model (Eq. 6):

$$\rho_i = k_m^o \cdot X_i \cdot \frac{S_d}{K_{s\_d} + S_d} \cdot \frac{S_a}{K_{s\_a} + S_a} \quad (6)$$

Where k_m^o: maximum uptake rate, X_i: concentration of active microorganisms, S_a and S_d are the concentration of the electron acceptor and donor, and K_{s_a} and K_{s_d}: corresponding half-saturation constants. Sulphide, S_{HS-}, is the electron donor (S_d), whereas nitrate, oxygen and the bioanode are the electron acceptors (S_a). By modifying Eq. 6, the following expressions for nitrate (Eq. 7) and oxygen (Eq. 8) were implemented in the model.

$$\rho_1 = k_m^o \cdot X_{snb} \cdot \frac{S_{HS^-}}{K_{s_{HS^-}} + S_{HS^-}} \cdot \frac{S_{NO_3^-}}{K_{s_{NO_3^-}} + S_{NO_3^-}} \quad (7)$$

$$\rho_2 = k_m^o \cdot X_{sob} \cdot \frac{S_{HS^-}}{K_{s_{HS^-}} + S_{HS^-}} \cdot \frac{S_{O_2}}{K_{s\_O_2} + S_{O_2}} \quad (8)$$

To describe the kinetics of a biotic anode, a modification of Eq. 6 is required because an electrical potential controls the bioelectrochemical reaction rate. This is accomplished by implementing a Nernst-type equation. Marcus *et al.* (2007) developed a dual-limitation Nernst-Monod kinetic expression. This expression was modified to apply for bioelectrochemical sulphide oxidation (Eq. 9).

$$\rho_3 = k_{m\_eet}^o \cdot X_{eet} \cdot \frac{S_{HS^-}}{K_{s_{HS^-}} + S_{HS-}} \cdot \frac{1}{1+\exp\left(-\frac{nF}{RT}\eta\right)} \quad (9)$$

Where F: Faradays constant, n: number of electrons transferred to the anode, η: the local potential ($E_{anode} - E_{KA}$), E_{anode}: anode potential. E_{KA} corresponds to K_{s_a} and can be determined experimentally (Markus *et al.*, 2007, Samarakoon *et al.*, 2019). In this model, E_{KA} is the reference point and was set to 0. Therefore, η is considered as the anode potential.

2.5 Stoichiometry

The stoichiometry of the relevant reactions depends on several factors, including the type of microorganisms, the ratio of electron donor to electron acceptor, system design and operational parameters. The reactions are incorporated as 100 % conversion to sulphur or 100 % sulphate. The following six stoichiometric equations were included in the model:

Nitrate:

$$HS^- + \frac{2}{5}NO_3^- + \frac{7}{5}H^+ \rightarrow S^o + \frac{1}{5}N_2 + \frac{6}{5}H_2O \quad (10)$$

$$HS^- + \frac{8}{5}NO_3^- + \frac{3}{5}H^+ \rightarrow SO_4^{2-} + \frac{4}{5}N_2 + \frac{4}{5}H_2O \quad (11)$$

Oxygen:

$$HS^- + \frac{1}{2}O_2 + H^+ \rightarrow S^o + H_2O \quad (12)$$

$$HS^- + 2O_2 \rightarrow SO_4^{2-} + H^+ \quad (13)$$

Anode:

$$HS^- \rightarrow S^o + H^+ + 2e^- \quad (14)$$

$$HS^- + 4H_2O \rightarrow SO_4^{2-} + 9H^+ + 8e^- \quad (15)$$

2.6 Parameters

Sulphide (S_{HS^-}), nitrate ($S_{NO_3^-}$), and oxygen (S_{O_2}) were included as both initial and influent concentrations. The operational parameters are presented in Table 1. The maximum sulphide uptake rate, k_m^o, is equal to μ_{max}/Y_i, where μ_{max} is the maximum microbial growth rate (Batstone *et al.* 2002). This rate depends on the microbial group, and the values vary in the literature. Other relevant parameters were obtained from the literature (Tab. 2).

2.7 Case study

A case study was performed to compare bio-oxidation of sulphide with the three different electron acceptors, and to estimate the dosage and time required to reduce the concentration to a predefined target concentration. The following base conditions were established: 1) Both the initial and inflow sulphide concentrations, S_{HS^-} , are 1.5 mM; 2) Nitrate and oxygen initial concentrations were based on the stoichiometric equations 10 and 12 with 100 % oxidation to sulphur, corresponding to 0.6 mM nitrate and 0.75 mM oxygen, and varied according to the scenarios described in 3.3; 3) Sulphide target concentration was set at 0.1 mM, which according to Figure 4a ensures a P_{H_2S} below 500 ppm with pH 7.2 and 35 ˚C temperature. The reactor pH was constant at 7.2. An initial active biomass of 0.1 mM was established in all three cases and the k_m^o was assumed to be 7.5 mole S mole^{-1} X d^{-1}.

Table 2: Parameters and constants related to the processes in Figure 1 implemented in Aquasim.

Parameter	Description	Value	Unit	Reference
$K_{s,sulphide,1}$	Half-saturation constant for sulphide oxidation, with nitrate	$4.6 \cdot 10^{-4}$	mole L^{-1}	Wanga *et al.*, 2010
$K_{s,nitrate}$	Half-saturation constant for nitrate	$1.0 \cdot 10^{-5}$	mole L^{-1}	Wanga *et al.*, 2010
$K_{s,sulphide,2}$	Half-saturation constant for sulphide oxidation, with oxygen	$1.0 \cdot 10^{-6}$	mole L^{-1}	Pokorna-Krayzelova *et al.*, 2018
$K_{s,oxygen}$	Half-saturation constant for oxygen	$1.0 \cdot 10^{-4}$	mole L^{-1}	Pokorna-Krayzelova *et al.*, 2018
$K_{s,sulphide,3}$	Half-saturation constant for sulphide oxidation with an anode	$7.0 \cdot 10^{-6}$	mole L^{-1}	Assumed
Y_i	Yield of biomass on uptake of sulphide. Used for all three types of microbes	0.03	mole S_X mole S^{-1}	Assumed
F	Faraday's constant	96485	C mole e^{-1}	-
R	Ideal gas constant	8.314	J $mole^{-1}$ K^{-1}	-
T	Temperature	288-328	K	-
η	Local potential	-0.1 to +0.3	V	-
$k_{H^0\_H_2S}$	Henry's constant at standard conditions	$9.86 \cdot 10^{-2}$	M bar^{-1}	Sander, 1999
$k_{H^0\_N_2}$	Henry's constant at standard conditions	$6.42 \cdot 10^{-4}$	M bar^{-1}	Sander, 1999
$k_{H^0\_CH_4}$	Henry's constant at standard conditions	$1.38 \cdot 10^{-3}$	M bar^{-1}	Sander, 1999
$k_{H^0\_CO_2}$	Henry's constant at standard conditions	$3.55 \cdot 10^{-2}$	M bar^{-1}	Sander, 1999
$\Delta H^0{}_{Ka\_H_2S}$	Enthalpy of reaction $HS^- + H^+ \rightarrow H_2S$	21670	J $mole^{-1}$	Batstone *et al.*, 2002
$\Delta H^0{}_{Ka\_CO_2}$	Enthalpy of reaction $CO_2 \rightarrow HCO_3^-$	7646	J $mole^{-1}$	Batstone *et al.*, 2002
$\Delta H^0{}_{KH\_H_2S}$	Enthalpy of reaction $H_2S(liq) \rightarrow H_2S(g)$	-17459	J $mole^{-1}$	Sander, 1999
$\Delta H^0{}_{KH\_CO_2}$	Enthalpy of reaction $CO_2(liq) \rightarrow CO_2(g)$	-19410	J $mole^{-1}$	Batstone *et al.*, 2002
$\Delta H^0{}_{KH\_CH_4}$	Enthalpy of reaction $CH_4(liq) \rightarrow CH_4(g)$	-14240	J $mole^{-1}$	Batstone *et al.*, 2002
$\Delta H^0{}_{KH\_N_2}$	Enthalpy of reaction $N_2(liq) \rightarrow N_2(g)$	-10808	J $mole^{-1}$	Sander, 1999
k_{La}	Mass flux coefficient	200	d^{-1}	Batstone *et al.*, 2002
k_{dec}	Decay rate of sulphide oxidising microbes	0.048	d^{-1}	Sun *et al.*, 2017

3. Results and discussion

3.1. Identification of key parameters

For the model's practical application, it is important to identify the key parameters which have the highest impact on the three most central state variables; 1) The H_2S-concentration in the headspace, $S_{H_2S;}$ 2) The concentration of sulphide in the liquid, $S_{HS}-$; and 3) The concentration of active biomass, $X_{sob/snb/eet}$, as a function of growth and decay. This was accomplished through both a sensitivity analysis and dissociation- and air-water equilibrium- calculations. The sensitivity analysis was performed with the sensitivity function in Aquasim. The dissociation- and equilibrium calculations are additional tools for developing the model and not a direct part of the model in Aquasim.

3.1.1 Sensitivity analysis

The sensitivity analysis indicates that the concentration of hydrogen sulphide, S_{H2S}, in the headspace displays the highest sensitivity towards Henry's law constant, K_{H,H_2S}, followed by the mass transfer coefficient, kL_a. K_{H,H_2S} is dependent on T, whereas kL_a vary depending on different properties, including T, mixing degree, and liquid properties (Yongsiri *et al.*, 2004). With multiplicative Monod kinetics, $S_{HS}-$ displayed the highest sensitivity towards the maximum uptake rate, k_m^o, and low sensitivity towards $K_{s,nitrate}$ $K_{s,sulphide}$, and T. The k_m^o-value also exhibited the highest impact on $S_{HS}-$ with Nernst- Monod kinetics, while $S_{HS}-$ displayed low sensitivity towards the anode potential (further discussed in chapter 3.2). The concentration of biomass, X_i, presented the highest sensitivity towards Y_i and k_m^o-value as expected, in addition to being highly dependent on the substrate concentrations. The pH

was not included in the sensitivity analysis due to the dependence on the concentration of protons, which is a state variable.

The sensitivity analysis revealed that the model is sensitive to k_m^o. This maximum specific uptake rate depends on the microbial species (Barrera *et al.*, 2015). To study the parameter's effect on the sulphide oxidation rate, simulations were performed with k_m^o -values corresponding to a μ_{max} in the range of 0.075 d^{-1} to 1.5 d^{-1} (Fig. 3). Too low uptake rates (Fig. 3: k_m^o= 2.5 and 5 mole S $mole^{-1}$ X d^{-1}) cause inefficient sulphide removal, sulphide accumulation, and potentially high volatilisation of H_2S(g) with both multiplicative Monod- and Nernst-Monod kinetics. The effect of the uptake rate is more prominent with a lower concentration of active biomass (results not included).

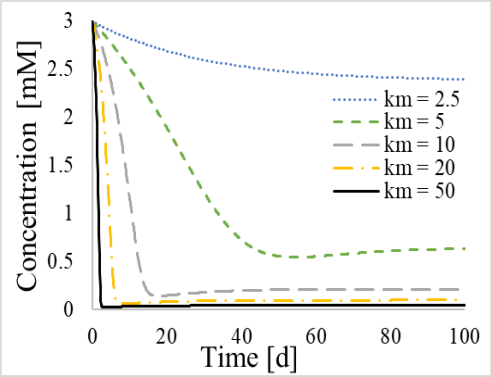

Figure 3: Sulphide oxidation with different uptake rates, here with nitrate as the electron acceptor. Initial biomass: 0.01 mM. Nitrate dosed as both initial and continuous supply (see discussion in 3.3).

The simulation results illustrate that access to a microbial group with an efficient uptake rate for sulphide increases the system's efficiency. In practice, this can be achieved with specialised and adapted microbial cultures or by increasing the concentration of active biomass.

3.1.2. Acid-base equilibrium and air-water equilibrium calculations

The main purpose of the acid-base equilibrium and air-water equilibrium calculations was to study the effect of T and pH, which are two important operational parameters. The dissociation of sulphide (Eq. 3) is highly dependent on pH and temperature, as demonstrated in Figure 4. At pH 6.8 and T = 35 °C, the H_2S/HS^- - ratio is 50/50. At a constant pH, a decrease in T causes an increase in the proportion of H_2S. In contrast, increasing the pH to 8 reduces the proportion of H_2S(liq) to less than 10 % for the whole temperature range.

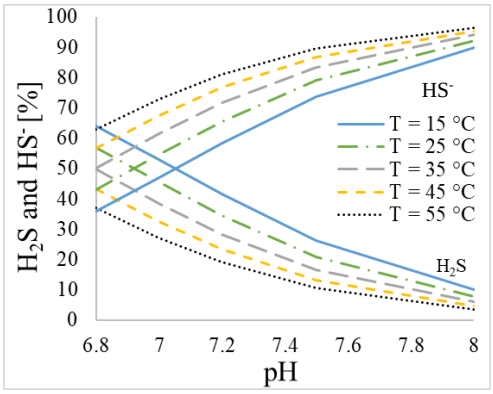

Figure 4: Equilibrium concentration of H_2S and HS^- as a function of pH and T

The partial pressure of H_2S(g), P_{H_2S}, was estimated with air-water equilibrium calculations for different total sulphide concentrations in the liquid phase. The calculation method was modified from Hvitved-Jacobsen *et al.* (2013) to account for dissociation, pH- and temperature dependence. The results illustrate that within the operational ranges for AD processes, the pH has a more significant impact on P_{H_2S} compared to temperature (Fig. 5a and b). As an example, the P_{H_2S} at T = 15 °C is 77 % of the P_{H_2S} at T = 55 °C, whereas an increase in pH from 6.8 to 8 reduces the P_{H_2S} to 12 % of the P_{H_2S} at pH 6.8. Despite the higher proportion of sulphide present as H_2S in the liquid phase at lower temperatures, an increase in temperature causes an increase in partial pressure of H_2S in the gas phase. This can be attributed to the increase in Henry's law constant, K_{H,H_2S}, with an increase in temperature.

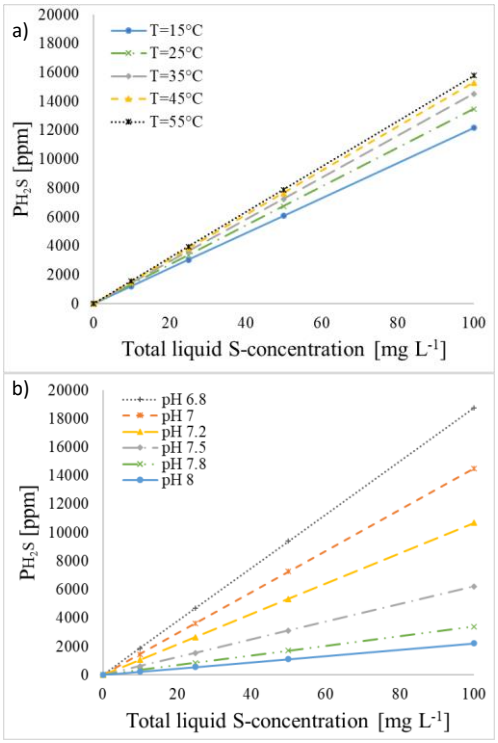

Figure 5: Partial pressure of H_2S estimated with air-water equilibrium calculations, as a function of a) T and b) pH.

Figures 5a and b illustrate that even low total sulphide concentrations in the liquid can cause high H_2S concentrations in biogas. The values should be considered maximum levels as the calculation assumes that all the H_2S in the liquid phase can volatilise. Due to different physical phenomena, including sulphide precipitation and biological or chemical oxidation, the actual values will be lower (Hvitved-Jacobsen *et al.*, 2013). However, due to the concerns and regulations related to releasing $H_2S(g)$, this simple method helps predicting the potential concentration of H_2S in the biogas.

3.2. Bioelectrochemical oxidation and the Nernst-Monod term

The anode potential and the number of electrons transferred from the microorganisms to the anode surface are important parameters in BESs. To study the impact of the anode potential, simulations were performed with an increase in the local potential from -0.1 to +0.3 V (stepsize = 0.05 V) (Fig. 6). By convention, n is set to 1, as yield and stoichiometric parameters can be defined per electron. The uptake rate of sulphide increases with an increase in the potential up to a certain threshold (here: 0.1- 0.15 V). With a local potential of 0.1 V or higher, the Nernst-Monod term is close to 1. Consequently, increasing the potential further would not improve the oxidation rate with the current model implementation. With a potential of 0.1 V or higher, Nernst-Monod kinetics resembles single Monod kinetics, as the uptake rate mainly depends on electron donor consumption (substrate consumption).

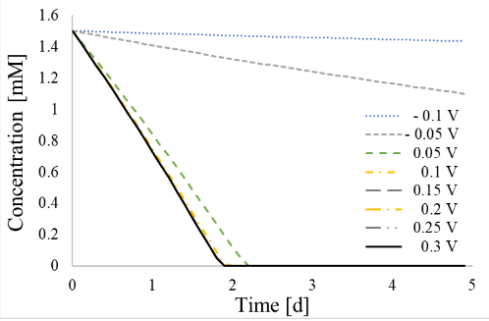

Figure 6: Bioelectrochemical sulphide oxidation rate with different local potentials. Initial biomass: 0.1 mM.

3.3 Case study: practical application of the model

The case study illustrates the differences between the three bio-oxidation processes. The simulation results show that the target concentration is reached within 3.9 days with nitrate, 2.4 days with oxygen, and 1.7 days with an anode potential of 0.1 V (Figures 7a, b, and c) under the given conditions.

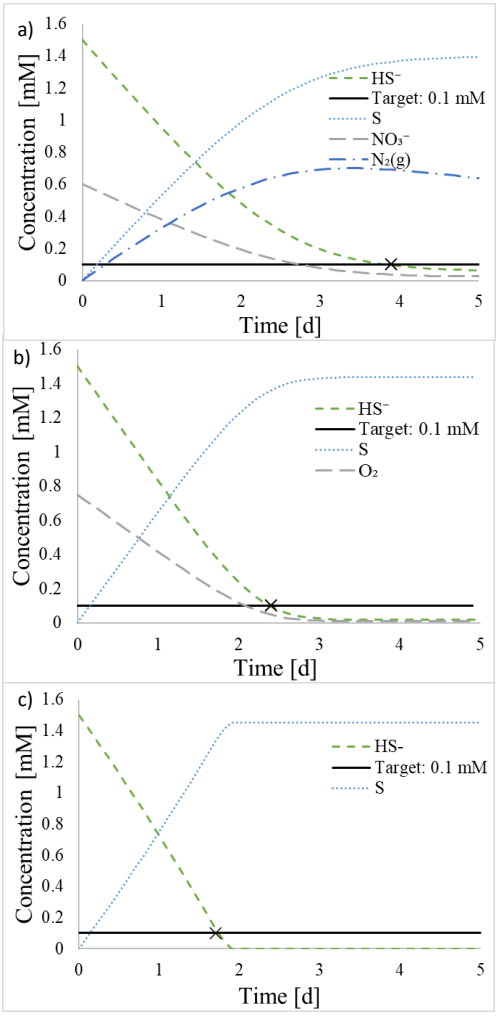

Figure 7: Estimation of required time until the target concentration is reached with a) nitrate, b) oxygen, and c) anode as the electron acceptors.

The estimated nitrate dosage required to ensure a sulphide concentration lower than 0.1 mM in continuous operation is an initial addition of 55.55 kg and a continuous supply of 2.60 kg d^{-1} with the assumed conditions. The corresponding oxygen dosage is an initial supply of 35.84 kg and a continuous supply of 1.68 kg d^{-1}. However, supplying high initial concentrations is unrealistic, as the microorganisms can be negatively affected by too high dosages of nitrate or oxygen. Therefore, simulations were repeated without supplying the initial dosage of nitrate or oxygen. The results show that a steady-state concentration of sulphide below the target concentration of 0.1 mM can be reached in 65.0 days and 76.1 days with a continuous supply of 1.68 kg d^{-1} oxygen and 2.60 kg d^{-1} nitrate, respectively (Fig. 8a and b). However, the required time will depend on different parameters, including the dosage, the microbial uptake rate (see Fig. 3), and the microbial density. By increasing the oxygen

dosage and nitrate dosage by a factor of 1.5, the target concentration is reached in 21.8 and 22.7 days, respectively (results not included). This is a considerable reduction in the required time to reach the target concentration, and it illustrates that the supplied dosage has a significant impact on the simulation results.

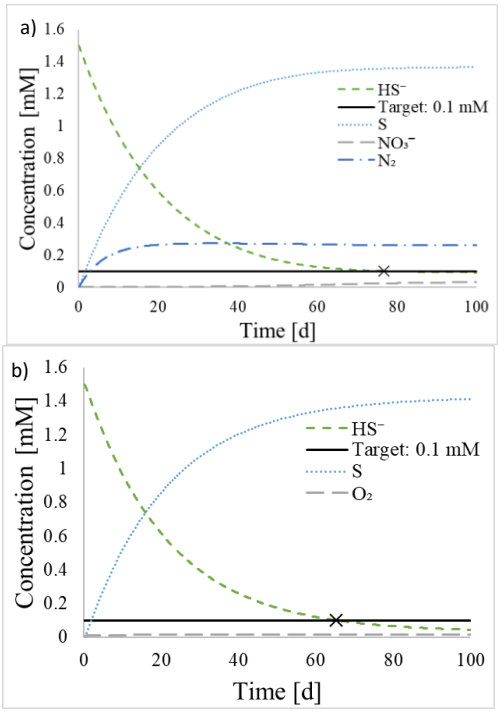

Figure 8: Sulphide removal in continuous operation mode with a) nitrate and b) oxygen.

An increased oxidation rate can be obtained by increasing the initial biomass concentration, using a microbial group with a higher maximum uptake rate, or gradually increasing the nitrate or oxygen dosage. Repeated simulations showed that by increasing the initial biomass from 0.1 to 1 mM, the target concentration of 0.1 mM sulphide was reached in less than 60 days, with nitrate or oxygen as the electron acceptors (results not included). Despite the faster sulphide removal obtained, the oxidation rate was restricted by the supply of the electron acceptor. Alternatively, by increasing the nitrate dosage stepwise every fifth day by 0.06 mM (10 % of the initial dosage), the target sulphide concentration was reached in 29.7 days. The corresponding number of days with oxygen (an increase of 0.075 mM every fifth day) was 28.7 days (results not included).

This case study illustrates the main advantage of developing a simple simulation tool for studying bio-oxidation processes and reactor operations. By adjusting the parameters in the model according to the reactor operation, different strategies could be evaluated. Simulation results can be obtained quickly without negatively affecting the reactor or the AD processes. Obtaining the same results experimentally would be costly, time-consuming, and potentially lead to reactor failure. An additional advantage is that the calculations can be based on both the concentration of H_2S(g) in the headspace or HS^-(liq) in the effluent streams from plants.

3.4 Evaluation of the model and further model development

The overall goal of the model is to develop a simple tool for estimation of H_2S(g) in biogas and to estimate the time, chemical dosage, or anode potential required to reduce HS^-(liq), H_2S(liq) and H_2S(g) to acceptable levels. At this modelling stage, a study of the substrate uptake rates and identification of the most sensitive parameters were accomplished. This initial modelling work provides the framework for further development of the model. However, certain model limitations have been identified at the current stage. To improve the model, other anaerobic microbial processes and competing reactions should be implemented. These processes can affect the oxidation rates through competition for substrates and inhibition. The proposed improvements would be more realistic, as the oxidation processes at the current modelling stage are only affected by the substrate concentrations, anode potential, and the specific microbial activity.

To improve the model implementation of bioelectrochemical sulphide oxidation, incorporation of different stoichiometry and other bioanode-related processes would be valuable. This includes biofilm thickness, mass transfer limitations, competing reactions at the bioanode surface, and electron transfer limitations (due to different electron sinks) (Pham *et al.*, 2009). A further study of anode potential implementation can improve the model, as the anode potential has a lower impact on the simulated bioelectrochemical sulphide oxidation rate than expected. Additionally, this model only considers the bioanodic reactions. Sulphide oxidation can contribute positively to biocathodic processes such as methane production by generating electrons and protons in a BES (Jiang *et al.*, 2014; Dykstra *et al.*, 2021). Modelling a complete bioelectrochemical reactor would require implementation of both the oxidation and the reduction processes. In this modelling work, the goal was to study sulphide removal. Therefore, only the bioanodic process was studied.

Lastly, different kinetic constants and parameters can be found in the literature related to the sulphide routes and the specific microbial groups. The variation will affect the simulation results. Therefore, calibration and validation of the model

with data from real plants will improve the model further.

4. Conclusion

The model provides a simple tool in Aquasim for studying H_2S liquid-gas mass transfer and sulphide bio-oxidation with three different electron acceptors: 1) Nitrate; 2) Oxygen; and 3) A bioanode with a given potential. Multiplicative Monod kinetics (nitrate and oxygen) and Nernst-Monod kinetics (bioanode) provide the framework for the respective biotic sulphide oxidation processes.

A sensitivity analysis revealed that the model is most sensitive toward the maximum microbial uptake rate, k_m^o. Low k_m^o-values can result in inefficient sulphide removal, accumulation of sulphide, and high concentrations of H_2S(g). A local potential of 0.1-0.15 V is defined as the plateau potential with Nernst-Monod kinetics in the current study, as further increasing the potential did not improve the sulphide oxidation rate.

At the current stage, the model can be used to study the defined processes. However, certain model limitations have been identified. Therefore, the model needs further improvements to function as a simulation tool for studying sulphide-related processes in AD and calculate the required dosage and oxidation time in full-scale processes.

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