Title: Modelling an aerobic biotrickling filter for biogas desulfurization through a multi-step oxidation mechanism

Abstract: A dynamic model describing physical-chemical and biological processes for the removal of high loads of H2S from biogas streams in biotrickling filters (BTFs) was developed, calibrated and validated for a wide range of experimental conditions in a lab-scale BTF. The model considers the main processes occurring in the three phases of a BTF (gas, liquid and biofilm) in a co-current flow mode configuration. Furthermore, this model attempts to describe accurately the intermediate (thiosulfate and elemental sulfur) and final products (sulfate) of H2S oxidation. A sensitivity analysis was performed in order to focus parameters estimation efforts on those parameters that showed the highest influence on the estimation of the H2S removal efficiency, the accumulated mass of sulfur and the sulfate concentration in the liquid phase. Biofilm and liquid layer thicknesses, specific growth rate of biomass over elemental sulfur and the H2S global mass transfer coefficient were the parameters that showed the highest influence on model outputs. Experimental data for model calibration corresponded to the operation of the BTF under stepwise increasing H2S concentrations between 2000 and 10000 ppmv. Once the model was calibrated, validation was performed by simulating a stationary feeding period of 42 days of operation of the BTF at an average concentration of 2000 ppmv and a dynamic operation period were the BTF was operated under variable inlet H2S concentration between 1000 and 5000 ppmv to simulate load fluctuations occurring in industrial facilities. The model described the reactor performance in terms of H2S removal and predicted satisfactorily the main intermediate and final products produced during the biological oxidation process.

Response to Reviewers: ANSWERS to Reviewer's comments to the Author:

We deeply thank the reviewer comments and observations since most of them helped to improve the quality and readability of the manuscript. We have addressed all comments point by point as detailed below. Changes in the manuscript are indicated with a P (page) and L (line) code.
Reviewer #1: Overall, I think this is a good paper. Some comments: Perhaps consider the mass transfer at the interfaces. Meaning, there will be some transfer at the gas to liquid and liquid to biomass interfaces. Also, I think it would be meaningful to consider wetted vs non wetted biofilms and how this would effect your model; having worked with biotrickling filters, there are differences in effluent concentrations when trickling rates are high enough to wet a decent fraction of the packing material.

Answer:

We thank the reviewer by his short but very interesting and useful comments. We agree with the reviewer that mass transfer at the interfaces must be considered in order to have a more realistic approach of the model. Regarding the first comment about gas-liquid mass transfer, a global mass transfer coefficient referred to the liquid phase (KL) was considered in this work (equation 3). Thus, such global coefficient already included the mass transfer both in the gas boundary layer an in the liquid boundary layer (assuming the concept of the double-film theory). In any case, the schematic of the model in the former version (figure 3) was confusing since it was drawn as if no mass transfer resistance occurred in the gas phase.

Derived from the reviewer comment, we thought interesting to include some short sentences about the contribution of both resistances to the overall G-L transport resistance. The individual mass transfer coefficients for both gas species oxygen (O2) and hydrogen sulfide (H2S) were determined using the Billet and Schultes correlations for kg and kl. Result showed that the contribution of the gas phase was only a 0.18% for O2 and a 9.7% for H2S. To clarify, the following modifications and comments were added:

(P3L24) "However, biogas desulfurization requires of much longer gas contact times and, consequently, lower gas velocities that may increase mass transfer resistance in the gas phase."

"Gas-liquid mass transport is described by a gas-liquid global mass transfer coefficient referred to the liquid phase (KL) that considers both the individual gas and liquid mass transfer resistances". This comment was added both in the description of model assumptions (assumption 6) in section SM2 of the Supplementary Material file and in section 2.2 of the main manuscript (P9L1)

The schematic of the model (now in figure 1) has been modified to show the concentration change in the gas boundary layer when approaching the G-L interface.

(P16L14) "The "K" ("L," "O" _"2") was determined using the Billet and Schultes correlations [34] for the gas and liquid individual mass transfer coefficients kg and kl, respectively, which was in close agreement with "K" ("L," "O" _"2") determined by Dorado et al. [9]. It is worth highlighting that only the liquid-side resistance was significant since based on Billet and Schultes correlations the contribution of individual mass transfer resistances in the gas phase to the overall resistance for both gas species oxygen (O2) and hydrogen sulfide (H2S) were only 0.18% and 9.7% for O2 and H2S, respectively."

Regarding to the second comment about liquid-biofilm mass transfer, we included a diffusion term described by Fick’s law in the liquid phase in the former version of the manuscript (equation 4). We agree with the
reviewer about its significance since we really verified running simulations without this term that this term was completely necessary to properly fit our experimental data. We did not deeply show with simulations that importance in the manuscript but to clarify, the following comments were added:

“Mass transfer resistance in the liquid-biofilm interface was described by Fick’s law considering that the whole thickness of the liquid phase acted as the liquid boundary layer for mass transport resistance” This comment was added both in the description of model assumptions (assumption 7) in section SM2 of the Supplementary Material file and in section 2.2 in the main manuscript (P9L12)

Regarding the modeling approach about the use of fully wetted or wetted/non-wetted biofilms we agree with the reviewer that this would have a clear impact due to the changing amount of water in the packed bed when the TLV is modified. This is not trivial and no clear consensus exists about the use of one or another modeling approach since lumping of certain parameters may result in similar modeling results. A careful analysis from a modeling perspective must be performed. However, this was not the scope of the manuscript since the TLV was kept constant throughout the study. The following sentence was added:

(P4L3) “Despite no clear consensus has been reached so far and a careful analysis from a modeling perspective must be performed, modeling of biotrickling filters using a wetted/non-wetted biofilm approach seems necessary when the TLV is modified due to the changing amount of water in the packed bed.”

Reviewer #2: This contribution presents a model for an aerobic biotrickling filter (BTF) for biogas desulfurization. The model applied to describe the biological processes is the one from Mora et al. [27]. The BTF setup and experimental results regarding the influence of trickling liquid velocity and flow pattern were presented before, by [26]. So the main novelty of this contribution lies in modelling the BTF as such, and in the model calibration and validation based on experimental data. Part of the experimental data used for calibration were published in [26] (Figure 4A and 5A&B from this contribution overlap with Figure 2a from [26]).

Overall, I think the objectives and novelty of the paper should be stated more clearly. The introduction needs to be rewritten in this respect. The results and discussion need to be more to the point. The whole text could be written more compactly without loss of essential information - in fact it could make the message more clear. Figures can be made more clear; the number of figures can be reduced; a graphical representation from the information from Table 2 would allow easier interpretation. The generality of the presented results and the general added value of this contribution needs to be elaborated on, given that the model is calibrated and validated for a specific model set-up.

Note: part of the results in this contribution were previously presented at the EMChIE2015 conference. In my view, they are definitely sufficiently interesting for a journal publication, but that conference paper was written more to-the-point and had a clearer structure than this contribution - so please reconsider it.
The present manuscript contains quite some typos and English language errors.

Answer:
We agree with the reviewer comments, thus, we have tried to focus the revised version on the BTF modeling. We want to stress that, in our opinion, the novelty of the paper was already clearly stated in the first version of the manuscript; however, the introduction has been modified following the reviewer comments in order to stress the novelty of this work and the contribution on BTF desulfurization modeling. The numbers of figures has been reduced, considering the specific comments of the reviewer. Table 2 (sensitivity results for key BTF model parameters) was not represented graphically since different figures would be need in order to represent the sensitivity value for each output variable for all the model parameter studied, and therefore a table was considered more appropriate to show in a compact manner the sensitivity analysis results.

SPECIFIC COMMENTS

1-Abstract
line 44: 'respirometric techniques': this is not the focus of this paper but was addressed by Mora et al. [27]
Answer:
(P1 L20) The sentence was removed

2- Abstract: lines 46-51: no need to give a definition of sensitivity analysis in the abstract. Leave out or specify output parameters and process variables.
Answer:
The output process variables studied were included in the sentence as follows:
(P1, L21) "...showed the highest influence on the estimation of the H2S removal efficiency the accumulated mass of sulfur and the sulfate concentration in the liquid phase."

3-Introduction
The introduction should introduce the subject and identify knowledge gaps that will be addressed in this contribution. I expect the introduction of BTF for H2S removal from biogas and the modelling of BTF in general.
Answer:
Knowledge gaps were already stated in the former version of the manuscript (now in P3,L6-24). According to the reviewer suggestions, the introduction was modified including a brief introduction about BTF for H2S removal from biogas. The following paragraph was added in the introduction:
(P2, L15) "Obtaining energy from non-renewable sources is becoming too expensive or too environmentally damaging nowadays. A energy source with high potential for green energy production is biogas. However, in order to have a suitable biogas utilization, impurities such as H2S and reduced sulfur compounds (RSC) produced during the anaerobic fermentation of S-bearing organic molecules must be removed [1]. Removal of H2S is strictly necessary to avoid corrosion of internal combustion engines during co-generation processes as well as for proper performance of further biogas upgrading technologies [2]. Biological technologies such as biotrickling filters (BTF) have demostrated to be a suitable, competitive treatment technology for biogas conditioning when compared to physical-chemical technologies. However, main effort has been focus on experimental works, studying different pollutant loads [3], using different packing materials [4], different oxygen mass transfer devices [5], pH conditions [6] or
gas-liquid flow pattern [7]. Tough process modeling has shown to be a crucial tool to evaluate the technical [1] and economical feasibility [2] of biological processes prior full-scale implementation, few efforts have been made in this direction on biogas desulfurization in BTFs."

4-Introduction
References cited should either be applicable to this topic or be very general; this is not the case for [1]–[4]. Also [5]–[8] seem to be 'thrown in'. Specify what the individual references are about rather than listing references all together.
Answer:
General references or not directly applicable to the topic have been removed. Former paragraph starting from P3L4 until P3L8 has been removed. In general, references have been cited individually and an individual explanation has been provided instead of referencing all together at the end of the sentence. However some references have been kept grouped where the sentence points to a common fact.

5-Introduction
The introduction on biodegradation mechanism and kinetics (p3 line 41 till p4 line 37) is not relevant for the introduction since the biological model was not developed in this contribution. At most, it could be summarized in the model description
Answer:
The introduction on biodegradation mechanism and kinetics has been removed from the introduction section and was summarized in the kinetic model description. Paragraph starting on P4L20 until P5L9 has been removed from the introduction section and summarized on section 2.2.2 (P11L4 to P12L2).

6-Introduction
part. p5 lines29–37 do not belong in the introduction either.
Answer:
This paragraph has been also moved to kinetic model description on P11.

7-Materials and Methods
Before giving details on the reactor dimension and packing, specify the general layout and operating principle (p5, line 48).
Answer:
The operating principle of the reactor is now explained just at the beginning of the section and rewritten as follows:
P5L22: "A laboratory-scale BTF reactor, with an ancillary unit for air supply, was used in this study to remove high loads of H2S from biogas mimics streams (Fig.1). The biogas mimics consisted in controlled mixtures of H2S and nitrogen (N2) fed at the top of the BTF (1). An air flow (2) was firstly fed to an aeration column (3) for air supply to increase the dissolved oxygen (DO) concentration in the liquid phase. Exhaust air (4) from the aeration column was fed at the top of the BTF under a co-current flow pattern and mixed with the biogas inlet stream at an O2/H2S supplied ratio of 41.2 (v v-1). After biological degradation on the BTF bed (5), the treated biogas stream (6) leaves the reactor. The liquid phase was continuously recycled from bottom-to-top of the BTF at a trickling liquid velocity (TLV) of 4.4 m h-1 (7). The liquid recirculation line (8) was previously oxygenated in an aeration column. The DO concentration in the recycle and purge lines was monitored in-situ in all the experiments. The reactor pH was also controlled at pHs of around 6.5 and 7 using an ON/OFF control system by automated addition of NaOH 1M or HCl 1 M. An empty bed residence time (EBRT) of 118 s and an average hydraulic retention time (HRT) of 30 ± 4 h were maintained
throughout the study by regulating the purge pump (9) and the mineral medium pump (10). Regarding the packing bed characteristics, the reactor diameter was 7.14 cm with a packed bed volume of 2.80·10⁻³ m³ (Vbed). Polypropylene Pall rings of 15.9 mm diameter (MACH engineering products, USA) with a specific surface area of 354 m² m⁻³ were used.”

8-Materials and Methods
Explicitly specify the experimental dataset and the periods 1-2-3. Are these periods consecutive?
Answer:
Experimental conditions presented on data provided on Table 1 (H2S inlet concentration, H2S Loading Rate, O2/H2S volumetric ratio) are commonly enough to describe the operating conditions to facilitate the comparison between different systems with different dimensions. Periods 1-2-3 were not consecutive, all experiments were performed in between a time span of 15 months. The following phrase was added to clarify:
(P7L10) “Periods of table 1 does not correspond to consecutive periods, all experiments were performed in between a time span of 15 months.”

9-Materials and Methods
Specify gas flow rate (constant for all experiments?).
Answer:
Gas flow rate is not specified since the key parameter is the gas contact time (EBRT). The gas flow rate can be determined relating the EBRT and the volume of the packed bed. The following phrase was added in order to clarify this:
(P7L4) “...in the lab-scale BTF set up (Fig. 1) operating at constant EBRT and constant biogas flow.”

10-Materials and Methods
Is O₂ concentration varying - O₂/H₂S variations only caused by varying H₂S?
Answer:
The O₂/H₂S volumetric ratio varied only due to H₂S inlet concentration increase since the air flow rate was kept constant in this work. The following phrase was added in order to clarify this:
(P7L4) “...in the lab-scale BTF set up (Fig. 1) operating at constant EBRT and constant biogas flow.”

11-Materials and Methods
Separate description of experimental setup and the model (lines 7, 12 and 42 do not fit here; also reconsider the paragraph starting on p6, line 48).
Answer:
Lines describing model variables on experimental setup description have been removed.

12-Materials and Methods
Figure 1 and Figure 3 could be left out and replaced by (and extended version of) Figure S2, detailing how the different layers in the BTF are described - the description on p7 referring to different indices is difficult to follow without a figure.
Answer:
Figure 1 and 3 and Figure S2 have been merged in order to have a complete description in a single figure (new Figure 1) to help the comprehension of the BTF set up, BTF discretization and biological mechanisms of H₂S biological oxidation.
13-Materials and Methods
The model description could be written more concisely by describing the meaning of the different balances and by listing the parameters in a 'nomenclature' section.
Answer: The parameters have been listed in a nomenclature section.

14-Materials and Methods
2.2.2. 'Kinetic model'. Not only kinetic, but also stoichiometry, right? Rather entitle this section 'modelling biological and chemical sulfur conversions'.
Answer: Right, the name has been changed. To avoid confusion with elemental sulfur, S-compounds has been used instead of sulfur. (P11L3) “2.2.2 Modeling of biological and chemical S-compounds conversions”

15-Materials and Methods
It would be a strong added value to summarize the biological reactions in Gujer matrix format, to have a clear overview of the state variables and the model stoichiometry and kinetics.
Answer: The model proposed by Mora et al. 2016 to describe the multi-step sulfide oxidation bioprocess has been summarized in the Gujer Matrix format in Tables 2 and 3 in which the stoichiometry and the kinetic expressions, respectively, are described.

16-Materials and Methods
This whole section needs to be significantly shortened, given that the model was developed by Mora et al. [27].
Answer: We agree with the reviewer. Since part of the introduction related to general considerations about biodegradation mechanism and kinetics has been moved to this section (see answer to comment #5) the description of the model by Mora et al has been moved to the supplementary material Section SM-4.

17-Materials and Methods
p11, line 28 'no previous works has intended to model such range of intermediate products of biological sulfide oxidation'. If this is a major novelty, it should already be stated in the introduction and. I would also expect a discussion later in the article on whether or not it is important to consider a multi-step oxidation mechanism.
Answer: This sentence has been moved to the introduction section (P5L16). The discussion about this major novelty has been added as a final discussion on the result section as follows:

(P21 L2) “Especially, accurate model predictions under high H2S-LR and O2 limiting conditions (period 1) could be useful for predicting elemental sulfur accumulation in industrial BTF installations. Therefore, maintenance tasks can be strategically planned”

18-Materials and Methods
2.3 Model implementation.
pl3 'set of PDE was discretized'. This information comes late - needed to interpret mass balances.
Answer:
Yes. This paragraph has been moved to (P8L8) in the model development section just before the mass balances.

19. Results and discussion
3.1 Give a definition of the sensitivity function. Did you consider relative or absolute sensitivity? This will of course impact the comparability of the numbers obtained.
Answer:
Sensitivity function definition was included as follows:

(P13L8) “Sensitivity was assessed by increasing and decreasing model parameters by 10% and comparing the relative change of the output variables to a relative change of the model parameter.”

Also the word “relative” was added before “sensitivity analysis” throughout the manuscript (mostly in section 3.1, page 13) to indicate that the relative sensitivity was assessed.

20. Results and discussion
Also reconsider the structure of this section, emphasizing the main points. First describe most sensitive parameters, then the least sensitive, afterwards discuss.
Answer:
In the former version of the manuscript the most sensitive output variables were firstly described and, afterwards, the less sensitive. Also, the discussion was already based only on the most sensitive parameters (with higher relative sensitivity function value than 0.1). However, the first sentence in P13L24 was changed to follow the same structure from more to less sensitive variables throughout the discussion.

(P13L24) “The most sensitive output variables were the RE and CL,SO42- that exhibited comparable sensitivities between them at a 10% increase while mS0 was the less sensitive output variable due to its cumulative nature.”

21. Results and discussion
p15 'O2 transport rather than H2S transport is the limiting step'. But O2 transport and H2S transport take place in separate reactors, right?
Answer:
The goal of using an external aeration column was to improve the O2 gas-liquid mass transport before air enters the BTF column. The total amount of oxygen supplied to the BTF was the contribution of that supplied to the liquid phase in the aeration column plus the excess air from the aeration column that passed through the packed bed of the reactor. The contribution of the O2 transferred in the aeration column was estimated to be between 10 and 30% of the total (aeration column + reactor) O2 transferred. This discussion has already been made in previous works by Lopez et al. No changes were made to the manuscript.

22. Results and discussion
3.2 The first paragraph (starting on p16 line 49) rather belongs to 'Materials and methods'.
Answer:
The paragraph was moved to the Materials and Methods section (now in P12L10)

23 Results and discussion
Since Kmax is the relation between the maximum amount of elemental sulfur that could be accumulated inside SOB cells before this accumulation completely blocked the biological sulfide consumption such maximum amount of elemental sulfur was determined using the substrate switch constant (Kmax) and the biomass concentration estimated by the model (X) according to K_max=m_(S^0 max)/X. This comment was added to the manuscript as:

(P16L7) “Since Kmax is the relation between the maximum amount of elemental sulfur that could be accumulated inside SOB cells before this accumulation completely blocked the biological sulfide consumption, this maximum amount of elemental sulfur was determined using the substrate switch constant (Kmax) and the biomass concentration estimated by the model (X) according to K_max=m_(S^0 max)/X. Thus, under the calibration conditions, a maximum amount of 157 g of elemental sulfur could be accumulated inside SOB cells, well above the amount of elemental sulfur produced.”

24. Results and discussion

Clarify that the results presented in Fig4 and Fig5 are the model calibration results (also in caption Fig 4).

Answer:

Caption in figure 4 was changed. The sentence in the manuscript was changed to:

(P17L4) “In Fig. 3 and Fig. 4 experimental results and model predictions of the effect of stepwise LR increases due to H2S inlet concentration increases corresponding to the model calibration period are presented”.

25. Results and discussion

line 59 'Fig 4'. Where to look exactly?

Answer:

Truly, in Figure 4 (now Figure 3) there was no RE plotted but the H2S concentration. The sentence was rewritten as follows:

(P21 L21) “Experimental data in both figures indicate that the system was able to remove almost 100% of H2S inlet concentration at all H2S-LR (Fig. 3A and 3B).”

26. Results and discussion

'Sulfate concentration increases during steady state'. If the concentration changes, steady state has not yet been reached. What causes the change - do you expect it to keep going on?

Answer:

We agree with the reviewer. We meant “stationary feeding period” instead because the inlet conditions were constant. In fact, a BTF hardly reaches steady-state conditions since there is biomass growth, changes in the preferential paths inside the packed bed etc... Pseudo-steady state conditions were replaced by stationary feeding period throughout the manuscript.

27. Results and discussion

'Overall, the model described processes occurring in the three phases'. Specify which figures correspond to which phase.

Answer:

The sentence was confusing. The sentence now reads as:
Overall, the model showed to be valid to describe the main processes occurring in the three phases of a BTF, gas phase (Fig. 3A and 3B), liquid phase (Fig. 4A) and solid phase as elemental sulfur (Fig. 4B) in a co-current flow mode configuration.

28. Conclusions
The conclusions are too general. Specify conclusions related to the model set-up, calibration and validation separately.
Answer:
The conclusions have been modified, describing separately each part of the work from the sensitivity analysis until the constant feeding validation period and the dynamic validation period.
Most of this section has been rewritten as follows:

…… A preliminary assessment through a relative sensitivity analysis allowed determining the most sensitive parameters of the model. Parameters related to O2 mass transport exhibited a larger influence to model output variables considered (RE, CL, SO42- and mS0). The proposed model was calibrated using experimental data, which allowed describing accurately the outlet H2S concentration profile along the BTF bed during H2S-LR increments. Besides describing properly sulfate production, elemental sulfur, the main intermediate product during H2S oxidation, was correctly predicted. Mass transfer parameters (δB, δL, KL,H2S) and kinetic parameters (X, μmax,2) were estimated during BTF model calibration.

Moreover, the BTF model was validated under a stationary feeding period and a dynamic H2S-LR period. Proper gas phase description during both periods was obtained. More importantly, elemental sulfur and sulfate were also in agreement with experimental data. Dynamic validation results demonstrated that the model is able to predict correctly the BTF operation when a variable H2S-LR profile is applied. Hence the BTF model here presented is capable to predict the BTF performance under similar conditions as those found in real plants, making it a suitable tool in order to develop and design control strategies towards process optimization of desulfurizing BTFs.”

29. Conclusions
The last part (p22 lines 19-29) belongs to the discussion rather than the conclusions section.
Answer:
This section was moved to the last part of the discussion on the results section

Especially, accurate model predictions under high H2S-LR and O2 limiting conditions (period 1) could be useful for predicting elemental sulfur accumulation in industrial BTF installations. Therefore, maintenance tasks can be strategically planned. Moreover, the development of the BTF model can be used for the development and simulation of control strategies towards process optimization. Parameters related to O2 transport are crucial in order to completely oxidize H2S and avoid the formation of elemental sulfur in the BTF bed, since an excessive accumulation of elemental sulfur can significantly diminish the reactor performance. Therefore, control strategies must be based on the improvement of the oxygen transfer to the liquid phase towards process optimization.”
OTHER REMARKS
Mind using uniform terminology throughout the manuscript:
- steady state (p6) or 'stationary'?
  Answer:
  See answer to comment #26
- ancillary column - oxygenation column - aeration column
  Answer:
  Aeration column has been used along the complete manuscript

'biogas mimics stream': just write 'biogas stream' and specify in the M&M section that it is a synthetic stream.
  Answer:
  Biogas stream has been used along the complete manuscript

p7 line34, sentence incomplete
  Answer:
  The sentence has been completed as follows
  
  (P7L24) “...interface occurring in the aeration column.”

p10 'sump' - you mean a buffer tank? Was not specified in the description of the installation.
  Answer:
  The sentence has been changed to:
  P6L22
  “Liquid present in the bottom section of the BTF (7) was recycled to the aeration column”

Figure 4A and Figure 5A&B should be grouped in one figure so it is clear to which LR the results correspond.
  Answer:
  We tried to group these figures in a single figure but it was too packed that was hardly understandable. We kept them split in two as it was presented in the first version of the manuscript. However to clarify Figure 5 (now figure 4), we added the H2S inlet concentration profile to have a clearer reference.

replace 'in coherence with', 'in concordance with' by 'in agreement with' or 'correspond with'.
  Answer:
  They have been changed along the manuscript

References
- all authors should be listed for each publication, do not use 'et al.'
  Answer:
  All authors are now listed in the references
- give full and accurate reference, including volume and page numbers, e.g. for [26] and [27]
  Answer:
  Reference [26] now reference [7] does not have a volume and page numbers yet.
  Reference [27] now reference [21] has been modified and the volume and page numbers have been added.
- avoid typos e.g. p22 line 53, p24 line 17,
  Answer:
Typos have been corrected in the manuscript
Re: Manuscript submission cover letter   February 19th, 2016

Dear Editor:

We are submitting a revised version of the manuscript entitled “Modelling an aerobic biotrickling filter for biogas desulfurization through a multi-step oxidation mechanism” authored by Luis R. López, Antonio D. Dorado, Mabel Mora, Xavier Gamisans, Javier Lafuente and David Gabriel.

The following author is responsible for correspondence:

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The manuscript has been revised according to reviewer comments. A separated file with a point-by-point answer to all reviewer comments is attached. We think we have answered all questions properly. For sure, the quality of the manuscript has improved a lot.

I look forward to your response with respect to possible publication.

Yours sincerely,

David Gabriel  
Associate Professor  
Department of Chemical Engineering  
Universitat Autonoma de Barcelona  
Barcelona, Spain
### LIST OF SUGGESTED REVIEWERS

<table>
<thead>
<tr>
<th>First Name</th>
<th>Last Name</th>
<th>Department</th>
<th>Institution</th>
<th>E-mail Address</th>
<th>Reason</th>
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<tr>
<td>Eveline</td>
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<td>Expert in modelling biological systems both in wastewater and wastegas treatment</td>
</tr>
<tr>
<td>German</td>
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<td><a href="mailto:garoca@ucv.cl">garoca@ucv.cl</a></td>
<td>Several publications in bioreactor modelling, including $\text{H}_2\text{S}$ removal in biotrickling filters</td>
</tr>
<tr>
<td>Zarook</td>
<td>Sharefdeen</td>
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<td>Expert in biofiltration modelling</td>
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ANSWERS to Reviewer's comments to the Author:

We deeply thank the reviewer comments and observations since most of them helped to improve the quality and readability of the manuscript. We have addressed all comments point by point as detailed below. Changes in the manuscript are indicated with a P (page) and L (line) code.

Reviewer #1: Overall, I think this is a good paper. Some comments: Perhaps consider the mass transfer at the interfaces. Meaning, there will be some transfer at the gas to liquid and liquid to biomass interfaces. Also, I think it would be meaningful to consider wetted vs non wetted biofilms and how this would effect your model; having worked with biotrickling filters, there are differences in effluent concentrations when trickling rates are high enough to wet a decent fraction of the packing material.

Answer:
We thank the reviewer by his short but very interesting and useful comments. We agree with the reviewer that mass transfer at the interfaces must be considered in order to have a more realistic approach of the model. Regarding the first comment about gas-liquid mass transfer, a global mass transfer coefficient referred to the liquid phase ($K_L$) was considered in this work (equation 3). Thus, such global coefficient already included the mass transfer both in the gas boundary layer and in the liquid boundary layer (assuming the concept of the double-film theory). In any case, the schematic of the model in the former version (figure 3) was confusing since it was drawn as if no mass transfer resistance occurred in the gas phase.

Derived from the reviewer comment, we thought interesting to include some short sentences about the contribution of both resistances to the overall G-L transport resistance. The individual mass transfer coefficients for both gas species oxygen ($O_2$) and hydrogen sulfide ($H_2S$) were determined using the Billet and Schultes correlations for $k_g$ and $k_l$. Result showed that the contribution of the gas phase was only a 0.18% for $O_2$ and a 9.7% for $H_2S$. To clarify, the following modifications and comments were added:

(P3L24) “However, biogas desulfurization requires of much longer gas contact times and, consequently, lower gas velocities that may increase mass transfer resistance in the gas phase.”

“Gas-Liquid mass transport is described by a gas-liquid global mass transfer coefficient referred to the liquid phase ($K_L$) that considers both the individual gas and liquid mass transfer resistances”. This comment was added both in the description of model assumptions (assumption 6) in section SM2 of the Supplementary Material file and in section 2.2 of the main manuscript (P9L1).

The schematic of the model (now in figure 1) has been modified to show the concentration change in the gas boundary layer when approaching the G-L interface.

(P16L14) “The $K_{L,O_2}$ was determined using the Billet and Schultes correlations [34] for the gas and liquid individual mass transfer coefficients $k_g$ and $k_l$, respectively, which was in close agreement with $K_{L,O_2}$ determined by Dorado et al. [9]. It is worth highlighting that only the liquid-side resistance was significant since based on Billet and Schultes correlations the contribution of
individual mass transfer resistances in the gas phase to the overall resistance for both gas species oxygen (O$_2$) and hydrogen sulfide (H$_2$S) were only 0.18% and 9.7% for O$_2$ and H$_2$S, respectively.”

Regarding to the second comment about liquid-biofilm mass transfer, we included a diffusion term described by Fick’s law in the liquid phase in the former version of the manuscript (equation 4). We agree with the reviewer about its significance since we really verified running simulations without this term that this term was completely necessary to properly fit our experimental data. We did not deeply show with simulations that importance in the manuscript but to clarify, the following comments were added:

“Mass transfer resistance in the liquid-biofilm interface was described by Fick’s law considering that the whole thickness of the liquid phase acted as the liquid boundary layer for mass transport resistance” This comment was added both in the description of model assumptions (assumption 7) in section SM2 of the Supplementary Material file and in section 2.2 in the main manuscript (P9L12)

Regarding the modeling approach about the use of fully wetted or wetted/non-wetted biofilms we agree with the reviewer that this would have a clear impact due to the changing amount of water in the packed bed when the TLV is modified. This is not trivial and no clear consensus exists about the use of one or another modeling approach since lumping of certain parameters may result in similar modeling results. A careful analysis from a modeling perspective must be performed. However, this was not the scope of the manuscript since the TLV was kept constant throughout the study. The following sentence was added:

(P4L3) “Despite no clear consensus has been reached so far and a careful analysis from a modeling perspective must be performed, modeling of biotrickling filters using a wetted/non-wetted biofilm approach seems necessary when the TLV is modified due to the changing amount of water in the packed bed.”

Reviewer #2: This contribution presents a model for an aerobic biotrickling filter (BTF) for biogas desulfurization. The model applied to describe the biological processes is the one from Mora et al. [27]. The BTF setup and experimental results regarding the influence of trickling liquid velocity and flow pattern were presented before, by [26]. So the main novelty of this contribution lies in modelling the BTF as such, and in the model calibration and validation based on experimental data. Part of the experimental data used for calibration were published in [26] (Figure 4A and 5A&B from this contribution overlap with Figure 2a from [26]).

Overall, I think the objectives and novelty of the paper should be stated more clearly. The introduction needs to be rewritten in this respect. The results and discussion need to be more to the point. The whole text could be written more compactly without loss of essential information - in fact it could make the message more clear. Figures can be made more clear; the number of figures can be reduced; a graphical representation from the information from Table 2 would allow easier interpretation. The generality of the presented results and the
general added value of this contribution needs to be elaborated on, given that the model is calibrated and validated for a specific model set-up.

Note: part of the results in this contribution were previously presented at the EMChIE2015 conference. In my view, they are definitely sufficiently interesting for a journal publication, but that conference paper was written more to-the-point and had a clearer structure than this contribution - so please reconsider it.

The present manuscript contains quite some typos and English language errors.

**Answer:**
We agree with the reviewer comments, thus, we have tried to focus the revised version on the BTF modeling. We want to stress that, in our opinion, the novelty of the paper was already clearly stated in the first version of the manuscript, however the introduction has been modified following the reviewer comments in order to stress the novelty of this work and the contribution on BTF desulfurization modelling. The numbers of figures has been reduced, considering the specific comments of the reviewer. Table 2 (sensitivity results for key BTF model parameters) was not represented graphically since different figures would be need in order to represent the sensitivity value for each output variable for all the model parameter studied, and therefore a table was considered more appropriate to show in a compact manner the sensitivity analysis results.

**SPECIFIC COMMENTS**

1-Abstract
line 44: 'respirometric techniques': this is not the focus of this paper but was addressed by Mora et al. [27]

**Answer:**
(P1 L20) The sentence was removed

2- Abstract: lines 46-51: no need to give a definition of sensitivity analysis in the abstract. Leave out or specify output parameters and process variables.

**Answer:**
The output process variables studied were included in the sentence as follows: (P1, L21) “…showed the highest influence on the estimation of the H2S removal efficiency the accumulated mass of sulfur and the sulfate concentration in the liquid phase.”

3-Introduction
The introduction should introduce the subject and identify knowledge gaps that will be addressed in this contribution. I expect the introduction of BTF for H2S removal from biogas and the modelling of BTF in general.

**Answer:**
Knowledge gaps were already stated in the former version of the manuscript (now in P3,L6-24). According to the reviewer suggestions, the introduction was modified including a brief introduction about BTF for H2S removal from biogas. The following paragraph was added in the introduction:
“Obtaining energy from non-renewable sources is becoming too expensive or too environmentally damaging nowadays. A energy source with high potential for green energy production is biogas. However, in order to have a suitable biogas utilization, impurities such as H2S and reduced sulfur compounds (RSC) produced during the anaerobic fermentation of S-bearing organic molecules must be removed [1]. Removal of H2S is strictly necessary to avoid corrosion of internal combustion engines during co-generation processes as well as for proper performance of further biogas upgrading technologies [2]. Biological technologies such as biotrickling filters (BTF) have demonstrated to be a suitable, competitive treatment technology for biogas conditioning when compared to physical-chemical technologies. However, main effort has been focus on experimental works, studying different pollutant loads [3], using different packing materials [4], different oxygen mass transfer devices [5], pH conditions [6] or gas-liquid flow pattern [7]. Tough process modeling has shown to be a crucial tool to evaluate the technical [1] and economical feasibility [2] of biological processes prior full-scale implementation, few efforts have been made in this direction on biogas desulfurization in BTFs.”

4-Introduction
References cited should either be applicable to this topic or be very general; this is not the case for [1]-[4]. Also [5]-[8] seem to be 'thrown in'. Specify what the individual references are about rather than listing references all together.

Answer:
General references or not directly applicable to the topic have been removed. Former paragraph starting from P3L4 until P3L8 has been removed. In general, references have been cited individually and an individual explanation has been provided instead of referencing all together at the end of the sentence. However some references have been kept grouped where the sentence points to a common fact.

5-Introduction
The introduction on biodegradation mechanism and kinetics (p3 line 41 till p4 line 37) is not relevant for the introduction since the biological model was not developed in this contribution. At most, it could be summarized in the model description.

Answer:
The introduction on biodegradation mechanism and kinetics has been removed from the introduction section and was summarized in the kinetic model description. Paragraph starting on P4L20 until P5L9 has been removed from the introduction section and summarized on section 2.2.2 (P11L4 to P12L2).

6-Introduction
part. p5 lines29-37 do not belong in the introduction either.

Answer:
This paragraph has been also moved to kinetic model description on P11.

7-Materials and Methods
Before giving details on the reactor dimension and packing, specify the general layout and operating principle (p5, line 48).

Answer:
The operating principle of the reactor is now explained just at the beginning of the section and rewritten as follows:

P5L22: “A laboratory-scale BTF reactor, with an ancillary unit for air supply, was used in this study to remove high loads of H$_2$S from biogas mimics streams (Fig.1). The biogas mimics consisted in controlled mixtures of H$_2$S and nitrogen (N$_2$) fed at the top of the BTF (1). An air flow (2) was firstly fed to an aeration column (3) for air supply to increase the dissolved oxygen (DO) concentration in the liquid phase. Exhaust air (4) from the aeration column was fed at the top of the BTF under a co-current flow pattern and mixed with the biogas inlet stream at an O$_2$/H$_2$S supplied ratio of 41.2 (v/v$^{-1}$). After biological degradation on the BTF bed (5), the treated biogas stream (6) leaves the reactor. The liquid phase was continuously recycled from bottom-to-top of the BTF at a trickling liquid velocity (TLV) of 4.4 m h$^{-1}$ (7). The liquid recirculation line (8) was previously oxygenated in an aeration column. The DO concentration in the recycle and purge lines was monitored in-situ in all the experiments. The reactor pH was also controlled at pHs of around 6.5 and 7 using an ON/OFF control system by automated addition of NaOH 1 M or HCl 1 M. An empty bed residence time (EBRT) of 118 s and an average hydraulic retention time (HRT) of 30 ± 4 h were maintained throughout the study by regulating the purge pump (9) and the mineral medium pump (10). Regarding the packing bed characteristics, the reactor diameter was 7.14 cm with a packed bed volume of 2.80$\times$10$^{-3}$ m$^3$ (V$_{bed}$). Polypropylene Pall rings of 15.9 mm diameter (MACH engineering products, USA) with a specific surface area of 354 m$^2$ m$^{-3}$ were used.”

8-Materials and Methods
Explicitly specify the experimental dataset and the periods 1-2-3. Are these periods consecutive?

Answer:
Experimental conditions presented on data provided on Table 1 (H$_2$S inlet concentration, H$_2$S Loading Rate, O$_2$/H$_2$S volumetric ratio) are commonly enough to describe the operating conditions to facilitate the comparison between different systems with different dimensions. Periods 1-2-3 were not consecutive, all experiments were performed in between a time span of 15 months. The following phrase was added to clarify:

(P7L10) “Periods of table 1 does not correspond to consecutive periods, all experiments were performed in between a time span of 15 months.”

9-Materials and Methods
Specify gas flow rate (constant for all experiments?).

Answer:
Gas flow rate is not specified since the key parameter is the gas contact time (EBRT). The gas flow rate can be determined relating the EBRT and the volume of the packed bed. The following phrase was added in order to clarify this.

(P7L4) “…in the lab-scale BTF set up (Fig. 1) operating at constant EBRT and constant biogas flow.”

10-Materials and Methods
Is O$_2$ concentration varying - O$_2$/H$_2$S variations only caused by varying H$_2$S?

Answer:
The O$_2$/H$_2$S volumetric ratio varied only due to H$_2$S inlet concentration increase since the air flow rate was kept constant in this work. The following phrase was added in order to clarify this:

(P7L4) “…in the lab-scale BTF set up (Fig. 1) operating at constant EBRT and constant biogas flow.”

11-Materials and Methods
Separate description of experimental setup and the model (lines 7, 12 and 42 do not fit here; also reconsider the paragraph starting on p6, line 48).

Answer:
Lines describing model variables on experimental setup description have been removed.

12-Materials and Methods
Figure 1 and Figure 3 could be left out and replaced by (and extended version of) Figure S2, detailing how the different layers in the BTF are described - the description on p7 referring to different indices is difficult to follow without a figure.

Answer:
Figure 1 and 3 and Figure S2 have been merged in order to have a complete description in a single figure (new Figure 1) to help the comprehension of the BTF set up, BTF discretization and biological mechanisms of H$_2$S biological oxidation.

13-Materials and Methods
The model description could be written more concisely by describing the meaning of the different balances and by listing the parameters in a 'nomenclature' section.

Answer:
The parameters have been listed in a nomenclature section.

14-Materials and Methods
2.2.2. 'Kinetic model'. Not only kinetic, but also stoichiometry, right? Rather entitle this section 'modelling biological and chemical sulfur conversions'.

Answer:
Right, the name has been changed. To avoid confusion with elemental sulfur, S-compounds has been used instead of sulfur.

(P11L3) “2.2.2 Modeling of biological and chemical S-compounds conversions”

15-Materials and Methods
It would be a strong added value to summarize the biological reactions in Gujer matrix format, to have a clear overview of the state variables and the model stoichiometry and kinetics.

Answer:
The model proposed by Mora et al. 2016 to describe the multi-step sulfide oxidation bioprocess has been summarized in the Gujer Matrix format in Tables 2 and 3 in which the stoichiometry and the kinetic expressions, respectively, are described.

16-Materials and Methods
This whole section needs to be significantly shortened, given that the model was developed by Mora et al. [27].

**Answer:**
We agree with the reviewer. Since part of the introduction related to general considerations about biodegradation mechanism and kinetics has been moved to this section (see answer to comment #5) the description of the model by Mora et al has been moved to the supplementary material Section SM-4.

17-Materials and Methods

p11, line 28 'no previous works has intended to model such range of intermediate products of biological sulfide oxidation'. If this is a major novelty, it should already be stated in the introduction and. I would also expect a discussion later in the article on whether or not it is important to consider a multi-step oxidation mechanism.

**Answer:**
This sentence has been moved to the introduction section (P5L16). The discussion about this major novelty has been added as a final discussion on the result section as follows:

(P21 L2) “Especially, accurate model predictions under high H₂S-LR and O₂ limiting conditions (period 1) could be useful for predicting elemental sulfur accumulation in industrial BTF installations. Therefore, maintenance tasks can be strategically planned”

18-Materials and Methods

2.3 Model implementation.

p13 'set of PDE was discretized'. This information comes late - needed to interpret mass balances.

**Answer:**
Yes. This paragraph has been moved to (P8L8) in the model development section just before the mass balances.

19. Results and discussion

3.1 Give a definition of the sensitivity function. Did you consider relative or absolute sensitivity? This will of course impact the comparability of the numbers obtained.

**Answer:**
Sensitivity function definition was included as follows:

(P13L8) “Sensitivity was assessed by increasing and decreasing model parameters by 10% and comparing the relative change of the output variables to a relative change of the model parameter.”

Also the word “relative” was added before “sensitivity analysis” throughout the manuscript (mostly in section 3.1, page 13) to indicate that the relative sensitivity was assessed.

20. Results and discussion

Also reconsider the structure of this section, emphasizing the main points. First describe most sensitive parameters, then the least sensitive, afterwards discuss.
In the former version of the manuscript the most sensitive output variables were firstly described and, afterwards, the less sensitive. Also, the discussion was already based only on the most sensitive parameters (with higher relative sensitivity function value than 0.1). However, the first sentence in P13L24 was changed to follow the same structure from more to less sensitive variables throughout the discussion.

(P13L24) “The most sensitive output variables were the RE and $C_{L_{SO4}}$ that exhibited comparable sensitivities between them at a 10% increase while $m_{SO}$ was the less sensitive output variable due to its cumulative nature.”

21. Results and discussion
p15 'O2 transport rather than H2S transport is the limiting step'. But O2 transport and H2S transport take place in separate reactors, right?

Answer: The goal of using an external aeration column was to improve the O2 gas-liquid mass transport before air enters the BTF column. The total amount of oxygen supplied to the BTF was the contribution of that supplied to the liquid phase in the aeration column plus the excess air from the aeration column that passed through the packed bed of the reactor. The contribution of the O2 transferred in the aeration column was estimated to be between 10 and 30% of the total (aeration column + reactor) O2 transferred. This discussion has already been made in previous works by Lopez et al. No changes were made to the manuscript.

22. Results and discussion
3.2 The first paragraph (starting on p16 line 49) rather belongs to 'Materials and methods'.

Answer: The paragraph was moved to the Materials and Methods section (now in P12L10)

23 Results and discussion
p17 '157g of elemental sulfur'. How was this amount determined?

Answer: Since $K_{max}$ is the relation between the maximum amount of elemental sulfur that could be accumulated inside SOB cells before this accumulation completely blocked the biological sulfide consumption such maximum amount of elemental sulfur was determined using the substrate switch constant ($K_{max}$) and the biomass concentration estimated by the model ($X$) according to $K_{max} = \frac{m_{SO}^{\max}}{X}$. This comment was added to the manuscript as:

(P16L7) “Since $K_{max}$ is the relation between the maximum amount of elemental sulfur that could be accumulated inside SOB cells before this accumulation completely blocked the biological sulfide consumption, this maximum amount of elemental sulfur was determined using the substrate switch constant ($K_{max}$) and the biomass concentration estimated by the model ($X$) according to $K_{max} = \frac{m_{SO}^{\max}}{X}$. Thus, under the calibration conditions, a maximum amount of 157 g of elemental
sulfur could be accumulated inside SOB cells, well above the amount of elemental sulfur produced.”

24. Results and discussion
p17 Clarify that the results presented in Fig 4 and Fig 5 are the model calibration results (also in caption Fig 4).
Answer:
Caption in figure 4 was changed. The sentence in the manuscript was changed to:

(P17L4) “In Fig. 3 and Fig. 4 experimental results and model predictions of the effect of stepwise LR increases due to H₂S inlet concentration increases corresponding to the model calibration period are presented”.

25. Results and discussion
p17 line 59 'Fig 4'. Where to look exactly?
Answer:
Truly, in Figure 4 (now Figure 3) there was no RE plotted but the H₂S concentration. The sentence was rewritten as follows:

(P21 L21) “Experimental data in both figures indicate that the system was able to remove almost 100% of H₂S inlet concentration at all H₂S-LR (Fig. 3A and 3B).”

26. Results and discussion
p20, line 26 'Sulfate concentration increases during steady state'. If the concentration changes, steady state has not yet been reached. What causes the change - do you expect it to keep going on?
Answer:
We agree with the reviewer. We meant “stationary feeding period” instead because the inlet conditions were constant. In fact, a BTF hardly reaches steady-state conditions since there is biomass growth, changes in the preferential paths inside the packed bed etc… Pseudo-steady state conditions were replaced by stationary feeding period throughout the manuscript.

27. Results and discussion
p21 'Overall, the model described processes occurring in the three phases'. Specify which figures correspond to which phase.
Answer:
The sentence was confusing. The sentence now reads as:

(P20L22) “Overall, the model showed to be valid to describe the main processes occurring in the three phases of a BTF, gas phase (Fig. 3A and 3B), liquid phase (Fig. 4A) and solid phase as elemental sulfur (Fig. 4B) in a co-current flow mode configuration”

28. Conclusions
The conclusions are too general. Specify conclusions related to the model set-up, calibration and validation separately.

Answer:
The conclusions have been modified, describing separately each part of the work from the sensitivity analysis until the constant feeding validation period and the dynamic validation period. Most of this section has been rewritten as follows:

(P21L21) “…… A preliminary assessment through a relative sensitivity analysis allowed determining the most sensitive parameters of the model. Parameters related to O2 mass transport exhibited a larger influence to model output variables considered (RE, C1,SO42- and mS0). The proposed model was calibrated using experimental data, which allowed describing accurately the outlet H2S concentration profile along the BTF bed during H2S-LR increments. Besides describing properly sulfate production, elemental sulfur, the main intermediate product during H2S oxidation, was correctly predicted. Mass transfer parameters (δb, δl, KL,H2S) and kinetic parameters (X, μmax,2) were estimated during BTF model calibration.

Moreover, the BTF model was validated under a stationary feeding period and a dynamic H2S-LR period. Proper gas phase description during both periods was obtained. More importantly, elemental sulfur and sulfate were also in agreement with experimental data. Dynamic validation results demonstrated that the model is able to predict correctly the BTF operation when a variable H2S-LR profile is applied. Hence the BTF model here presented is capable to predict the BTF performance under similar conditions as those found in real plants, making it a suitable tool in order to develop and design control strategies towards process optimization of desulfurizing BTFs.”

29. Conclusions
The last part (p22 lines 19-29) belongs to the discussion rather than the conclusions section.

Answer:
This section was moved to the last part of the discussion on the results section

(P21L2) “Especially, accurate model predictions under high H2S-LR and O2 limiting conditions (period 1) could be useful for predicting elemental sulfur accumulation in industrial BTF installations. Therefore, maintenance tasks can be strategically planned. Moreover, the development of the BTF model can be used for the development and simulation of control strategies towards process optimization. Parameters related to O2 transport are crucial in order to completely oxidize H2S and avoid the formation of elemental sulfur in the BTF bed, since an excessive accumulation of elemental sulfur can significantly diminish the reactor performance. Therefore, control strategies must be based on the improvement of the oxygen transfer to the liquid phase towards process optimization.”

OTHER REMARKS
Mind using uniform terminology throughout the manuscript:
- steady state (p6) or 'stationary'?

Answer:
See answer to comment #26
ancillary column - oxygenation column - aeration column

**Answer:**
Aeration column has been used along the complete manuscript.

'biogas mimics stream': just write 'biogas stream' and specify in the M&M section that it is a synthetic stream.

**Answer:**
Biogas stream has been used along the complete manuscript.

**p7 line34, sentence incomplete**

**Answer:**
The sentence has been completed as follows:

(P7L24) “…interface occurring in the aeration column.”

**p10 'sump' - you mean a buffer tank? Was not specified in the description of the installation.**

**Answer:**
The sentence has been changed to:

P6L22

“Liquid present in the bottom section of the BTF (7) was recycled to the aeration column”

**Figure 4A and Figure 5A&B should be grouped in one figure so it is clear to which LR the results correspond.**

**Answer:**
We tried to group these figures in a single figure but it was too packed that was hardly understandable. We kept them split in two as it was presented in the first version of the manuscript. However to clarify Figure 5 (now figure 4), we added the H2S inlet concentration profile to have a clearer reference.

**replace 'in coherence with', 'in concordance with' by 'in agreement with' or 'correspond with'.**

**Answer:**
They have been changed along the manuscript.

**References**
- all authors should be listed for each publication, do not use 'et al.'

**Answer:**
All authors are now listed in the references.

- give full and accurate reference, including volume and page numbers, e.g. for [26] and [27]

**Answer:**
Reference [26] now reference [7] does not have a volume and page numbers yet. Reference [27] now reference [21] has been modified and the volume and page numbers have been added.

- avoid typos e.g. p22 line 53, p24 line 17,

**Answer:**
Typos have been corrected in the manuscript.
**Highlights**

- A model describing desulfurization of biogas in a biotrickling filter was developed.
- Calibration at 5 H₂S loading rates allowed estimating 5 model parameters.
- Model validation was performed with dynamic elemental sulfur and sulfate profiles.
- H₂S removal was influenced by G-L mass transfer and by biological degradation.
- G-L oxygen transfer is crucial to avoid sulfur accumulation in the packed bed.
Modeling an aerobic biotrickling filter for biogas desulfurization through a multi-step oxidation mechanism

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Abstract

A dynamic model describing physical-chemical and biological processes for the removal of high loads of H\textsubscript{2}S from biogas streams in biotrickling filters (BTFs) was developed, calibrated and validated for a wide range of experimental conditions in a lab-scale BTF. The model considers the main processes occurring in the three phases of a BTF (gas, liquid and biofilm) in a co-current flow mode configuration. Furthermore, this model attempts to describe accurately the intermediate (thiosulfate and elemental sulfur) and final products (sulfate) of H\textsubscript{2}S oxidation through a kinetic model developed using respirometric techniques. A sensitivity analysis was performed in order to focus parameters estimation efforts on those parameters that showed the highest influence on modeling results over the estimation of the H\textsubscript{2}S removal efficiency, the accumulated mass of sulfur and the sulfate concentration in the
Biofilm and liquid layer thicknesses, specific growth rate of biomass over elemental sulfur and the H$_2$S global mass transfer coefficient were the parameters that showed the highest influence on model outputs. Experimental data for model calibration corresponded to the operation of the BTF under stepwise increasing H$_2$S concentrations between 2000 and 10000 ppm. Once the model was calibrated, validation was performed by simulating a stationary feeding period of 42 days of operation of the BTF at an average concentration of 2000 ppm, and a dynamic operation period were the BTF was operated under variable inlet H$_2$S concentration between 1000 and 5000 ppm, to simulate load fluctuations occurring in industrial facilities. The model described the reactor performance in terms of H$_2$S removal and predicted satisfactorily the main intermediate and final products produced during the biological oxidation process.

Keywords
Desulfurizing biotrickling filter; biogas; modeling; kinetics; sensitivity analysis; elemental sulfur

1. Introduction

Obtaining energy related to non-renewable sources is becoming too expensive or too environmentally damaging to retrieve nowadays. A stream energy source with high potential for green energy production is biogas. However, in order to have a suitable biogas utilization, impurities such as H$_2$S and reduced sulfur compounds (RSC) coming from produced during the anaerobic fermentation of S-bearing organic molecules must be removed [1]. Removal of H$_2$S is strictly necessary to avoid corrosion of internal combustion engines during co-generation processes as well as for proper performance of further biogas upgrading technologies [2]. Biological technologies such as biotrickling filters (BTF) when
compared to physical-chemical technologies, such as biotrickling filters (BTF), have demonstrated to be a suitable, competitive treatment technology for biogas conditioning when compared to physical-chemical technologies. However, main effort has been focus on experimental works, studying different pollutant loads [3], using different packing materials [4], different oxygen mass transfer devices [5], pH conditions [6] or gas-liquid flow pattern [7]. Tough process modeling has shown to be a crucial tool to evaluate the technical [1] and economical feasibility [2] of biological processes prior full-scale implementation, few efforts have been made in this direction on biogas desulfurization in BTFs.

Process modeling has shown to be a crucial tool to evaluate the technical and economical feasibility of biological processes prior to full-scale implementation [1,2] and for the development of control strategies [3,4]. Mathematical modeling of liquid phase biological processes, such as those related to nutrients removal through different biological technologies, has been extensively studied and reported [5–8]. Also multiphase biological processes, such as biofiltration in biofilters and biotrickling filters (BTF) for the removal of different type of contaminants like volatile organic compounds (VOCs) [7–9] and ammonia [10,11], have been modeled describing both transient and steady-state conditions.

However, most BTF models have focused on VOCs removal [12], while literature available for H₂S BTFs modeling is scarce [13–15]. Therefore, a model describing properly the removal of high loads of H₂S in BTFs is still lacking in literature. Previous models for H₂S removal in BTFs have focused on removal of H₂S at odor level concentrations [13,14,16], while only few models in literature dealt with high loads of H₂S [17,18]. In most cases, the inherent complexity of such plug-flow, heterogeneous, multiphase bioreactors has been strongly simplified to avoid facing a large number of unidentifiable parameters. Often, G-L
mass transport, diffusion in the biofilm and biological degradation kinetics have been identified as the most relevant processes. The heterogeneity of the water-biofilm layers, as well as the kinetics and mechanisms considered to model H₂S removal in BTFs, are the two main aspects that have been addressed differently by several authors. Most models consider an homogeneous biofilm density, a biofilm completely wetted along the packed bed height \[13,17,19\] and H₂S and O₂ mass transfer from the gas to the liquid phase prior to their diffusion to the biofilm were degradation takes place. Usually, only mass transfer resistance in the liquid phase is considered for modeling G-L mass transport due to the high interstitial gas velocity in the packed bed. However, biogas desulfurization requires of much longer gas contact times and, consequently, lower gas velocities that may increase mass transfer resistance in the gas phase. Also, several alternatives have been proposed to model such bioreactors such as considering a partially or a fully wetted biofilm as well as considering or not adsorption of a fraction of the pollutant by the biofilm \[14,20\]. However, despite no clear consensus has been reached so far, and a careful analysis from a modeling perspective must be performed, modeling of biotrickling filters using a wetted/non-wetted biofilm approach seems necessary when the TLV is modified due to the changing amount of water in the packed bed.

One of the most critical parts in the development of a model is how biodegradation mechanisms and kinetics are described, since depending on the operational conditions, the process might become biodegradation rate-controlled \[15\]. Different biodegradation kinetics models and degradation mechanisms have been used in order to describe the substrate consumption in BTFs models for H₂S removal. Eqs. 1 and 2 are usually lumped in a single equation describing the complete oxidation of sulfide to sulfate \[14\]. However, partial oxidation to elemental sulfur has been often observed in BTFs for biogas desulfurization \[5\]. For this reason, a two-step mechanism (Eqs. 1 and 2) is needed for proper system modeling.
A Monod-type kinetic expression is often used to describe substrate consumption \[13,14\] in desulfurizing systems, being H$_2$S the only rate-limiting substrate. However, different authors have shown that the treatment of high loads of H$_2$S, such as those found in biogas desulfurization processes, may lead to substrate inhibition or oxygen limiting conditions. A multi-substrate type equation with a Haldane term for H$_2$S and a Monod term depending on the dissolved oxygen (DO) concentration inside the biofilm have been shown to describe well experimental oxygen uptake rate (OUR) and H$_2$S uptake rate profiles \[20\] during the characterization of H$_2$S-oxidizing biofilms in BTFs. Some authors have also proposed the use of a kinetic equation in which the ratio of elemental sulfur/sulfate produced is based on the DO concentration \[21\]. A product selectivity function for elemental sulfur or sulfate based on the sulfide oxidation activity and the OUR has been also considered \[22,23\]. It is well-known that elemental sulfur, the main intermediate product of H$_2$S biological oxidation, is formed due to O$_2$ transport limitations inside the BTF bed \[24,7\]. Thus, obtaining an accurate model that describes well the production and accumulation of intermediate products of H$_2$S biological oxidation is crucial to describe accurately biogas desulfurization in BTFs.

Recently, Mora et al. \[21\] have proposed a multi-step pathway for describing sulfide-oxidizing bacteria (SOB) as catalyst of H$_2$S oxidation to SO$_4^{2-}$ considering the partial sulfide oxidation to elemental sulfur, as an intracellular product, and the sulfite and thiosulfate production as additional intermediates. Such mechanistic model was calibrated and...
validated through homogeneous respirometric tests providing successful results in describing the main species of the \( \text{H}_2\text{S} \) oxidation process.

From a practical point of view, prediction of desulfurizing BTFs performance is essential. Low sulfate production rates can lead to an excessively elemental sulfur formation that accumulates into the packed bed. Consequently, a significant increase in pressure drop inside BTF bed occurs [22], with a considerable reduction of BTF operational life-span and process security. However, few works have addressed this topic so far. There is still the need for the development of tools that impulse the industrial application of this emerging biological-based technology. BTF models are essential in design steps, besides useful in the development of control strategies towards process optimization.

From the stated above, the aim of this work was to develop, calibrate and validate a dynamic model of an aerobic BTF for the removal of high-loads of \( \text{H}_2\text{S} \) from biogas streams. The BTF model attempts to describe intermediate and final products obtained from \( \text{H}_2\text{S} \) oxidation under stationary feeding periods, pseudo steady-state, transient and dynamic conditions. It has to be remarked that no previous works have intended to model such range of intermediate products of biological sulfide oxidation in BTFs for biogas desulfurization. To reduce the uncertainty due to general assumptions and parameters based on literature correlations, the model herein uses a multi-step kinetic model previously developed by Mora et al. [21] and calibrated using respirometric techniques with biomass samples obtained from the BTF set-up used herein.

2. Material and methods

2.1 Experimental setup and operating conditions
A laboratory-scale biotrickling filter (BTF) reactor, with an ancillary unit for air supply, was used in this study to remove high loads of H$_2$S from biogas mimics streams (Fig. 1). The biogas mimics operating principle of the BTF setup is as follows accordingly to in Fig. 1:

Biogas consisted in controlled mixtures of H$_2$S and nitrogen (N$_2$). Inlet stream is located at the top of the BTF (1). A, which was an synthetic stream composed by H$_2$S and nitrogen (N$_2$), was first fed to the ancillary unit aeration column (3) for air supply to increase the dissolved oxygen (DO) concentration in the liquid phase. Exhaust air (4) from the aeration column was fed at the top of the BTF under a co-current flow pattern and mixed with the biogas inlet stream at an O$_2$/H$_2$S supplied ratio of 41.2 (v/v$^{-1}$). After biological degradation on the BTF bed (5), the treated biogas stream (6) leaves the reactor. The liquid present phase was continuously recycled from bottom-to-top in the bottom section of the of the BTF at a trickling liquid velocity (TLV) of 4.4 m h$^{-1}$ (7) was recycled to the aeration column. The liquid recirculation line (8) stream was previously oxygenated in the aeration column was directly fed from the top of the BTF at a trickling liquid velocity (TLV) of 4.4 m h$^{-1}$. The DO concentration in the recycle and purge lines were monitored in situ for all the experiments. The reactor pH was also controlled at pHs of around 6.5 and 7 using an ON/OFF control system by automated addition of NaOH 1M or HCl 1 M.

An empty bed residence time (EBRT) of 118 s and an average hydraulic retention time (HRT) of 30 ± 4 h were maintained throughout the study by regulating the purge pump (9) and the mineral medium pump (10) during reference conditions. Regarding the packing bed characteristics, the reactor diameter was 7.14 cm with a packed bed volume of 2.80 L. Polypropylene Pall rings of 15.9 mm diameter (MACH engineering products, USA) with a specific surface area per volume unit of packed bed $a$ of 354 m$^2$ m$^{-3}$ were used.
of 354 m² m⁻³ were used. An empty bed residence time (EBRT) of 118 s and an average hydraulic retention time (HRT) of 30 ± 4 h were maintained during reference conditions. Air was supplied to the liquid phase by continuous aeration at an O₂:H₂S supplied ratio of 41.2 (v:v) using a digital mass flow controller (Bronkhorst, The Netherlands). Air flow was first fed to the ancillary unit for air supply to increase the dissolved oxygen (DO) concentration in the liquid phase. Inlet and outlet DO concentrations from the oxygenation column where also simulated. Exhaust air from the oxygenation column was fed at the top of the BTF under co-current flow pattern. Oxygen consumption along the BTF column is also described by model equations. The liquid recirculation stream previously oxygenated in the aeration column was directly fed from the top of the BTF at a trickling liquid velocity (TLV) of 4.4 m h⁻¹. The DO concentration in the recycle and purge line were monitored in-situ for all the experiments; pH was also controlled around 6.5 and 7 using an ON/OFF control system by automated addition of NaOH 1M or HCl 1 M.

Furthermore, H₂S, O₂ and carbon dioxide (CO₂) in the gas phase were monitored on-line through three gas phase streams obtained from the gas outlet stream and from gas sampling ports were monitored on-line with an electrochemical H₂S(g) sensor (Sure-cell, Euro-Gas Management Services, UK), O₂ gas sensor (O₂ SL sensor, Euro-Gas Management Services, UK) an CO₂ gas sensor (CO₂ probe GMP343 Vaisala Carbocap, Vaisala, Finland). Sampling ports were located along the BTF height at 0.24 m, 0.51 m and 0.7 m in order to monitor the H₂S concentration profile along the BTF bed and therefore compare it with simulated data. Further information about gas concentration measurement can be founded on Supplementary Material, section SM-1. Also, detailed information of the BTF inoculation, analytical methods and related information can be found elsewhere [7].
The calibration of model parameters was performed using data obtained during stepwise H$_2$S Loading Rate (H$_2$S-LR) increments as a consequence of H$_2$S inlet concentration increase (Period 1 - Table 1) in the lab-scale BTF set up (Fig. 1) operating at constant EBRT and constant bioaerobic gas flow. For model validation under stationary H$_2$S feeding pseudo-steady-state conditions, a period of 42 days was simulated at a constant H$_2$S inlet concentration of 2000 ppm (Period 2 - Table 1). In addition, model was also validated under dynamic conditions (Period 3 - Table 1) by simulating variable H$_2$S-LR conditions due to C$_{g,H2S,in}$ increase (Fig. 2) emulating daily load fluctuations as those commonly found in real facilities. The averages of maximum and minimum H$_2$S-LR loading rate values are shown in Table 1. All experiments were performed in between a time span of 15 months.

2.2 Model development

A three phase model (gas, liquid and biofilm) was considered to model reactor dynamics under a co-current flow pattern configuration. The model also considered the main processes occurring in the aeration column attached to the bioreactor (Supplementary Material, Fig. S1).

2.2.1 Biotrickling filter model

The BTF model incorporates mathematical expressions for the following mechanisms occurring in the packed bed: mass transport by advective flow in the gas and liquid phases, mass transfer at the gas-liquid interface, mass transfer by diffusion at the liquid-biofilm interface, internal diffusion in the liquid and biofilm phases and biological reaction in the biofilm as schematized in Fig. 1. Also, the model considered oxygen mass transfer at the gas-liquid interface occurring in the aeration column.
Model equations were built based on the above mentioned mechanisms and assumptions often assumed in BTF models in literature [13,14,20], which can be found in Supplementary Material, section SM-2. Since transport of compounds in the axial direction is modeled as plug flow, the BTF bed was discretized in vertical layers in order to simulate a sequence of continuous stirred tank reactors (CSTR) [23]. Vertical layers \((n_{\text{vs}})\) were numbered starting from the top of the BTF \((n_{\text{vs}}=1)\) to the biogas outlet \((n_{\text{so}})\). Similarly, the biofilm layers \((nb)\) was were also divided in different subdivisions starting from the biofilm surface \((nb=1)\) to the biofilm subdivision in contact with the packed material \((nbp)\). The set of partial differential equations was discretized in space along the bed height and biofilm thickness. The conversion of the tubular reactor into a serial of stirred reactors was verified running simulations at different discretizations and optimizing results and time computing. As a result, an optimal discretization of the biofilter was found, resulting in eight nodes along the bed height \((n_{\text{vs}}=8)\) and ten nodes along the biofilm thickness \((nb=10)\).

The following equations describe the mass balances in the gas, liquid and biofilm phases mass balances and their initial conditions in the BTF:

**Mass balance for the gas phase in the BTF**

\[
\frac{dC_{g,i}}{dt} = \frac{F_T}{V_{g,\text{vs}}} \left( C_{g,i}^{n_{\text{vs}}-1} - C_{g,i}^{n_{\text{vs}}} \right) - \frac{K_{L,a}}{H_L} \left( C_{g,i}^{n_{\text{vs}}} - C_{L,i}^{n_{\text{vs}}} \right) \tag{3}
\]

initial conditions:
\[
t=0, \quad C_{g,i}^{n_{\text{vs}}}=0
\]

at the BTF inlet \((n_{\text{vs}}=1)\):
\[
C_{g,i}^{n_{\text{vs}}-1}=C_{g,i}^{\text{in}}
\]

subindex. Where superscripts/subscripts \(i\) refers to either gaseous \(H_2S\) or \(O_2\), while \(C_{g,i}^{n_{\text{vs}}}\) and \(C_{L,i}^{n_{\text{vs}}}\) are the concentrations of component \(i\) in the bulk gas phase and bulk liquid phase for a certain layer, respectively \((\text{g m}^{-3})\); \(F_T\) is the total (biogas + air) gas flow rate \((\text{m}^3 \text{ h}^{-1})\); \(V_{g,\text{vs}}\) is
the empty volume of the packed bed (m$^3$) of layer nvs; $H_i$ is the gas-liquid dimensionless Henry coefficient for component $i$ ( ); $k_{L,i}$ is the gas-liquid mass transfer coefficient of component $i$ (m·h$^{-1}$) and $a$ is the specific surface area per volume unit of packed bed (m$^2$·m$^{-3}$). $V_{G,nvs}$ (m$^3$) is calculated as $V_{G,nvs} = \frac{F_{L,nvs} \cdot \rho_{L,nvs}}{\rho_g}$ where $\epsilon_g$ is the gas phase porosity, which represents the volume fraction occupied by the gas phase in the packed and $V_{bed}$ is the empty volume of the packed bed. Notice that G-L mass transport is described by a gas-liquid global mass transfer coefficient referred to the liquid phase ($K_L$) that considers both the individual gas and liquid mass transfer resistances.

**Mass balance for the liquid phase in the BTF**

\[
\frac{dC_{L,i}^{nvs}}{dt} = \frac{F_{L,nvs}}{V_{L,nvs}} \left( C_{L,i}^{nvs-1} - C_{L,i}^{nvs} \right) + \frac{K_{L,i}}{\varphi} \left( \frac{C_{G,i}^{nvs}}{H_i} - C_{L,i}^{nvs} \right) \left( \frac{a \cdot D_i}{\varphi \cdot \delta_L} \right) \left( C_{L,i}^{nvs} - C_{L,i}^{nvs-1} \right) \tag{4}
\]

initial conditions: $t = 0$, $C_{L,i}^{nvs} = C_{L,i}^{nvs-1} = 0$

at the BTF inlet (nvs=1): $C_{L,i}^{nvs} = C_{L,i}^{nvs-1} = C_{RE}$

**subscripts and indices** $i$ refers to $S^2$, $SO_4^{2-}, S_2O_3^{2-}$ and DO concentration, the compounds considered in the liquid phase of the BTF, while $V_{L,nvs}$ is liquid volume (m$^3$) of layer nvs; $C_{L,i}^{nvs}$ is the concentration of component $i$ at the biofilm surface (g·m$^{-3}$); $C_{L,i}^{nvs-1}$ is the concentration of compound $i$ in the recirculation flow (g·m$^{-3}$); $F_L$ is the liquid flow rate (m$^3$·h$^{-1}$); $D_i$ is the diffusivity of component $i$ in water (m$^2$·h$^{-1}$) and $\delta_L$ is thickness of the water layer (m). $V_{L,nvs}$ (m$^3$) is calculated as $V_{L,nvs} = \frac{V_{bed} \cdot \varphi_{nvs}}{\rho_{nvs}}$ where $\varphi$ is the volume fraction occupied by the liquid phase in the packed bed according to the dynamic hold-up measured (-). Notice that mass transfer resistance in the liquid-biofilm interface was described by Fick’s law considering that the whole thickness of the liquid phase acted as the liquid boundary layer for mass transport resistance.
Mass balances for the biofilm of in the BTF

For the first layer of the biofilm (\(nb=1\)) and all BTF layers (\(nvs=1\) to \(nvs0\))

\[
\frac{dC_{B,i}^{\text{mv},1}}{dt} = \frac{D_i}{\delta_{B-NB}} \left( C_{L,i}^{\text{mv},1} - C_{B,i}^{\text{nv},1} \right) - \frac{D_i}{\delta_{B-NB}} \sum r_{B,j}^{\text{mv},1} + \sum V_{B,i}^{\text{mv},1} \delta_{B-NB}
\]  

\(5\)

where subindex \(j\) indicates the rate equation in which component \(i\) is participating.

For the inner layers of the biofilm (\(nb=2\) to \(nb=nbp-1\)) and all BTF layers (\(nvs=1\) to \(nvs0\))

\[
\frac{dC_{B,i}^{\text{mv},nbp}}{dt} = \frac{D_i}{\delta_{B-NB}} \left( C_{B,i}^{\text{mv},nbp} - C_{B,i}^{\text{nv},nbp} \right) + \sum V_{B,i}^{\text{mv},nbp} \delta_{B-NB} \]  

\(6\)

For the closest layer to the packing material (\(nb=nbp\)) and all BTF layers (\(nvs=1\) to \(nvs0\))

\[
\frac{dC_{B,i}^{\text{mv},nbp}}{dt} = \frac{D_i}{\delta_{B-NB}} \left( C_{B,i}^{\text{mv},nbp} - C_{B,i}^{\text{nv},nbp} \right) + \sum V_{B,i}^{\text{mv},nbp} \delta_{B-NB}
\]  

\(7\)

Initial conditions in Eqs. 5, 6 and 7:

\(t=0, \quad C_{B,i}^{\text{mv},1} = 0\)

Boundary conditions in Eqs. 5, 6 and 7:

\(x=0, \quad C_{B,i} = C_{B,i}^{L}\)

\(x=\delta_{B}, \quad \frac{C_{B,i}^{\text{mv},nbp}}{\delta_{B}} = 0\)

in Eqs. 5, 6 and 7, subscript subindex \(i\) refers to \(S^2, SO_4^{2-}, S_2O_3^{2-}\) and DO concentration, the compounds considered in the biofilm phase of the BTF, while subscripts \(j\) indicates the rate equation in which component \(i\) is participating. \(C_{B,i}^{\text{mv},1}\) is the concentration of component \(i\) at the biofilm subdivision \(nb\) (\(g m^{-3}\)), \(\delta_{B-NB}\) is the thickness of one biofilm subdivision (\(m\)) and \(\delta_{B}\) is the biofilm thickness (\(m\)); \(\upsilon\) is the stoichiometric coefficient for compound \(i\) in each process rate (\(\cdot \)), and \(r_{B,j}\) is the rate equation for each biological process considered (\(g m^{-3} h^{-1}\)).

According to the BTF configuration, mass balances in the sump of the reactor (Eq. 8) and in the aeration column (Eqs. 9-10) were included.

Mass balance for the liquid phase in the sump of the BTF

\[
\frac{dF_i^L}{dt} = \frac{V_{L,D} F_i^{L-BF} C_{L,i}^{B-F}}{V_{L,D}} + \frac{V_{L,B} C_{L,i}^{B-F}}{V_{L,D}} + \frac{V_{L,D} C_{L,i}^{B-F}}{V_{L,D}}
\]  

\(8\)
initial conditions: $t=0, C_{L,i}^p=0$

subscript $i$ refers to $S^2$, $SO_4^{2-}$, $S_2O_4^{2-}$ and DO concentration, the compounds considered in the liquid phase of the BTF, while $E_{L}$, $E_{L,m}$ and $E_{L,m}$ are the liquid flow rate, the liquid purge rate and the fresh liquid mineral medium flow rate, respectively ($m^3 \cdot h^{-1}$). $V_{L,i}$ is the volume of liquid in the sump of the BTF ($m^3$); $C_{L,i}^p$ is the concentration of compound $i$ in the purge flow ($g \cdot m^{-3}$); $C_{L,i}^{RE}$ is the concentration of compound $i$ in the recirculation flow ($g \cdot m^{-3}$); and $C_{L,i}^{RE}$ is the concentration of compound $i$ in the mineral medium ($g \cdot m^{-3}$). Notice that $C_{L,i}^p$ and $C_{L,i}^{RE}$ are equal except for dissolved oxygen because of the aeration column located in the recirculation line.

Mass balance for the gas phase in the aeration column

\[
\frac{dC_{O_2}}{dt} = \frac{F_{O_2}}{V_{g,AC}} \left( C_{g,AC} - C_{g,AC}^{out} \right) \cdot K_{L,O_2;AC} \left( \frac{C_{g,AC}^{in}}{H_{O_2}} - C_{L,O_2}^p \right) \quad (9)
\]

initial conditions: $t=0, C_{g,AC}^{AC}=0$

$F_{O_2}$ is the inlet air flow rate to the aeration column ($m^3 \cdot h^{-1}$); $V_{g,AC}$ is the gas phase volume of the aeration column ($m^3$); $C_{g,AC}^{in}$ and $C_{g,AC}^{out}$ are the oxygen inlet and outlet concentration in the aeration column, respectively ($g \cdot m^{-3}$); $K_{L,O_2;AC}$ is the gas-liquid mass transfer coefficient for oxygen in the aeration column ($h^{-1}$); $H_{O_2}$ is the $O_2$ gas-liquid dimensionless Henry coefficient ($\cdot$).

Mass balance for the liquid phase in the aeration column

\[
\frac{dC_{L,O_2}}{dt} = \frac{F_L}{V_{L,AC}} \left( C_{L,O_2}^p - C_{L,i}^{RE} \right) \cdot K_{L,O_2;AC} \left( \frac{C_{g,AC}^{in}}{H_{O_2}} - C_{L,i}^{RE} \right) \quad (10)
\]
initial conditions: $t=0, C_{L,O_2}^p=0$

$L_{aer}$ is the liquid volume of the aeration column (m$^3$)

2.2.2 Modelling of biological and chemical sulfides

A Monod-type kinetic expression is often used to describe substrate consumption [13,14] in desulfurizing systems, being $H_2S$ the only rate-limiting substrate. However, different authors have shown that the treatment of high-loads of $H_2S$, such as those found in biogas desulfurization processes, may lead to substrate inhibition or oxygen-limiting conditions. A multi-substrate type equation with a Haldane term for $H_2S$ and a Monod term depending on the dissolved oxygen (DO) concentration inside the biofilm have been shown to describe well experimental oxygen uptake rate (OUR) and $H_2S$ uptake rate profiles [20] during the characterization of $H_2S$-oxidizing biofilms in BTFs. Some authors have also proposed the use of a kinetic equation in which the ratio of elemental sulfur/sulfate produced is based on the DO concentration [24]. A product selectivity function for elemental sulfur or sulfate based on the sulfide oxidation activity and the OUR has been also considered by other authors [25,26].

It is well-known that elemental sulfur, the main intermediate product of $H_2S$ biological oxidation, is formed due to $O_2$ transport limitations inside the BTF bed [7,27].

According to the abovementioned findings in literature, the kinetic model proposed by Mora et al. [21] was used herein. The multi-step sulfide oxidation mechanism (Figure 1D) has been summarized in Tables 2 and 3, in which the stoichiometry and the kinetic expressions that describe each of the reactions occurring during the process have been specified. In short, the kinetic model considers that $H_2S$ is partially oxidized to elemental sulfur, which is intracellularly stored, but also to sulfite, which in presence of sulfide reacts to subsequently...
form thiosulfate. Then, once sulfide is completely depleted, elemental sulfur and thiosulfate are further oxidized to sulfate, the end product of the reaction. Further information about the biological and chemical sulfide conversions can be found on Supplementary Material, section SM-4 and elsewhere [21].

**Kinetic model: multi-step sulfide oxidation**

A Monod-type kinetic expression is often used to describe substrate consumption [13,14] in desulfurizing systems, being H$_2$S the only rate-limiting substrate. However, different authors have shown that the treatment of high loads of H$_2$S, such as those found in biogas desulfurization processes, may lead to substrate inhibition or oxygen limiting conditions. A multi-substrate type equation with a Haldane term for H$_2$S and a Monod term depending on the dissolved oxygen (DO) concentration inside the biofilm have been shown to describe well experimental oxygen uptake rate (OUR) and H$_2$S uptake rate profiles [20] during the characterization of H$_2$S-oxidizing biofilms in BTFs. Some authors have also proposed the use of a kinetic equation in which the ratio of elemental sulfur/sulfate produced is based on the DO concentration [24]. A product selectivity function for elemental sulfur or sulfate based on the sulfide oxidation activity and the OUR has been also considered [25,26]. It is well known that elemental sulfur, the main intermediate product of H$_2$S biological oxidation, is formed due to O$_2$ transport limitations inside the BTF bed [7,27]. Thus, obtaining an accurate model that describes well the production and accumulation of intermediate products of H$_2$S biological oxidation is crucial to describe accurately biogas desulfurization in BTFs. To reduce the uncertainty due to general assumptions and parameters based on literature correlations, the model herein uses a multi-step kinetic model (Fig. 1) previously developed by Mora et al. [21] and calibrated using respirometric techniques with biomass samples obtained from the BTF set up used herein.
Biological degradation of H$_2$S is described with a multi-step sulfide oxidation kinetic model (Fig. 3) based on Mora et al. [27]. The kinetic model considers that H$_2$S is partially oxidized to elemental sulfur, which is intracellularly stored, but also to sulfite, which in presence of sulfide reacts to subsequently form thiosulfate. Then, once sulfide is completely depleted, elemental sulfur and thiosulfate are further oxidized to sulfate, the end product of the reaction.

It has to be remarked that no previous works has intended to model such range of intermediate products of biological sulfide oxidation in BTFs for biogas desulfurization. Eqs. 11 to 13 correspond to the biological oxidation rates of sulfide, elemental sulfur and thiosulfate. Eq. 14 describes thiosulfate chemical production rate.

$$r_B = \frac{1}{Y_{max}} \cdot \left( \frac{\text{max} \cdot \mu_{max}}{K} \right) \cdot \left( \text{max} \cdot k_o \cdot X \right) \cdot (11)$$

$$r_B = \frac{1}{Y_{max}} \cdot \left( \frac{\text{max} \cdot \mu_{max}}{K} \right) \cdot \left( \text{max} \cdot k_o \cdot X \right) \cdot (12)$$

$$r_B = \frac{1}{Y_{max}} \cdot \left( \frac{\text{max} \cdot \mu_{max}}{K} \right) \cdot \left( \text{max} \cdot k_o \cdot X \right) \cdot (13)$$

$$r_{TS} = k \cdot C_{TS} \cdot \frac{\theta}{X} \cdot (14)$$

Subscripts: SS, S and TS refer to the reaction rate for S$_2^-$, S$_0^-$ and S$_2$O$_3^{2-}$ consumption, respectively, while $Y_{SS}$, $Y_S$ and $Y_{TS}$ are the biomass yield using S$_2^-$, S$_0^-$ and S$_2$O$_3^{2-}$ as substrate respectively (g VSS g$^{-1}$ S). $\mu_{max}$, $\mu_{max}$, and $\mu_{max}$ are the specific growth rates for SOB over S$_2^-$, S$_0^-$ and S$_2$O$_3^{2-}$, respectively in h$^{-1}$, g X g$^{-1}$ S, h$^{-1}$ and h$^{-1}$.

$k_{max}$, $k_{max}$ and $k_{max}$ are the affinity constants for sulfide and for oxygen, respectively, in g S m$^{-3}$ and g DO m$^{-3}$.

$K_{SS}$ is the sulfide inhibition constant in g S m$^{-3}$; $K_{max}$ is the maximum intracellular elemental sulfur stored to biomass in g S g$^{-1}$ VSS; $\alpha$ is a constant (dimensionless); $X$ is the biomass concentration in g X m$^{-3}$; $K_{SS}$ is the substrate switch constant g S m$^{-3}$. $K_{max}$ is the
affinity constant for $S_2O_3^{2-}$ consumption in g S m$^{-3}$; $k$ is the kinetic constant for $S_2O_3^{2-}$ production under biotic conditions; and $\beta$ is a constant (dimensionless). The model proposed by Mora et al. [21] to describe the multi-step sulfide oxidation bioprocess has been summarized in Tables 2 and 3 in which the stoichiometry and the kinetic expressions, respectively, used to describe each of the reactions occurring during the process have been specified. Further information about the biological and chemical sulfide conversions can be found on Supplementary Material, section SM-4 and elsewhere [21].

$H_2S$ biodegradation kinetics (Eq. 11) is described by a Haldane equation since substrate inhibition caused by sulfide over sulfide oxidation is considered. Furthermore, oxygen limitation was described by including a Monod-type kinetic term in the rate equations. In addition, accumulation of intracellular elemental sulfur by SOB was considered in order to describe the experimental decrease of the sulfide oxidation rate observed due to accumulation of intracellular elemental sulfur. SOB in the BTF was *Thiotrix* sp. according to pyrosequencing analysis performed during the kinetic model development [21]. Such filamentous $\gamma$-proteobacteria forms intracellular deposits of elemental sulfur as intermediary product during sulfide oxidation [28].

Elemental sulfur biodegradation kinetics (Eq. 12) was described using a shrinking particle model analogous to that used for biological consumption of other solid substrates such as Poly-hydroxy-butyrate (PHB). A non-competitive inhibition term was included in order to describe the substrate switch. Dissolved oxygen and thiosulfate limitation were described by a multi-substrate Monod-type kinetic expression. Similarly, thiosulfate oxidation to sulfate (Eq-
18

13) was described considering a Monod type kinetic for substrate consumption, while
potential chemical oxidation of sulfide to form thiosulfate was also considered (Eq. 14).

2.3 Model implementation

The set of partial differential equations was discretized in space along the bed height and
biofilm thickness. The conversion of the tubular reactor into a serial of stirred reactors was
verified running simulations at different discretizations and optimizing results and time
computing. As a result, an optimal discretization of the biofilter was found, resulting in eight
nodes along the bed height ($n_v$) and ten nodes along the biofilm thickness ($n_b$).

The resulting set of ordinary differential equations was solved using MATLAB in a home-
made modeling environment. A variable order method was used for solving stiff differential
equations based on the numerical differentiation formulas (NDFs), which are generally more
efficient than the closely related family of backward differentiation formulas (BDFs), also
known as Gear's methods. Since the inlet H$_2$S concentration was changed throughout the BTF
operation, inlet concentration profiles were used as input variable of the model.

Model parameters were estimated during calibration by curve-fitting of experimental data to
model predictions to describe the dynamics of a lab-scale BTF for biogas desulfurization. A
minimization routine on MATLAB, based on a non-linear multidimensional minimization
(Nelder-Mead) was used. The objective function to minimize was based on RE and $C_{\text{SO}_4^{2-}}$
according to the sensitivity analysis, and also to take into account both the gas-phase and the
liquid-phase dynamics, respectively. Also, $m_{\text{SO}_2}^0$ was not included in the objective function
because experimental $m_{\text{SO}_2}^0$ was not analytically measured but determined through mass
balances [7].
In order to evaluate the goodness of model predictions to experimental data, the efficiency criterion proposed by Nash and Sutcliffe [28] was used. Such efficiency criterion mathematically measures how well a model simulation fits the available experimental data. The efficiency coefficient (NSE) is defined as one minus the sum of the absolute squared differences between the predicted and observed data normalized by the variance of the observed data during the period under investigation according to Eq. (1511). Essentially, the closer the model efficiency to 1, the more accurate the model is.

\[
\text{NSE} = 1 - \frac{\sum_i (y_i - \bar{y}_i)^2}{\sum_i (y_i - \bar{y})^2} \quad (1511)
\]

3. Results and discussion

3.1 Sensitivity analysis

Before the model calibration, a sensitivity analysis was performed in order to determine the parameters that showed the highest influence on model outputs over the main process variables. Sensitivity analysis was assessed by increasing and decreasing by 10% the values of model parameters by 10% and comparing the relative change of the output variables to a relative change of the value of the model parameter. As stated in Deshusses et al. [14], model parameters fall in the following categories: physical-chemical properties, system specifications (dimensions), biokinetics and mass transfer parameters. In the present work, parameters belonging to all parameter categories were included to perform the relative
sensitivity analysis of the main output variables on biofiltration such as the H₂S removal efficiency (RE), the accumulated mass of elemental sulfur (m₅⁰) and the sulfate concentration in the liquid phase (C₅₆₂⁰). To perform the sensitivity analysis, model parameters were varied 0.9 and 1.1 times the reference value while simulating the stepwise load increase of period 1 (Table 1). Relative sensitivity results were chosen as those corresponding to the H₂S inlet concentration of 10000 ppmv (Table 24) because of a larger relative sensitivity of the model at these inlet concentrations. Only those parameters that showed a relative sensitivity higher than 0.10 in at least one of the output variables are shown in Table 24. Similar results in terms of relative sensitivity were obtained for the 4000, 6000 and 8000 ppmv concentration steps simulated (results not shown).

The most sensitive output variables were the RE and C₅₆₂⁰, which exhibited comparable sensitivities between them at a 10% increase while m₅⁰ was the less sensitive output variable due to its cumulative nature. Because of its cumulative nature, m₅⁰ was the less sensitive output variable compared to RE and C₅₆₂⁰, which exhibited comparable sensitivities between them at a 10% increase. However, at a 10% decrease results indicated that RE was highly influenced by parameters of all categories abovementioned to a higher extent than C₅₆₂⁰. Thus, both RE and C₅₆₂⁰ were the sole output variables selected to be included in the objective function during the calibration stage. Despite the low relative sensitivity of m₅⁰, the most sensitive parameters were those parameters related to its formation, i.e. O₂ and H₂S mass transfer coefficients (K₉₅₂, K₉₆₂⁰D₉₂), physical-chemical properties (H₉₂,H₉₂₂) and parameters related to its consumption (μ₉₅₂). This result was somehow expected since elemental sulfur formation directly depends on the oxygen availability and the S/DO ratio in the liquid phase that result from their transfer efficiency and solubility.
Besides the system specific parameters and physical-chemical parameters, the relative sensitivity analysis showed that biokinetic and mass transfer parameters were the most sensitive, which are often the most difficult to determine experimentally [29,30] and usually obtained by curve fitting of model estimations to experimental data [31,32]. Both RE and $C_{\text{L,SO}_4^{2-}}$ were mostly influenced by physical-chemical parameters such as $O_2$ and $H_2S$ Henry coefficients ($H_{O_2}$, $H_{H_2S}$); system specific parameters such as the specific interfacial area ($a$); by mass transfer parameters such as the $O_2$ and $H_2S$ mass transfer coefficients, liquid layer thickness and $O_2$ diffusivity $\left(K_{L,O_2}, K_{L,H_2S}, \delta_L, D_{O_2}\right)$; and by kinetic parameters such as the specific growth rate for sulfur and to the $O_2$ half-saturation constant $\left(\mu_{\text{max},2}, \alpha\right)$.

Consequently, the relative sensitivity analysis indicated that $H_2S$ removal was either influenced by gas-liquid mass transfer and by biological degradation. However, parameters related with $O_2$ mass transfer such as $K_{L,O_2}$, $H_{O_2}$ and $D_{O_2}$ exhibited a larger influence compared to the corresponding $H_2S$ parameters. Such result is in consonance with previous works that reported that $O_2$ transport rather than $H_2S$ transport is usually the limiting step in high-load $H_2S$ biogas desulfurization [3,33]. López et al. [7] showed that the effectiveness of $O_2$ G-L mass transfer due the trickling liquid velocity (TLV) regulation was a key factor to improve $H_2S$ oxidation in high-load $H_2S$ biogas desulfurization.

Regarding the biokinetic parameters, $\mu_{\text{max},2}$ was the most sensitive parameter, even if it exhibited lower sensitivities compared with mass transport and physical-chemical parameters. This result indicates that elemental sulfur accumulation plays a major role as intermediate and that must be included and properly described by any kinetic model. Sulfide oxidation rate can be limited by excessive elemental sulfur accumulation, which is directly influenced by the rate at which elemental sulfur is consumed ($\mu_{\text{max},2}$). In the kinetic model used in the present
work, intermediate reactions such as elemental sulfur production and biodegradation are considered, which means that both the inhibitory or the catalytic effect caused by each species over other bioreactions are reflected.

Excluding those parameters that can be determined using correlations ($K_{L,02}$), or physical-chemical parameters that can be found in literature ($D_{O2}$, $H_{H2S}$, $H_{O2}$), or provided by the packing manufacturer ($a$), the most sensitive parameters were selected for model calibration. Five parameters were selected for curve-fitting estimation during model calibration: namely, biomass and liquid layer thickness ($\delta_B$, $\delta_L$), specific growth rate for sulfur ($\mu_{max,2}$), biomass concentration ($X$) and $H_2S$ global mass transfer coefficient ($K_{L,H2S}$). The number of parameters was selected according to the number of variables assessed ($H_2S$ gas concentrations along the bed height, sulfate concentration and mass of elemental sulfur accumulated).

### 3.2 Model parameters estimation

Model parameters were estimated during calibration by curve-fitting of experimental data to model predictions to describe the dynamics of a lab-scale BTF for biogas desulfurization. A minimization routine on MATLAB, based on a non-linear multidimensional minimization (Nelder-Mead) was used. The objective function to minimize was based on RE and $C_{L,SO4}^2$ according to the sensitivity analysis, and also to take into account both the gas phase and the liquid phase dynamics, respectively. Also, $m_0^L$ was not included in the objective function because experimental $m_0^L$ was not analytically measured but determined through mass balances [7]. A summary of the BTF model parameters is shown in Tables 53 and 46, while Fig. 4–3 and Fig. 5–4 show the comparison of model predictions using the parameters estimated and the experimental data corresponding to the calibration period (Table 1).
Biomass concentration ($X$) estimated by the model (Table 53) was in coherence-agreement with the amount of elemental sulfur produced (22.37 g) and the $K_{\text{max}}$ determined by Mora et al. [21][26]. Since $K_{\text{max}}$ is the relation between the maximum amount of elemental sulfur that could be accumulated inside SOB cells before this accumulation completely blocked the biological sulfide consumption, this maximum amount of elemental sulfur was determined using the substrate switch constant ($K_{\text{max}}$) and the biomass concentration estimated by the model ($X$) according to $K_{\text{max}} = m_\text{max} / X$. Thus, under the calibration conditions, a maximum amount of 157 g of elemental sulfur could be accumulated inside SOB cells, well above the amount of elemental sulfur produced before this accumulation completely blocked the biological sulfide consumption. The $K_{LHS}$ was in concordance-agreement with $K_{LO_2}$ since both $K_{L}$ values were related by the square root of the diffusivity of each species [13]. The $K_{LO_2}$ was determined using the Onda-Billet and Schultes correlations [34] for the gas and liquid individual mass transfer coefficients $k_g$ and $k_l$, respectively, which was in close agreement with $K_{LO_2}$ determined by Dorado et al. [9]. It is worth highlighting that only the liquid-side resistance was significant since based on Billet and Schultes correlations the contribution of individual mass transfer resistances in the gas phase to the overall resistance for both gas species oxygen ($O_2$) and hydrogen sulfide ($H_2S$) were only 0.18% and 9.7% for $O_2$ and $H_2S$, respectively. In addition, $\mu_{\text{max},2}$ lies close to the range of values determined by Mora et al. [21] (5·10⁻⁴ -1.1·10⁻² h⁻¹). The $\delta_B$ denotes that the biofilm was thick enough to contain active and inactive biomass inside the biofilm and that $\delta_B$ is in the typical range for $H_2S$-degrading biofilms [13]. Kim and Deshusses [14] reported a $\delta_B$ of 23 μm concluding that, in order to perform the removal of high $H_2S$ loads in biogas, higher $\delta_B$ must be achieved. The $\delta_L$ estimated during model calibration was in agreement with the value obtained by dividing $D_{H_2S}$ by the $K_{LHS}$ [13].
In Fig. 4A and Fig. 5A experimental results and model predictions of the effect of stepwise LR increases due to H$_2$S inlet concentration increases are presented. Corresponding to the model calibration period are presented. Experimental data in both figures indicate that the system was able to remove almost 100% of inlet H$_2$S inlet concentration at RE close to 100% at all H$_2$S-LR (Fig. 4A and 3B). However, 100% sulfate production only occurred at the lowest H$_2$S-LR corresponding to an inlet concentration of 2000 ppmv. Further information related to sulfate production in this experiment values can be found elsewhere [7]. Thereafter, elemental sulfur was accumulated in the packed bed (Fig. 5A4A). At the highest H$_2$S-LR tested the sulfate production was lower than the elemental sulfur produced, which lead to a decrease of the concentration of sulfate measured in the liquid phase (Fig. 5B4B). Such behavior was directly related to the oxygen availability and the S/DO ratio in the liquid phase. A linear decrease of the inlet O$_2$/H$_2$S volumetric ratio (from 42.2 up to 8.4 % v/v) along the experiment led to limiting oxygen conditions. Thus, elemental sulfur production over sulfate production was favored. No thiosulfate production was detected experimentally neither was predicted by the model.

Regarding the goodness of model predictions to experimental data, high NSE values were obtained for the fitting of H$_2$S concentration measured at different bed heights (Fig. 4A3A and 3B). In the range of 2000 to 10000 ppmv, the model described well experimental H$_2$S concentrations measured in the first and second sections, with NSE coefficients of E=0.90 and E=0.93, respectively. At an inlet concentration of 10000 ppmv, a Nash-Sutcliffe efficiency coefficient of 0.43 was obtained for the H$_2$S concentration measured at the BTF outlet, mainly due to a mismatch between model predictions and experimental data. However, the Nash-Sutcliffe efficiency coefficient at the BTF outlet in the range of 2000 to 8000 ppmv, was E=0.90.
Mismatch between model prediction and experimental data of the BTF outlet concentration during the 10000 ppm\textsubscript{v} step might be related with the H\textsubscript{2}S measurement system. At 10000 ppm\textsubscript{v}, a higher airflow rate is needed to dilute the biogas flow rate in order to measure H\textsubscript{2}S concentrations inside the sensor measurement range. Therefore, less exact and precise experimental data is obtained. Additional details of BTF gas measurement system can be found in Supplementary Material, section S1 (Fig. S1).

Regarding to the predictions on the elemental sulfur accumulation (\(m_s\)), a Nash-Sutcliffe efficiency coefficient of \(E=0.94\) was obtained, indicating an accurate fit of the model to experimental data for the production of elemental sulfur. From Fig. 5B-4B it can be observed how the predicted sulfate concentration values fits almost perfectly to all experimental points, although during the step concentration of 4000 ppm\textsubscript{v} the simulated \(C_{L,SO_4^{2-}}\) was a 15\% higher than the experimental measure. Such difference was attributed to a biological delay time of microorganisms in the BTF to start to produce sulfate, since the first step-wise LR increment up to 4000 ppm\textsubscript{v}, was the first performed in the reactor after a long stationary feeding period of pseudo steady-state operation at 2000 ppm\textsubscript{v} of 42 days. The model reproduced well the sudden \(C_{L,SO_4^{2-}}\) concentration decrease during the last concentration step of 10000 ppm\textsubscript{v} as a consequence of both the unfavorable S/DO ratio and the amount of elemental sulfur accumulated in the BTF bed. A NSE coefficient of \(E=0.75\) was calculated for sulfate concentration predicted considering the whole period of the 2000-10000 ppm\textsubscript{v} stepwise increase experiment (Fig. 5B4B).

### 3.3 Model Validation

After calibration, the response of the model was evaluated in a different experimental period from that used for calibration. A stationary feeding period of 42 days of pseudo steady-state
Experimental data of cumulative mass of elemental sulfur and sulfate concentration and model predictions under the stationary feeding period pseudo-steady state conditions for model validation are presented in Fig. 65. The BTF performance during period 2 was always close to the optimal, since \( \text{H}_2\text{S} \text{ RE} \) was 100% and sulfate selectivity higher than 100% was calculated. Since the \( \text{H}_2\text{S-LR} \) during the experimental period corresponded to more than 100% sulfate production, elemental sulfur was progressively de-accumulated from the packed bed (Fig. 6A5A). The relatively small amount of sulfate produced from such elemental sulfur de-accumulation compared to that produced due to the \( \text{H}_2\text{S fed} \) led to a relatively constant sulfate profile along the monitored period.

The above mentioned elemental sulfur de-accumulation was verified in order to determine if it was a miscalculation in the mass balance or during sulfate concentration by ionic chromatography (IC). For this reason sulfate concentration, directly related to elemental sulfur de-accumulation, was determined when sulfate production was higher than 100% (see Supplementary Material, section SM-3 for further detail).

Results showed that the sulfate concentration produced from elemental sulfur de-accumulation was higher than the experimental error of IC (5%) (Fig. S3). Therefore the sulfate concentration increases during pseudo-steady state feeding conditions due to elemental sulfur de-accumulation. Elemental sulfur de-accumulated during this period correspond to the elemental sulfur previously accumulated, especially during the star-up period where 36 g of elemental sulfur were accumulated.
The model was able to accurately reproduce the elemental sulfur de-accumulation along this period. Despite of experimental data variability, model predictions showed an excellent agreement with experimental data. NSE of $E=0.87$ and $E=0.92$ were obtained along period 2 for the cumulative mass of sulfur and sulfate concentration, respectively, reflecting that there were no significant difference between experimental sulfate concentration and that predicted by the model.

Moreover, the model was used to simulate the performance of the reactor under dynamic conditions (Table 1), in order to simulate daily load fluctuations commonly found in real facilities. Dynamic model validation results are shown in Fig. 65. To properly assess the dynamics, the plant was fed a constant H$_2$S-LR of 56 g m$^{-3}$ h$^{-1}$ during 190h. Thereafter, the inlet dynamic profile was activated at an average H$_2$S-LR of 79 g m$^{-3}$ h$^{-1}$ with maximum and minimum peak H$_2$S-LR of 141 and 28 g m$^{-3}$ h$^{-1}$.

The BTF model response properly fits the experimental data during the change of dynamics represented in Fig. 76. During the first stage of 190h under pseudo steady-state conditions, the model predicted correctly the $C_{\text{LSO}_4^{2-}}$ experimental data. When variable H$_2$S-LR conditions were applied, a transient period with an increased sulfate concentration was observed until $t=240$h. Thereafter, $C_{\text{LSO}_4^{2-}}$ concentration remained oscillating in a constant range. The model was able to reproduce properly both the transient period and the pseudo steady-state period under a variable inlet load. The goodness of the fitting was confirmed with a NSE coefficient of $E=0.60$.

Overall, the model showed to be valid to describe the main processes occurring in the three phases of a BTF (gas, liquid and biofilm), gas phase (Fig 3A and 3B), liquid phase (Fig. 4A).
and solid phase as elemental sulfur (Fig. 4B), in a co-current flow mode configuration. Thus, this model becomes a powerful tool to predict the main intermediate (elemental sulfur) and final product (sulfate) of H$_2$S oxidation along different operational conditions such as pseudo steady-state conditions and variable LR conditions. Especially, accurate model predictions under high H$_2$S-LR and O$_2$ limiting conditions (period 1) could be useful for predicting elemental sulfur accumulation in industrial BTF installations. Therefore, maintenance tasks could be strategically planned. Moreover, the development of the BTF model can be used for the development and simulation of control strategies towards process optimization. Information obtained during the relative sensitivity analysis can be useful at the time of developing control strategies. Parameters related to O$_2$ transport are crucial in order to obtain the completely oxidation of H$_2$S and avoid the formation of elemental sulfur in the BTF bed, since an excessive accumulation of elemental sulfur can significantly diminish the reactor performance. Therefore, control strategies must be based on the improvement of the oxygen transfer to the liquid phase towards process optimization.

As an example, this model can help to develop control strategies in order to optimize process performance obtaining increasing RE while minimizing elemental sulfur accumulation.

Conclusions

A dynamic model for a BTF for high H$_2$S-LR biogas desulfurization in aerobic conditions operating under high H$_2$S-LR conditions was developed and successfully calibrated and validated, allowing a proper description of different operational scenarios such as LR increments due to H$_2$S concentration increases in the biogas stream. Furthermore the behavior of the different phases (gas, liquid and elemental sulfur) involved in the biogas desulfurization were correctly simulated predicted. Also the application of a two-step sulfide oxidation
A kinetic model was successfully performed in order to describe intermediate oxidation products.

A preliminary assessment through a relative sensitivity analysis, allowed to determining the most sensitive parameters to determine during model calibration of the model. The relative sensitivity analysis indicate that parameters. Parameters related to O₂ mass transport, exhibited a larger influence to model the output variables studied considered (RE and ClSO₄²⁻ and mₙ₀), compared to the corresponding H₂S parameters.

The proposed model was calibrated using experimental data, which allowing to describing accurately the H₂S—outlet H₂S concentration profile along the BTF bed during H₂S-LR increments. Besides describing properly sulfate production, additionally elemental sulfur, the main intermediate product during H₂S oxidation product, was correctly modeled predicted. Mass transfer parameters (δB, δL, KL,H₂S) and kinetic parameters (X, μmax,2) were estimated during BTF model calibration.

Moreover, the BTF model was correctly validated, describing two different periods, a pseudo under a stationary H₂S-LR feeding period and a dynamic H₂S-LR period. Proper gas phase description during both periods was obtained, but more importantly, elemental sulfur and sulfate were also in agreement with experimental data. Dynamic validations results demonstrated that the model is able to predict correctly the BTF operation when a variable H₂S-LR profile is applied. Hence the BTF model here presented expose that is capable to work and predict the BTF performance under similar conditions as those found in real plants, making it a suitable tool in order to develop and design control strategies towards process optimization of desulfurizing BTFs-S.
Accurate model predictions under high H$_2$S-LR and O$_2$-limiting conditions (period 1) could be useful for predicting elemental sulfur accumulation in industrial BTF installations. Therefore, maintenance tasks could be strategically planned. Moreover, the development of the BTF model can be used for the development and simulation of control strategies towards process optimization. From the sensitivity analysis results, it can be concluded that parameters related to O$_2$ are crucial in order to obtain the complete oxidation of H$_2$S and avoid the formation of elemental sulfur in the BTF bed, since an excessive accumulation of elemental sulfur can significantly diminish the reactor performance. Therefore, control strategies must be based on the improvement of the oxygen transfer to the liquid phase towards process optimization.

**Nomenclature Section**

**List of symbols**

- $a$: Specific surface area per volume unit of packed bed, m$^2$ m$^{-3}$
- $C_{nvs,i}$: Concentration of component $i$ at the biofilm surface in layer $nvs$, g m$^{-3}$
- $C_{nvs,nb}$: Concentration of component $i$ at the biofilm subdivision $nb$ in layer $nvs$, g m$^{-3}$
- $C_{B,SS}$: Concentration of sulfide in the biofilm phase, g m$^{-3}$
- $C_{B,S}$: Concentration of elemental sulfur in the biofilm phase, g m$^{-3}$
- $C_{B,TS}$: Concentration of thiosulfate in the biofilm phase, g m$^{-3}$
- $C_{B,DO}$: Concentration of dissolved oxygen in the biofilm phase, g m$^{-3}$
- $C_{AC,i}$: Oxygen inlet concentration in the aeration column, g m$^{-3}$
- $C_{out,i}$: Oxygen outlet concentration in the aeration column, g m$^{-3}$
- $C_{g,i}$: Concentrations of component $i$ in the bulk gas in layer $nvs$, g m$^{-3}$
Concentration of compound $i$ in the mineral medium, g m$^{-3}$

Concentrations of component $i$ in the bulk liquid in layer $n$, g m$^{-3}$

Concentration of compound $i$ in the purge flow, g m$^{-3}$

Concentration of compound $i$ in the recirculation flow, g m$^{-3}$

Concentration of sulfate in the liquid phase, g m$^{-3}$

Diffusivity of component $i$ in water, m$^{2}$ h$^{-1}$

Empty Bed Residence Time, s

Fresh liquid mineral medium flow rate, m$^{3}$ h$^{-1}$

Liquid purge flow rate, m$^{3}$ h$^{-1}$

Liquid flow rate, m$^{3}$ h$^{-1}$

Total (biogas + air) gas flow rate, m$^{3}$ h$^{-1}$

Hydraulic retention time, h

Gas-liquid dimensionless Henry coefficient for component $I$.

Gas-liquid global mass transfer coefficient for O$_2$ in the aeration column, h$^{-1}$

Gas-liquid global mass transfer coefficient of component $i$, h$^{-1}$

Maximum intracellular S$^{0}$ stored to biomass, g S g$^{-1}$ VSS

Substrate switch constant, g S m$^{-3}$

Affinity constant for S$_2$O$_3^{2-}$ consumption, g S m$^{-3}$

Affinity constants for sulfide, g S m$^{-3}$

Sulfide inhibition constant, g S m$^{-3}$

Affinity constants for oxygen, g DO m$^{-3}$

Kinetic constant for S$_2$O$_3^{2-}$ production under biotic conditions, h$^{-1}$

Cumulative mass of elemental sulfur, g

Rate equation for each biological process considered, g m$^{-3}$ h$^{-1}$

Trickling Liquid Velocity, m h$^{-1}$
V_{bed} — Packed bed volume, m³

V_{g,nvs} — Empty volume of the packed bed of layer nvs m³

V_{l,nvs} — Liquid volume of layer nvs, m³

V_{L,D} — Volume of liquid in the sump of the BTF, m³

V_{L,AC} — Liquid volume of the aeration column, m³

V_{g,AC} — Gas phase volume of the aeration column, m³

Y_{X/S_2} — Biomass growth yield using S^{0}, g VSS g^{-1} S

Y_{X/NS} — Biomass growth yield using S^{2}, g VSS g^{-1} S

Y_{X/TS} — Biomass growth yield using S_2O_3^{2-}, g VSS g^{-1} S

X — Biomass concentration, g X m⁻³

\nu_{ij} — Stoichiometric coefficient for compound i in process rate j

Greek letters

\alpha — Kinetic constant for elemental sulfur accumulation

\epsilon_g — Gas phase porosity

\eta — Packed bed porosity

\delta_p — Thickness of the water layer, m

\delta_{b,nb} — Thickness of one biofilm subdivision, m

\phi — Dynamic hold-up

\beta — Kinetic constant for thiosulfate

\mu_{max,1} — Specific growth rates for SOB over S^{2-}, h⁻¹

\mu_{max,2} — Specific growth rates for SOB over S^{0}, h⁻¹ g X^{1/3} g S^{4/3}

\mu_{max,3} — Specific growth rates for SOB over S_2O_3^{2-}, h⁻¹

Superscripts
Aknowledgements

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References


**TABLES**

Table 1. Experimental conditions for the simulated periods

<table>
<thead>
<tr>
<th>Period</th>
<th>[H$_2$S] (ppm)</th>
<th>LR (g S-H$_2$S m$^{-3}$ h$^{-1}$)</th>
<th>O$_2$/H$_2$S (% v v$^{-1}$)</th>
<th>Period simulated (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1: Calibration and sensitivity analysis</td>
<td>2000</td>
<td>56.3</td>
<td>42.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4000</td>
<td>112.9</td>
<td>21.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6000</td>
<td>169.6</td>
<td>14.0</td>
<td>5</td>
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<tr>
<td></td>
<td>8000</td>
<td>226.6</td>
<td>10.5</td>
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</tr>
<tr>
<td></td>
<td>10000</td>
<td>283.8</td>
<td>8.4</td>
<td></td>
</tr>
<tr>
<td>2: Stationary Validation</td>
<td>2000</td>
<td>56.3</td>
<td>42.2</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>2758$^a$</td>
<td>78.9</td>
<td>35.8</td>
<td></td>
</tr>
<tr>
<td>3: Dynamic Validation</td>
<td>5000$^b$</td>
<td>141.1</td>
<td>84.4</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>1000$^c$</td>
<td>28.1</td>
<td>16.8</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Average concentration

$^b$Maximum concentration

$^c$Minimum concentration
Table 2. Process stoichiometry for the aerobic sulfide, thiosulfate and elemental sulfur oxidation by S-oxidizing biomass.

<table>
<thead>
<tr>
<th>Process</th>
<th>Compounds</th>
<th>Sulfide</th>
<th>Thiosulfate</th>
<th>Sulfur</th>
<th>Sulfate</th>
<th>Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Growth on sulfide</td>
<td></td>
<td>$\frac{1}{Y_{X_1S_2}}$</td>
<td>$\frac{1}{Y_{X_1S_2}}$</td>
<td>$0.42^*$</td>
<td>$Y_{X_1S_2}$</td>
<td></td>
</tr>
<tr>
<td>2. Growth on elemental sulfur</td>
<td></td>
<td>$\frac{1}{Y_{X_1S}}$</td>
<td>$\frac{1}{Y_{X_1S}}$</td>
<td>$1.22^*$</td>
<td>$Y_{X_1S}$</td>
<td></td>
</tr>
<tr>
<td>3. Growth on thiosulfate</td>
<td></td>
<td>$\frac{1}{Y_{X_1TS}}$</td>
<td>$\frac{2}{Y_{X_1TS}}$</td>
<td>$1.65^*$</td>
<td>$Y_{X_1TS}$</td>
<td></td>
</tr>
<tr>
<td>4. Thiosulfate production</td>
<td></td>
<td>$1$</td>
<td>$2$</td>
<td>$-1.5$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Mora et al. [21]

Table 3. Process kinetics for the aerobic sulfide, thiosulfate and elemental sulfur oxidation by S-oxidizing biomass.

<table>
<thead>
<tr>
<th>Process</th>
<th>Process rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Growth on sulfide</td>
<td>$\mu_{max,1} \left( \frac{C_{B,SS}^{max}}{k_{SS} + C_{B,SS}^{max}} \right) \cdot \left( 1 - \frac{C_{B,SS}^{max}}{K_{max}} \right)^{\frac{2}{3}} \cdot \frac{C_{B,DO}^{max}}{C_{B,DO}^{max} + \frac{k_{SS}^{max}}{k_{SS}} + K} \cdot \frac{C_{B,DO}^{max}}{C_{B,DO}^{max} + k_{0} + k_{SS}} \cdot X$</td>
</tr>
<tr>
<td>2. Growth on elemental sulfur</td>
<td>$\mu_{max,2} \left( \frac{C_{B,SS}^{max}}{k_{SS} + C_{B,SS}^{max}} \right) \cdot \left( 1 - \frac{C_{B,SS}^{max}}{K_{max}} \right)^{\frac{2}{3}} \cdot \frac{C_{B,DO}^{max}}{C_{B,DO}^{max} + \frac{k_{SS}^{max}}{k_{SS}} + K} \cdot \frac{C_{B,DO}^{max}}{C_{B,DO}^{max} + k_{0} + k_{SS}} \cdot X$</td>
</tr>
<tr>
<td>3. Growth on thiosulfate</td>
<td>$\mu_{max,3} \left( \frac{C_{B,SS}^{max}}{k_{SS} + C_{B,SS}^{max}} \right) \cdot \left( 1 - \frac{C_{B,SS}^{max}}{K_{max}} \right)^{\frac{2}{3}} \cdot \frac{C_{B,DO}^{max}}{C_{B,DO}^{max} + \frac{k_{SS}^{max}}{k_{SS}} + K} \cdot \frac{C_{B,DO}^{max}}{C_{B,DO}^{max} + k_{0} + k_{SS}} \cdot X$</td>
</tr>
<tr>
<td>4. Thiosulfate production</td>
<td>$k_{B,SS}^\beta$</td>
</tr>
</tbody>
</table>
Table 24. Sensitivity results for key BTF model parameters assessed at an inlet H$_2$S concentration of 10000 ppmv,

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Units</th>
<th>Sensitivity, +Δ10 %</th>
<th>Sensitivity, -Δ10 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific interfacial area</td>
<td>a</td>
<td>m$^2$ m$^{-3}$</td>
<td>0.79 0.00 1.09</td>
<td>1.51 0.31 0.90</td>
</tr>
<tr>
<td>O$_2$ mass transfer coefficient</td>
<td>$K_{L02}$</td>
<td>m h$^{-1}$</td>
<td>0.45 -0.30 0.68</td>
<td>1.20 -0.19 0.53</td>
</tr>
<tr>
<td>O$_2$ Diffusivity</td>
<td>$D_{O2}$</td>
<td>m$^2$ h$^{-1}$</td>
<td>0.40 -0.10 0.33</td>
<td>1.02 -0.05 0.25</td>
</tr>
<tr>
<td>Specific growth rate over sulfur</td>
<td>$\mu_{max,2}$</td>
<td>h$^{-1}$</td>
<td>-0.40 -0.22 0.27</td>
<td>-0.48 0.04 0.51</td>
</tr>
<tr>
<td>H$_2$S Henry’s constant</td>
<td>$H_{H2S}$</td>
<td>dimensionless</td>
<td>-0.30 -0.46 0.24</td>
<td>-0.08 -0.50 0.25</td>
</tr>
<tr>
<td>Biofilm layer thickness</td>
<td>$\delta_B$</td>
<td>μm</td>
<td>-0.05 0.05 0.13</td>
<td>1.42 0.04 0.13</td>
</tr>
<tr>
<td>Biomass concentration</td>
<td>X</td>
<td>g X m$^{-3}$</td>
<td>0.06 0.12 0.11</td>
<td>1.31 0.12 0.11</td>
</tr>
<tr>
<td>Substrate switch</td>
<td>$K_{max}$</td>
<td>g S g X$^{-1}$</td>
<td>0.11 0.18 0.04</td>
<td>1.21 0.21 0.01</td>
</tr>
<tr>
<td>H$_2$S mass transfer coefficient</td>
<td>$K_{LH2S}$</td>
<td>m h$^{-1}$</td>
<td>-0.10 0.21 -0.04</td>
<td>-0.04 0.25 -0.07</td>
</tr>
<tr>
<td>O$_2$ half-saturation constant</td>
<td>$k_o$</td>
<td>g DO m$^{-3}$</td>
<td>0.14 0.08 -0.08</td>
<td>0.11 0.08 -0.09</td>
</tr>
<tr>
<td>Liquid layer thickness</td>
<td>$\delta_L$</td>
<td>μm</td>
<td>-0.50 0.02 -0.25</td>
<td>-0.37 0.04 -0.31</td>
</tr>
<tr>
<td>O$_2$ Henry’s constant</td>
<td>$H_{O2}$</td>
<td>dimensionless</td>
<td>-1.41 0.22 -0.76</td>
<td>-0.72 0.55 -1.23</td>
</tr>
<tr>
<td>Parameter</td>
<td>Symbol</td>
<td>Value</td>
<td>Units</td>
<td>Reference</td>
</tr>
<tr>
<td>----------------------------------------------------</td>
<td>--------</td>
<td>-----------</td>
<td>------------</td>
<td>------------</td>
</tr>
<tr>
<td>Biomass concentration</td>
<td>X</td>
<td>139.7·10³</td>
<td>g X m⁻³</td>
<td>Calibrated</td>
</tr>
<tr>
<td>Biofilm layer thickness</td>
<td>δ_B</td>
<td>200</td>
<td>µm</td>
<td>Calibrated</td>
</tr>
<tr>
<td>Liquid layer thickness</td>
<td>δ_L</td>
<td>10</td>
<td>µm</td>
<td>Calibrated</td>
</tr>
<tr>
<td>Specific growth rate for sulfur</td>
<td>μ_max2</td>
<td>2.17·10⁻²</td>
<td>h⁻¹</td>
<td>Calibrated</td>
</tr>
<tr>
<td>H₂S Global mass transfer coefficient</td>
<td>K_LH₂S</td>
<td>0.23</td>
<td>m h⁻¹</td>
<td>[34]</td>
</tr>
<tr>
<td>O₂ Global mass transfer coefficient in the BTF</td>
<td>K_LO₂</td>
<td>0.38</td>
<td>m h⁻¹</td>
<td>[34]</td>
</tr>
<tr>
<td>O₂ mass transfer coefficient in the Aeration column</td>
<td>K_LO₂AC</td>
<td>0.4</td>
<td>h⁻¹</td>
<td>Experimentally determined</td>
</tr>
<tr>
<td>Liquid hold-up</td>
<td>φ</td>
<td>3.57·10⁻²</td>
<td>dimensionless</td>
<td>Experimentally determined</td>
</tr>
<tr>
<td>Specific interfacial area</td>
<td>a</td>
<td>354.33</td>
<td>m² m⁻³</td>
<td>Packing material manufacturer</td>
</tr>
<tr>
<td>Packing material porosity</td>
<td>ε</td>
<td>0.85</td>
<td>dimensionless</td>
<td></td>
</tr>
<tr>
<td>H₂S diffusivity</td>
<td>D_H₂S</td>
<td>5.80·10⁻⁶</td>
<td>m² h⁻¹</td>
<td>[35]</td>
</tr>
<tr>
<td>O₂ diffusivity</td>
<td>D_O₂</td>
<td>9.00·10⁻⁶</td>
<td>m² h⁻¹</td>
<td>[35]</td>
</tr>
<tr>
<td>SO₄²⁻ diffusivity</td>
<td>D_SO₄²⁻</td>
<td>3.80·10⁻³</td>
<td>m² h⁻¹</td>
<td>[35]</td>
</tr>
<tr>
<td>H₂S Henry’s constant</td>
<td>H_H₂S</td>
<td>0.42</td>
<td>dimensionless</td>
<td>[36]</td>
</tr>
<tr>
<td>O₂ Henry’s constant</td>
<td>H_O₂</td>
<td>32.80</td>
<td>dimensionless</td>
<td>[36]</td>
</tr>
</tbody>
</table>
Table 46. Summary of main biokinetic parameters of the BTF model for biogas desulfurization calibrated by Mora et al. [21] (2015) through respirometry for the biotrickling filter modeled herein.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific growth rate for sulfide</td>
<td>$\mu_{\text{max,}1}$</td>
<td>0.41</td>
<td>h(^{-1})</td>
</tr>
<tr>
<td>Specific growth rate for sulfide</td>
<td>$\mu_{\text{max,}3}$</td>
<td>0.012</td>
<td>h(^{-1})</td>
</tr>
<tr>
<td>Sulfide affinity constant</td>
<td>$k_{SS}$</td>
<td>0.32</td>
<td>g S m(^{-3})</td>
</tr>
<tr>
<td>Sulfide inhibition constant</td>
<td>$k_{ia}$</td>
<td>42.4</td>
<td>g S m(^{-3})</td>
</tr>
<tr>
<td>Oxygen affinity constant</td>
<td>$k_o$</td>
<td>0.11</td>
<td>g DO m(^{-3})</td>
</tr>
<tr>
<td>maximum intracellular elemental sulfur stored in the biomass</td>
<td>$K_{max}$</td>
<td>0.252</td>
<td>g S g(^{1/3}) VSS</td>
</tr>
<tr>
<td>Thiosulfate affinity constant</td>
<td>$K_{TS}$</td>
<td>0.0023</td>
<td>g S m(^{-3})</td>
</tr>
<tr>
<td>Kinetic constant for thiosulfate</td>
<td>$k$</td>
<td>6.35</td>
<td>h(^{-1})</td>
</tr>
<tr>
<td>Substrate switch constant</td>
<td>$K$</td>
<td>0.014</td>
<td>g S m(^{-3})</td>
</tr>
<tr>
<td>Kinetic constant for thiosulfate</td>
<td>$\beta$</td>
<td>0.530</td>
<td>dimensionless</td>
</tr>
<tr>
<td>Kinetic constant</td>
<td>$\alpha$</td>
<td>1.71</td>
<td>dimensionless</td>
</tr>
</tbody>
</table>
List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>Specific surface area per volume unit of packed bed, m$^{-2}$ m$^{-3}$</td>
</tr>
<tr>
<td>$C_{i,m}$</td>
<td>Concentration of component $i$ at the biofilm surface, g m$^{-2}$</td>
</tr>
<tr>
<td>$C_{i,mv}$</td>
<td>Concentration of component $i$ at the biofilm subdivision nb, g m$^{-2}$</td>
</tr>
<tr>
<td>$C_{i,p}$</td>
<td>Oxygen inlet concentration in the aeration column, g m$^{-3}$</td>
</tr>
<tr>
<td>$C_{i,e}$</td>
<td>Oxygen outlet concentration in the aeration column, g m$^{-3}$</td>
</tr>
<tr>
<td>$C_{i,B}$</td>
<td>Concentration of component $i$ in the bulk gas phase for a certain layer, g m$^{-3}$</td>
</tr>
<tr>
<td>$C_{i,M}$</td>
<td>Concentration of component $i$ in the mineral medium, g m$^{-3}$</td>
</tr>
<tr>
<td>$C_{i,L}$</td>
<td>Concentration of component $i$ in the bulk liquid phase for a certain layer, g m$^{-3}$</td>
</tr>
<tr>
<td>$C_{i,R}$</td>
<td>Concentration of component $i$ in the recirculation flow, g m$^{-3}$</td>
</tr>
<tr>
<td>$C_{i,S}$</td>
<td>Concentration of sulfate in the liquid phase, g m$^{-3}$</td>
</tr>
<tr>
<td>$D_i$</td>
<td>Diffusivity of component $i$ in water, m$^2$ h$^{-1}$</td>
</tr>
<tr>
<td>$EBRT$</td>
<td>Empty Bed Residence Time, s</td>
</tr>
<tr>
<td>$F_{L,m}$</td>
<td>Fresh liquid mineral medium flow rate, m$^3$ h$^{-1}$</td>
</tr>
<tr>
<td>$F_{L,p}$</td>
<td>Liquid purge flow rate, m$^3$ h$^{-1}$</td>
</tr>
<tr>
<td>$F_L$</td>
<td>Liquid flow rate, m$^3$ h$^{-1}$</td>
</tr>
<tr>
<td>$F_{g}$</td>
<td>Total (biogas + air) gas flow rate, m$^3$ h$^{-1}$</td>
</tr>
<tr>
<td>$HRT$</td>
<td>Hydraulic retention time, h</td>
</tr>
<tr>
<td>$H$</td>
<td>Gas-liquid dimensionless Henry coefficient for component $i$</td>
</tr>
<tr>
<td>$K_{L,CO2}$</td>
<td>Gas-liquid mass transfer coefficient for oxygen in the aeration column, h$^{-1}$</td>
</tr>
<tr>
<td>$K_e$</td>
<td>Gas-liquid global mass transfer coefficient of component $e$</td>
</tr>
<tr>
<td>$K_{max}$</td>
<td>Maximum intracellular S$^{2-}$ stored to biomass, g S g$^{-1}$ VSS</td>
</tr>
<tr>
<td>$K_s$</td>
<td>Substrate switch constant, g S m$^{-3}$</td>
</tr>
<tr>
<td>$K_{a,s}$</td>
<td>affinity constant for S$_2$O$_3^{2-}$ consumption, g S m$^{-3}$</td>
</tr>
<tr>
<td>$K_{a,s}$</td>
<td>Affinity constants for sulfide, g S m$^{-3}$</td>
</tr>
<tr>
<td>$k$</td>
<td>Sulfide inhibition constant in g S m$^{-3}$</td>
</tr>
<tr>
<td>$k$</td>
<td>Affinity constants for oxygen, g DO m$^{-3}$</td>
</tr>
<tr>
<td>$k$</td>
<td>kinetic constant for S$_2$O$_3^{2-}$ production under biotic conditions, h$^{-1}$</td>
</tr>
<tr>
<td>$v_{max}$</td>
<td>Rate equation for each biological process considered, g m$^{-3}$ h$^{-1}$</td>
</tr>
<tr>
<td>$TLV$</td>
<td>Trickling Liquid Velocity, m h$^{-1}$</td>
</tr>
<tr>
<td>$V_{cb}$</td>
<td>Packbed volume, m$^3$</td>
</tr>
<tr>
<td>$V_{emp}$</td>
<td>Empty volume of the packed bed of layer, m$^3$</td>
</tr>
<tr>
<td>$V_{ls}$</td>
<td>Liquid volume of layer, m$^3$</td>
</tr>
<tr>
<td>$V_{s}$</td>
<td>Volume of liquid in the sump of the BTF, m$^3$</td>
</tr>
<tr>
<td>$V_{L}$</td>
<td>Liquid volume of the aeration column, m$^3$</td>
</tr>
<tr>
<td>$V_{g}$</td>
<td>Gas phase volume of the aeration column, m$^3$</td>
</tr>
<tr>
<td>$V_{bi}$</td>
<td>Biomass growth yield using S$^{2-}$, g VSS g$^{-1}$ S</td>
</tr>
<tr>
<td>$V_{bi}$</td>
<td>Biomass growth yield using S$^{2-}$, g VSS g$^{-1}$ S</td>
</tr>
</tbody>
</table>
Biomass growth yield using \( \text{SO}_2^- \), g VSS g \( \text{SO}_2^- \) g^{-1}

Biomass concentration, g X m^{-3}

Stoichiometric coefficient for compound \( i \) in each process rate

Greek letters

\( \varepsilon \) — Gas phase porosity

\( \varepsilon \) — Packed bed porosity

\( \delta_L \) — Thickness of the water layer, m

\( \delta_{\text{nb}} \) — Thickness of one biofilm subdivision, m

\( \phi \) — Dynamic hold-up

\( \beta \) — Kinetic constant for thiosulfate

\( \mu_{\text{SOB}} \) — Specific growth rates for SOB over \( \text{SO}_2^- \cdot \text{h}^{-1} \cdot \text{g} \cdot \text{X}^{1/3} \cdot \text{g}^{-1/3} \)

\( \mu_{\text{SOB}} \) — Specific growth rates for SOB over \( \text{SO}_3^2^- \cdot \text{h}^{-1} \cdot \text{g} \cdot \text{X}^{1/3} \cdot \text{g}^{-1/3} \)

\( \mu_{\text{SOB}} \) — Specific growth rates for SOB over \( \text{SO}_2^- \cdot \text{h}^{-1} \cdot \text{g} \cdot \text{X}^{1/3} \cdot \text{g}^{-1/3} \)

Superscripts

ns — Vertical layers

Subscripts

\( i \) — Component \( i \)

\( b \)
Modeling an aerobic biotrickling filter for biogas desulfurization through a multi-step oxidation mechanism

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b Universitat Politècnica de Catalunya, Department of Mining Engineering and Natural Resources, Bases de Manresa 61-73, 08240 Manresa, Spain.
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Abstract

A dynamic model describing physical-chemical and biological processes for the removal of high loads of H₂S from biogas streams in biotrickling filters (BTFs) was developed, calibrated and validated for a wide range of experimental conditions in a lab-scale BTF. The model considers the main processes occurring in the three phases of a BTF (gas, liquid and biofilm) in a co-current flow mode configuration. Furthermore, this model attempts to describe accurately the intermediate (thiosulfate and elemental sulfur) and final products (sulfate) of H₂S oxidation. A sensitivity analysis was performed in order to focus parameters estimation efforts on those parameters that showed the highest influence on the estimation of the H₂S removal efficiency, the accumulated mass of sulfur and the sulfate concentration in the liquid phase. Biofilm and liquid layer thicknesses, specific growth rate of biomass over elemental sulfur and the H₂S global mass transfer coefficient were the parameters that showed the highest influence on model outputs. Experimental data for model calibration corresponded to
the operation of the BTF under stepwise increasing H$_2$S concentrations between 2000 and 10000 ppm$_v$. Once the model was calibrated, validation was performed by simulating a stationary feeding period of 42 days of operation of the BTF at an average concentration of 2000 ppm$_v$ and a dynamic operation period were the BTF was operated under variable inlet H$_2$S concentration between 1000 and 5000 ppm$_v$ to simulate load fluctuations occurring in industrial facilities. The model described the reactor performance in terms of H$_2$S removal and predicted satisfactorily the main intermediate and final products produced during the biological oxidation process.

**Keywords**

Desulfurizing biotrickling filter; biogas; modeling; kinetics; sensitivity analysis; elemental sulfur

**1. Introduction**

Obtaining energy from non-renewable sources is becoming too expensive or too environmentally damaging nowadays. An energy source with high potential for green energy production is biogas. However, in order to have a suitable biogas utilization, impurities such as H$_2$S and reduced sulfur compounds (RSC) produced during the anaerobic fermentation of S-bearing organic molecules must be removed [1]. Removal of H$_2$S is strictly necessary to avoid corrosion of internal combustion engines during co-generation processes as well as for proper performance of further biogas upgrading technologies [2]. Biological technologies such as biotrickling filters (BTF) have demonstrated to be a suitable, competitive treatment technology for biogas conditioning when compared to physical-chemical technologies. However, main efforts have focused on experimental works, studying different pollutant loads [3], using different packing materials [4], different oxygen mass transfer devices [5], pH
conditions [6] or the gas-liquid flow pattern [7]. Tough process modeling has shown to be a crucial tool to evaluate the technical [1] and economical feasibility [2] of biological processes prior to full-scale implementation, few efforts have been made in this direction on biogas desulfurization in BTFs.

Multiphase biological processes, such as biofiltration in biofilters and biotrickling filters (BTF) for the removal of different type of contaminants like volatile organic compounds (VOCs) [7–9] and ammonia [10,11], have been modeled describing both transient and steady-state conditions. However, most BTF models have focused on VOCs removal [12], while literature available for H$_2$S BTFs modeling is scarce [13–15]. Therefore, a model describing properly the removal of high loads of H$_2$S in BTFs is still lacking in literature. Previous models for H$_2$S removal in BTFs have focused on removal of H$_2$S at odor level concentrations [13,14,16], while only few models in literature dealt with high loads of H$_2$S [17,18]. In most cases, the inherent complexity of such plug-flow, heterogeneous, multiphase bioreactors has been strongly simplified to avoid facing a large number of unidentifiable parameters. Often, G-L mass transport, diffusion in the biofilm and biological degradation kinetics have been identified as the most relevant processes. The heterogeneity of the water-biofilm layers as well as the kinetics and mechanisms considered to model H$_2$S removal in BTFs are the two main aspects that have been addressed differently by several authors. Most models consider an homogeneous biofilm density, a biofilm completely wetted along the packed bed height [13,17,19] and H$_2$S and O$_2$ mass transfer from the gas to the liquid phase prior to their diffusion to the biofilm were degradation takes place. Usually, only mass transfer resistance in the liquid phase is considered for modeling G-L mass transport due to the high interstitial gas velocity in the packed bed. However, biogas desulfurization requires of much longer gas contact times and, consequently, lower gas velocities that may increase mass transfer
resistance in the gas phase. Also, several alternatives have been proposed to model such
bioreactors such as considering a partially or a fully wetted biofilm as well as considering or
not adsorption of a fraction of the pollutant by the biofilm [14,20]. Despite no clear consensus
has been reached so far and a careful analysis from a modeling perspective must be
performed, modeling of biotrickling filters using a wetted/non-wetted biofilm approach seems
necessary when the TLV is modified due to the variable amount of water in the packed bed.

One of the most critical parts in the development of a model is how biodegradation
mechanisms and kinetics are described, since depending on the operational conditions, the
process might become biodegradation rate-controlled [15]. Different biodegradation kinetics
models and degradation mechanisms have been reported in order to describe the substrate
consumption in BTFs models for H₂S removal. Eqs. 1 and 2 are usually lumped in a single
equation describing the complete oxidation of sulfide to sulfate [14]. However, partial
oxidation to elemental sulfur has been often observed in BTFs for biogas desulfurization [5].
For this reason, a two-step mechanism (Eqs. 1 and 2) is needed for proper system modeling.

\[
\begin{align*}
    \text{H}_2\text{S} + 0.5\text{O}_2 & \rightarrow \text{S}^0 + \text{H}_2\text{O} \quad (1) \\
    \text{S}^0 + 1.5\text{O}_2 & \rightarrow \text{SO}_4^{2-} + \text{H}^+ \quad (2) 
\end{align*}
\]

Obtaining an accurate model that describes well the production and accumulation of
intermediate products of H₂S biological oxidation is crucial to describe accurately biogas
desulfurization in BTFs. Recently, Mora et al. [21] have proposed a multi-step pathway for
describing sulfide-oxidizing bacteria (SOB) as catalyst of H₂S oxidation to \( \text{SO}_4^{2-} \) considering
the partial sulfide oxidation to elemental sulfur as an intracellular product, and the sulfite and
thiosulfate production as additional intermediates. Such mechanistic model was calibrated and
validated through homogeneous respirometric tests providing successful results in describing
the main species of the H$_2$S oxidation process.

From a practical point of view, prediction of desulfurizing BTFs performance is essential.
Low sulfate production rates can lead to an excessive elemental sulfur formation that
accumulates into the packed bed. Consequently, a significant increase in pressure drop inside
BTF bed occurs [22], with a considerable reduction of BTF operational life-span and process
security. However, few works have addressed this topic so far. There is still the need for the
development of tools that impulse the industrial application of this emerging biological-based
technology. BTF models are essential in design steps, besides useful in the development of
control strategies towards process optimization.

From the stated above, the aim of this work was to develop, calibrate and validate a dynamic
model of an aerobic BTF for the removal of high-loads of H$_2$S from biogas streams. The BTF
model attempts to describe intermediate and final products obtained from H$_2$S oxidation under
stationary feeding periods, transient and dynamic conditions. It has to be remarked that no
previous works have intended to model such range of intermediate products of biological
sulfide oxidation in BTFs for biogas desulfurization

2. Material and methods

2.1 Experimental setup and operating conditions

A laboratory-scale BTF reactor, with an ancillary unit for air supply, was used in this study to
remove high loads of H$_2$S from biogas streams (Fig.1). The synthetic biogas consisted in
controlled mixtures of H$_2$S and nitrogen (N$_2$) fed at the top of the BTF (1). An air flow (2)
was firstly fed to an aeration column (3) for air supply to increase the dissolved oxygen (DO)
concentration in the liquid phase. Exhaust air (4) from the aeration column was fed at the top of the BTF under a co-current flow pattern and mixed with the biogas inlet stream at an O₂/H₂S supplied ratio of 41.2 (v v⁻¹). After biological degradation on the BTF bed (5), the treated biogas stream (6) leaves the reactor. The liquid phase was continuously recycled from bottom-to-top of the BTF at a trickling liquid velocity (TLV) of 4.4 m h⁻¹ (7). The liquid recirculation line (8) was previously oxygenated in an aeration column. The DO concentration in the recycle and purge lines was monitored in-situ in all the experiments. The reactor pH was also controlled at pHs of around 6.5 and 7 using an ON/OFF control system by automated addition of NaOH 1M or HCl 1 M. An empty bed residence time (EBRT) of 118 s and an average hydraulic retention time (HRT) of 30 ± 4 h were maintained throughout the study by regulating the purge pump (9) and the mineral medium pump (10). Regarding the packed bed characteristics, the reactor diameter was 7.14 cm with a packed bed volume of 2.80·10⁻³ m³ (V_bed). Polypropylene Pall rings of 15.9 mm diameter (MACH engineering products, USA) with a specific surface area of 354 m² m⁻³ were used.

Furthermore, H₂S, O₂ and carbon dioxide (CO₂) in the gas phase were measured by through three side streams obtained from the outlet gas stream and from gas sampling ports. On-line monitoring was performed with an electrochemical H₂S(g) sensor (Sure-cell, Euro-Gas Management Services, UK), O₂ gas sensor (O₂ SL sensor, Euro-Gas Management Services, UK) and a CO₂ gas sensor (CO₂ probe GMP343 Vaisala Carbocap, Vaisala, Finland). Sampling ports were located along the BTF height at 0.24 m, 0.51 m and 0.7 m in order to monitor the H₂S concentration profile along the BTF bed and therefore compare it with simulated data. Further information about gas concentration measurement can be found on Supplementary Material, section SM.-1. Also, detailed information of the BTF inoculation, analytical methods and related information can be found elsewhere [7].
The calibration of model parameters was performed using data obtained during stepwise H$_2$S Loading Rate (H$_2$S-LR) increments as a consequence of H$_2$S inlet concentration (C$_{g_{\text{in-H}_2S}}$) increase (Period 1-Table 1) in the lab-scale BTF set up (Fig. 1) operating at constant EBRT and constant biogas flow. For model validation under stationary H$_2$S feeding, a period of 42 days was simulated at a constant C$_{g_{\text{in-H}_2S}}$ of 2000 ppm$_v$ (Period 2-Table 1). In addition, model was also validated under dynamic conditions (Period 3-table 1) by simulating variable H$_2$S-LR conditions due to C$_{g_{\text{in-H}_2S}}$ increase (Fig. 2) emulating daily load fluctuations as those commonly found in real facilities. The averages of maximum and minimum H$_2$S-LR are shown in Table 1. Periods in Table 1 do not correspond to consecutive periods. All experiments were performed in between a time span of 15 months.

2.2 Model development
A three phase model (gas, liquid and biofilm) was considered to model reactor dynamics under a co-current flow pattern configuration. The model also considered the main processes occurring in the aeration column attached to the bioreactor (Supplementary Material, Fig. S1).

2.2.1 Biotrickling filter model
The BTF model incorporates mathematical expressions for the following mechanisms occurring in the packed bed: mass transport by advective flow in the gas and liquid phases, mass transfer at the gas-liquid interface, mass transfer by diffusion at the liquid-biofilm interface, internal diffusion in the biofilm phase and biological reaction in the biofilm as schematized in Fig. 1. Also, the model considered oxygen mass transfer at the gas-liquid interface occurring in the aeration column.
Model equations were built based on the above mentioned mechanisms and assumptions often assumed in BTF models in literature [13,14,20], which can be found in Supplementary Material, section SM-2. Since transport of compounds in the axial direction is modeled as plug flow, the BTF bed was discretized in vertical layers in order to simulate a sequence of continuous stirred tank reactors (CSTR) [23]. Vertical layers ($n_{vs}$) were numbered starting from the top of the BTF ($n_{vs}=1$) to the biogas outlet ($n_{vso}$). Similarly, the biofilm layers ($n_b$) were also divided in different subdivisions starting from the biofilm surface ($n_b=1$) to the biofilm subdivision in contact with the packed material ($n_{bp}$). The set of partial differential equations was discretized in space along the bed height and biofilm thickness. The conversion of the tubular reactor into a serial of stirred reactors was verified running simulations at different discretizations and optimizing results and time computing. As a result, an optimal discretization of the biofilter was found, resulting in eight nodes along the bed height ($n_{vs}=8$) and ten nodes along the biofilm thickness ($n_b=10$).

The following equations describe the mass balances in the gas, liquid and biofilm phases and their initial conditions in the BTF:

**Mass balance for the gas phase in the BTF**

\[
\frac{dC_{g,i}^{n_{vs}}}{dt} = \frac{F_T}{V_{g,n_{vs}}} \cdot \left(C_{g,i}^{n_{vs}-1} - C_{g,i}^{n_{vs}}\right) - \frac{K_{L,i} a}{\varepsilon_g} \cdot \left(\frac{C_{g,i}^{n_{vs}}}{H_i} - C_{L,i}^{n_{vs}}\right) \tag{3}
\]

initial conditions: \( t=0, C_{g,i}^{n_{vs}}=0 \)

at the BTF inlet \( (n_{vs}=1) \): \( C_{g,i}^{n_{vs}-1} = C_{g,i}^{in} \)

Where subscripts \( i \) refers to either gaseous $H_2S$ or $O_2$, while $C_{g,i}^{n_{vs}}$ and $C_{L,i}^{n_{vs}}$ are the concentrations of component $i$ in the bulk gas phase and bulk liquid phase for a certain layer \( (g m^{-3}) \), respectively; $V_{g,n_{vs}} (m^3)$ is calculated as $V_{g,n_{vs}} = \frac{V_{b,n_{vs}}}{n_{vs}}$ where $\varepsilon_g$ is the gas phase porosity,
which represents the volume fraction occupied by the gas phase in the packed and $V_b$ is the empty volume of the packed bed. Notice that G-L mass transport is described by a gas-liquid global mass transfer coefficient referred to the liquid phase ($K_{L,i}$) that considers both the individual gas and liquid mass transfer resistances.

Mass balance for the liquid phase in the BTF

$$\frac{dC_{L,i}^{nv}}{dt} = \frac{F_i}{V_{L,nv}} \cdot \left( C_{L,i}^{nv-1} - C_{L,i}^{nv} \right) + \frac{K_{L,i}a}{\varphi} \cdot \left( \frac{C_{g,i}^{nv}}{H_i} - C_{L,i}^{nv} \right) - \frac{aD_i}{\varphi \delta_L} \cdot \left( C_{L,i}^{nv} - C_{B,i}^{nv+1} \right) \quad (4)$$

Initial conditions:

$$t=0, \ C_{L,i}^{nv-1} = 0$$

at the BTF inlet ($nvs=1$):

$$C_{L,i}^{nv+1} = C_{L,i}^{RE}$$

subscripts $i$ refers to $S^{2-}, \ SO_4^{2-}, \ S_2O_3^{2-}$ and DO concentration, the compounds considered in the liquid phase of the BTF; $V_{L, nvs} (m^3)$ is calculated as $V_{L,nv} = \frac{V_b \varphi}{nvs}$ where $\varphi$ is the volume fraction occupied by the liquid phase in the packed bed according to the dynamic hold-up measured (-). Notice that mass transfer resistance in the liquid-biofilm interface was described by Fick’s law considering that the whole thickness of the liquid phase acted as the liquid boundary layer for mass transport resistance.

Mass balances for the biofilm in the BTF

For the first layer of the biofilm ($nb=1$) and all BTF layers ($nvs=1$ to $nvso$)

$$\frac{dC_{B,i}^{nv-1}}{dt} = \frac{D_i}{\delta_{B,L}^2} \cdot \left( C_{L,i}^{nv} - C_{B,i}^{nv} \right) - \frac{D_i}{\delta_{B,ab}^2} \cdot \left( C_{B,i}^{nv} - C_{B,i}^{nv+1} + 1 \right) + \sum V_{ij} \cdot r_{B,j} \quad (5)$$

For the inner layers of the biofilm ($nb=2$ to $nb=nbp-1$) and all BTF layers ($nvs=1$ to $nvso$)

$$\frac{dC_{B,i}^{nv+1}}{dt} = \frac{D_i}{\delta_{B,ab}^2} \cdot \left( C_{B,i}^{nv} + V_{ij} \cdot r_{B,j} \right) \quad (6)$$

For the closest layer to the packing material ($nbp$) and all BTF layers ($nvs=1$ to $nvso$)
\[
\frac{dC_{B,i}^{\text{vns,nbp}}}{dt} = \frac{D_i}{\delta_{B,ab}} \left( C_{B,i}^{\text{vns,nb}} - C_{B,i}^{\text{vns,nbp}} \right) + \sum v_{ij} \cdot r_{B,j} \tag{7}
\]

initial conditions in Eqs. 5, 6 and 7:
\[ t=0, \quad C_{B,i}^{\text{vns,nb}} = 0 \]

boundary conditions in Eqs. 5, 6 and 7:
\[ x=0, \quad C_{B,i} = C_{i,j} \]
\[ x=\delta_B, \quad \frac{dC_{B,i}^{\text{vns,nbp}}}{dt} = 0 \]

in Eqs. 5, 6 and 7, subscripts \( i \) refers to \( S^{2-}, SO_4^{2-}, S_2O_3^{2-} \) and DO concentration, the compounds considered in the biofilm phase of the BTF, while subscripts \( j \) indicates the rate equation in which component \( i \) is participating.

According to the BTF configuration, mass balances in the sump of the reactor (Eq. 8) and in the aeration column (Eqs. 9-10) were included.

Mass balance for the liquid phase in the sump of the BTF
\[
\frac{dC_{L,i}^P}{dt} = \frac{F_{L}C_{L,i}^{\text{vns}} - F_{L}C_{L,i}^{P} + F_{L}C_{L,i}^{\text{in}} - F_{L}C_{L,i}^{RE}}{V_{L,D}} \tag{8}
\]

initial conditions: \( t=0, C_{L,i}^P = 0 \)

subscript \( i \) refers to \( S^{2-}, SO_4^{2-}, S_2O_3^{2-} \) and DO concentration, the compounds considered in the liquid phase of the BTF. Notice that \( C_{L,i}^P \) and \( C_{L,i}^{RE} \) are equal except for dissolved oxygen because of the aeration column located in the recirculation line.

Mass balance for the gas phase in the aeration column
\[
\frac{dC_{g,O_2}^{\text{out}}}{dt} = \frac{F_{O_2}}{V_{g,AC}} \left( C_{g,O_2}^{AC} - C_{g,O_2}^{\text{out}} - K_{L,O_2}A \left( \frac{C_{g,O_2}^{\text{out}}}{H_{O_2}} - C_{L,O_2}^{RE} \right) \right) \tag{9}
\]

initial conditions: \( t=0, C_{g,O_2}^{AC} = 0 \)
Mass balance for the liquid phase in the aeration column

\[
\frac{dC_{L,O_2}}{dt} = \frac{F_{L}}{V_{L,AC}} \left( C^{P}_{L,O_2} - C^{RE}_{L,i} \right) + K_{L,O_2,AC} \left( \frac{C^{\text{out}}_{O_2}}{H_{O_2}} - C^{RE}_{L,i} \right) \tag{10}
\]

initial conditions: \( t=0, C^{P}_{L,O_2}=0 \)

2.2.2 Modeling of biological and chemical sulfides-compounds conversions

A Monod-type kinetic expression is often used to describe substrate consumption [13,14] in desulfurizing systems with \( H_2S \) as the sole rate-limiting substrate. However, different authors have shown that the treatment of high-loads of \( H_2S \), such as those found in biogas desulfurization processes, may lead to substrate inhibition or oxygen-limiting conditions. A multi-substrate type equation with a Haldane term for \( H_2S \) and a Monod term depending on the dissolved oxygen (DO) concentration inside the biofilm have been shown to describe well experimental oxygen uptake rate (OUR) and \( H_2S \) uptake rate profiles [20] during the characterization of \( H_2S \)-oxidizing biofilms in BTFs. Some authors have also proposed the use of a kinetic equation in which the ratio of elemental sulfur/sulfate produced is based on the DO concentration [24]. A product selectivity function for elemental sulfur or sulfate based on the sulfide oxidation activity and the OUR has been also considered by other authors [25,26].

It is well-known that elemental sulfur, the main intermediate product of \( H_2S \) biological oxidation, is formed due to \( O_2 \) transport limitations inside the BTF bed [7,27].

According to the abovementioned findings in literature, the kinetic model proposed by Mora et al. [21] was used herein. The multi-step sulfide oxidation mechanism (Figure 1D) has been summarized in Tables 2 and 3, in which the stoichiometry and the kinetic expressions that describe each of the reactions occurring during the process have been specified. In short, the kinetic model considers that \( H_2S \) is partially oxidized to elemental sulfur, which is intracellularly stored, but also to sulfite, which in presence of sulfide reacts to subsequently
form thiosulfate. Then, once sulfide is completely depleted, elemental sulfur and thiosulfate are further oxidized to sulfate, the end product of the reaction. Further information about the biological and chemical sulfide conversions can be found on Supplementary Material, section SM-4 and elsewhere [21].

2.3 Model implementation

The resulting set of ordinary differential equations was solved using MATLAB in a homemade modeling environment. A variable order method was used for solving stiff differential equations based on numerical differentiation formulas (NDFs), which are generally more efficient than the closely related family of backward differentiation formulas (BDFs), also known as Gear’s methods. Since the inlet \( \text{H}_2\text{S} \) concentration was changed throughout the BTF operation, inlet concentration profiles were used as input variable of the model. Model parameters were estimated during calibration by curve-fitting of experimental data to model predictions to describe the dynamics of a lab-scale BTF for biogas desulfurization. A minimization routine on MATLAB, based on a non-linear multidimensional minimization (Nelder-Mead) was used. The objective function to minimize was based on the \( \text{H}_2\text{S} \) removal efficiency (RE) and the concentration of sulfate in the liquid phase \( C_{\text{L,SO}_4^{2-}} \) according to the sensitivity analysis, and also to take into account both the gas-phase and the liquid-phase dynamics, respectively. Also, the cumulative mass of elemental sulfur \( m_S^0 \) was not included in the objective function because experimental \( m_S^0 \) was not analytically measured but determined through mass balances [7].

In order to evaluate the goodness of model predictions to experimental data, the efficiency criterion proposed by Nash and Sutcliffe [28] was used. Such efficiency criterion mathematically measures how well a model simulation fits the available experimental data. The efficiency coefficient (NSE) is defined as one minus the sum of the absolute squared
differences between the predicted and observed data normalized by the variance of the observed data during the period under investigation according to Eq. 11. Essentially, the closer the model efficiency to 1, the more accurate the model is.

\[
\text{NSE} = 1 - \frac{\sum_{i=1}^{n}(y_i - y_{mi})^2}{\sum_{i=1}^{n}(y_i - \bar{y}_o)^2}
\]  

(11)

3. Results and discussion

3.1 Sensitivity analysis

Before model calibration, a sensitivity analysis was performed in order to determine the parameters that showed the highest influence on model outputs over the main process variables. Sensitivity was assessed by increasing and decreasing model parameters by 10% and comparing the relative change of the output variables to a relative change of the model parameter. As stated in Deshusses et al. [14], model parameters fall in the following categories: physical-chemical properties, system specifications (dimensions), biokinetics and mass transfer parameters. In the present work, parameters belonging to all parameter categories were included to perform the relative sensitivity analysis of the main output variables on biofiltration such as \( RE \), \( m_S^0 \) and \( C_{LSO_4}^2 \). In order to determine the relative sensitivity, model parameters were varied 0.9 and 1.1 times the reference value while simulating the stepwise load increase of period 1 (Table 1). Relative sensitivity analysis results were chosen as those corresponding to the \( H_2S \) inlet concentration of 10000 ppm, (Table 4) because of a larger relative sensitivity of the model at these inlet concentration. Only those parameters that showed a relative sensitivity higher than 0.10 in at least one of the output variables are shown in Table 4. Similar results in terms of relative sensitivity were obtained for the 4000, 6000 and 8000 ppmv concentration steps simulated (results not shown).
The most sensitive output variables were the RE and $C_{L,SO_4^{2-}}$ that exhibited comparable sensitivities between them at a 10% increase while $m_S^0$ was the less sensitive output variable due to its cumulative nature. However, at a 10% decrease results indicated that RE was highly influenced by parameters of all categories abovementioned to a higher extent than $C_{L,SO_4^{2-}}$.

Thus, both RE and $C_{L,SO_4^{2-}}$ were the sole output variables selected to be included in the objective function during the calibration stage. Despite the low relative sensitivity of $m_S^0$, the most sensitive parameters were those parameters related to its formation, i.e. $O_2$ and $H_2S$ mass transfer coefficients ($K_{L,O_2}, K_{L,H_2S,DO_2}$), physical-chemical properties ($H_{O_2}, H_{H_2S}$) and parameters related to its consumption ($\mu_{max,2}$). This result was somehow expected since elemental sulfur formation directly depends on the oxygen availability and the S/DO ratio in the liquid phase that result from their transfer efficiency and solubility.

Besides the system specific parameters and physical-chemical parameters, the relative sensitivity analysis showed that biokinetic and mass transfer parameters were the most sensitive, which are often the most difficult to determine experimentally [29,30] and usually obtained by curve fitting of model estimations to experimental data [31,32]. Both RE and $C_{L,SO_4^{2-}}$ were mostly influenced by physical-chemical parameters such as $O_2$ and $H_2S$ Henry coefficients ($H_{O_2}, H_{H_2S}$); system specific parameters such as the specific surface area ($a$); by mass transfer parameters such as the $O_2$ and $H_2S$ mass transfer coefficients, liquid layer thickness and $O_2$ diffusivity ($K_{L,O_2}, K_{L,H_2S,DO_2}$); and by kinetic parameters such as the specific growth rate for sulfur and the $O_2$ half-saturation constant ($\mu_{max,2}, k_o$). Consequently, the relative sensitivity analysis indicated that $H_2S$ removal was either influenced by gas-liquid mass transfer and by biological degradation. However, parameters related with $O_2$ mass transfer such as $K_{L,O_2}$, $H_{O_2}$ and $D_{O_2}$ exhibited a larger influence compared to the
corresponding H$_2$S parameters. Such result is in consonance with previous works that reported that O$_2$ transport rather than H$_2$S transport is usually the limiting step in high-load H$_2$S biogas desulfurization [3,33]. López et al. [7] showed that the effectiveness of O$_2$ G-L mass transfer due the trickling liquid velocity (TLV) regulation was a key factor to improve H$_2$S oxidation in high-load H$_2$S biogas desulfurization.

Regarding the biokinetic parameters, $\mu_{\text{max,2}}$ was the most sensitive parameter, even if exhibited lower sensitivities compared with mass transport and physical-chemical parameters. This result indicates that elemental sulfur accumulation plays a major role as intermediate and that must be included and properly described by any kinetic model. Sulfide oxidation rate can be limited by excessive elemental sulfur accumulation, which is directly influenced by the rate at which elemental sulfur is consumed ($\mu_{\text{max,2}}$). In the kinetic model used in the present work, intermediate reactions such as elemental sulfur production and biodegradation are considered, which means that both the inhibitory or the catalytic effect caused by each species over other bioreactions are reflected.

Excluding those parameters that can be determined using correlations ($K_{L,\text{O}_2}$), or physical-chemical parameters that can be found in literature ($D_{\text{O}_2}$, $H_{\text{H}_2\text{S}}$, $H_{\text{O}_2}$), or provided by the packing manufacturer ($a$), the most sensitive parameters were selected for model calibration. Five parameters were selected for curve-fitting estimation during model calibration: namely, biomass and liquid layer thickness ($\delta_B$, $\delta_L$), specific growth rate for sulfur ($\mu_{\text{max,2}}$), biomass concentration ($X$) and H$_2$S global mass transfer coefficient ($K_{L,H_2S}$). The number of parameters was selected according to the number of variables assessed (H$_2$S gas concentrations along the bed height, sulfate concentration and mass of elemental sulfur accumulated).
3.2 Model parameters estimation

A summary of the BTF model parameters is shown in Tables 5 and 6, while Fig. 3 and Fig. 4 show the comparison of model predictions using the parameters estimated and the experimental data corresponding to the calibration period (Table 1).

Biomass concentration ($X$) estimated by the model (Table 5) was in agreement with the amount of elemental sulfur produced (22.37 g) and the $K_{\text{max}}$ determined by Mora et al. [21]. Since $K_{\text{max}}$ is the relation between the maximum amount of elemental sulfur that could be accumulated inside SOB cells before this accumulation completely blocked the biological sulfide consumption, this maximum amount of elemental sulfur was determined using the substrate switch constant ($K_{\text{max}}$) and the biomass concentration estimated by the model ($X$) according to $K_{\text{max}} = \frac{m_{\text{max}}}{X}$. Thus, under the calibration conditions, a maximum amount of 157 g of elemental sulfur could be accumulated inside SOB cells, well above the amount of elemental sulfur produced. The $K_{L,H_2S}$ was in agreement with $K_{L,O_2}$ since both $K_L$ values were related by the square root of the diffusivity of each species [13]. The $K_{L,O_2}$ was determined using the Billet and Schultes correlations [34] for the gas and liquid individual mass transfer coefficients $kg$ and $kl$, respectively, which was in close agreement with $K_{L,O_2}$ determined by Dorado et al. [9]. It is worth highlighting that only the liquid-side resistance was significant since based on Billet and Schultes correlations the contribution of individual mass transfer resistances in the gas phase to the overall resistance for both gas species oxygen ($O_2$) and hydrogen sulfide ($H_2S$) were only 0.18% and 9.7% for $O_2$ and $H_2S$, respectively. In addition, $\mu_{\text{max},2}$ lies close to the range of values determined by Mora et al. [21] ($5\cdot10^{-4}$ - $1.1\cdot10^{-2}$ h$^{-1}$).

The $\delta_B$ denotes that the biofilm was thick enough to contain active and inactive biomass inside the biofilm and that $\delta_B$ is in the typical range of $H_2S$-degrading biofilms [13]. Kim and Deshusses [14] reported a $\delta_B$ of 23 μm concluding that, in order to perform the removal of
high $\text{H}_2\text{S}$ loads in biogas, higher $\delta_B$ must be achieved. The $\delta_L$ estimated during model calibration was in agreement with the value obtained by dividing $D_{\text{H}_2\text{S}}$ by the $K_{L, \text{H}_2\text{S}}$. [13].

In Fig. 3 and Fig. 4 experimental results and model predictions of the effect of stepwise LR increases due to $\text{H}_2\text{S}$ inlet concentration increases corresponding to the model calibration period are presented. Experimental data in both figures indicate that the system was able to remove almost 100% of inlet $\text{H}_2\text{S}$ at all $\text{H}_2\text{S}$-LR (Fig. 3A and 3B). However, 100% sulfate production only occurred at the lowest $\text{H}_2\text{S}$-LR corresponding to an inlet concentration of 2000 ppmv. Further information related to sulfate production in this experiment can be found elsewhere [7]. Thereafter, elemental sulfur was accumulated in the packed bed (Fig. 4A). At the highest $\text{H}_2\text{S}$-LR tested the sulfate production was lower than the elemental sulfur produced, which lead to a decrease of the concentration of sulfate measured in the liquid phase (Fig. 4B). Such behavior was directly related to the oxygen availability and the S/DO ratio in the liquid phase. A linear decrease of the inlet $\text{O}_2$/$\text{H}_2\text{S}$ volumetric ratio (from 42.2 down to 8.4 % $v$/$v^-$) along the experiment led to limiting oxygen conditions. Thus, elemental sulfur production over sulfate production was favored. No thiosulfate production was detected experimentally neither was predicted by the model.

Regarding the goodness of model predictions to experimental data, high NSE values were obtained for the fitting of $\text{H}_2\text{S}$ concentration measured at different bed heights (Fig. 3A and 3B). In the range of 2000 to 10000 ppmv, the model described well experimental $\text{H}_2\text{S}$ concentrations measured in the first and second sections, with NSE coefficients of E=0.90 and E=0.93, respectively. At an inlet concentration of 10000 ppmv, a Nash-Sutcliffe efficiency coefficient of 0.43 was obtained for the $\text{H}_2\text{S}$ concentration measured at the BTF outlet, mainly due to a mismatch between model predictions and experimental data. However, the Nash-
Sutcliffe efficiency coefficient at the BTF outlet in the range of 2000 to 8000 ppmv was $E=0.90$.

Mismatch between model prediction and experimental data of the BTF outlet concentration during the 10000 ppmv step might be related with the $H_2S$ measurement system. At 10000 ppmv, a higher airflow rate is needed to dilute the biogas flow rate in order to measure $H_2S$ concentrations inside the sensor measurement range. Therefore, less exact and precise experimental data is obtained. Additional details of BTF gas measurement system can be found in Supplementary Material, section S1 (Fig. S1).

Regarding to the predictions on the elemental sulfur accumulation ($m_S^0$), a Nash-Sutcliffe efficiency coefficient of $E=0.94$ was obtained, indicating an accurate fit of the model to experimental data for the production of elemental sulfur. From Fig. 4B it can be observed how the predicted sulfate concentration values fits almost perfectly to all experimental points, although during the step concentration of 4000 ppmv the simulated $C_{LSO_4}^{2-}$ was a 15% higher than the experimental measure. Such difference was attributed to a biological delay time of microorganisms in the BTF to start to produce sulfate, since the first step-wise LR increment up to 4000 ppmv was the first performed in the reactor after a long stationary feeding period at 2000 ppmv of 42 days. The model reproduced well the sudden $C_{LSO_4}^{2-}$ concentration decrease during the last concentration step of 10000 ppmv as a consequence of both the unfavorable S/DO ratio and the amount of elemental sulfur accumulated in the BTF bed. A NSE coefficient of $E=0.75$ was calculated for sulfate concentration predicted considering the whole period of the 2000-10000 ppmv stepwise increase experiment (Fig. 4B).

3.3 Model Validation
After calibration, the response of the model was evaluated in a different experimental period from that used for calibration. A stationary feeding period of 42 days was used to validate the model, corresponding to period 2 in Table 1. Experimental data of cumulative mass of elemental sulfur and sulfate concentration and model predictions under the stationary feeding period for model validation are presented in Fig. 5. The BTF performance during period 2 was always close to the optimal, since H₂S RE was 100% and sulfate selectivity higher than 100% was calculated. Since the H₂S-LR during the experimental period corresponded to more than 100% sulfate production, elemental sulfur was progressively de-accumulated from the packed bed (Fig. 5A). The relatively small amount of sulfate produced from such elemental sulfur de-accumulation compared to that produced due to the H₂S fed led to a relatively constant sulfate profile along the monitored period.

The abovementioned elemental sulfur de-accumulation was verified in order to determine if it was a miscalculation in the mass balance or during sulfate concentration by ionic chromatography (IC). For this reason sulfate concentration, directly related to elemental sulfur de-accumulation, was determined when sulfate production was higher than 100% (see Supplementary Material, section SM-3 for further detail). Results showed that the sulfate concentration produced from elemental sulfur de-accumulation was higher than the experimental error of IC (5%) (Fig. S3). Therefore the sulfate concentration increases during a stationary feeding period due to elemental sulfur de-accumulation.

The model was able to accurately reproduce the elemental sulfur de-accumulation along this period. Despite of experimental data variability, model predictions showed an excellent agreement with experimental data. NSE of E=0.87 and E= 0.92 were obtained along period 2 for the cumulative mass of sulfur and sulfate concentration, respectively, reflecting that there
were no significant difference between experimental sulfate concentration and that predicted by the model.

Moreover, the model was used to simulate the performance of the reactor under dynamic conditions (Table 1), in order to simulate daily load fluctuations commonly found in real facilities. Dynamic model validation results are shown in Fig. 5. To properly assess the dynamics, the plant was fed a constant H₂S-LR of 56 g m⁻³ h⁻¹ during 190h. Thereafter, the inlet dynamic profile was activated at an average H₂S-LR of 79 g m⁻³ h⁻¹ with maximum and minimum peak H₂S-LR of 141 and 28 g m⁻³ h⁻¹.

The BTF model response properly fits the experimental data during the change of dynamics represented in Fig. 6. During the first stage of 190h during the stationary feeding period, the model predicted correctly the C_{L,SO₄}²⁻ experimental data. When variable H₂S-LR conditions were applied, a transient period with an increased sulfate concentration was observed until t=240h. Thereafter, C_{L,SO₄}²⁻ concentration remained oscillating in a constant range. The model was able to reproduce properly both the transient period and the pseudo steady-state period under a variable inlet load. The goodness of the fitting was confirmed with a NSE coefficient of E=0.60.

Overall, the model showed to be valid to describe the main processes occurring in the three phases of a BTF, gas phase (Fig 3A and 3B), liquid phase (Fig. 4A) and solid phase as elemental sulfur (Fig. 4B), in a co-current flow mode configuration. Thus, this model becomes a powerful tool to predict the main intermediate (elemental sulfur) and final product (sulfate) of H₂S oxidation along different operational conditions such as pseudo steady-state conditions and variable LR conditions. Especially, accurate model predictions under high
H₂S-LR and O₂ limiting conditions (period 1) could be useful for predicting elemental sulfur accumulation in industrial BTF installations. Therefore, maintenance tasks can be strategically planned. Moreover, the development of the BTF model can be used for the development and simulation of control strategies towards process optimization. Parameters related to O₂ transport are crucial in order to completely oxidize H₂S and avoid the formation of elemental sulfur in the BTF bed, since an excessive accumulation of elemental sulfur can significantly diminish the reactor performance. Therefore, control strategies must be based on the improvement of the oxygen transfer to the liquid phase towards process optimization.

4. Conclusions

A dynamic model for a BTF for high H₂S-LR biogas desulfurization in aerobic conditions was developed and successfully calibrated and validated, allowing a proper description of different operational scenarios such as LR increments due to H₂S concentration increases in the biogas stream. Furthermore, the behavior of the different phases (gas, liquid and elemental sulfur) involved in the biogas desulfurization were correctly predicted. Also, the application of a two-step sulfide oxidation kinetic model was successfully performed in order to describe intermediate oxidation products.

A preliminary assessment through a relative sensitivity analysis allowed determining the most sensitive parameters of the model. Parameters related to O₂ mass transport exhibited a larger influence to model output variables considered (RE, C₉SO₄²⁻ and mₘ²). The proposed model was calibrated using experimental data, which allowed describing accurately the outlet H₂S concentration profile along the BTF bed during H₂S-LR increments. Besides describing properly sulfate production, elemental sulfur, the main intermediate product during H₂S
oxidation, was correctly predicted. Mass transfer parameters (δ_B, δ_L, K_L,H2S) and kinetic parameters (X, μ_max,2) were estimated during BTF model calibration.

Moreover, the BTF model was validated under a stationary feeding period and a dynamic H_2S-LR period. Proper gas phase description during both periods was obtained. More importantly, elemental sulfur and sulfate were also in agreement with experimental data. Dynamic validation results demonstrated that the model is able to predict correctly the BTF operation when a variable H_2S-LR profile is applied. Hence the BTF model here presented is capable to predict the BTF performance under similar conditions as those found in real plants, making it a suitable tool in order to develop and design control strategies towards process optimization of desulfurizing BTFs.

Nomenclature Section

List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>a</td>
<td>Specific surface area per volume unit of packed bed, m^2 m^-3</td>
</tr>
<tr>
<td>C_{B,i}^{nvs,I}</td>
<td>Concentration of component i at the biofilm surface in layer nvs, g m^-3</td>
</tr>
<tr>
<td>C_{B,i}^{nvs,nb}</td>
<td>Concentration of component i at the biofilm subdivision nb in layer nvs, g m^-3</td>
</tr>
<tr>
<td>C_{B,SS}</td>
<td>Concentration of sulfide in the biofilm phase, g m^-3</td>
</tr>
<tr>
<td>C_{B,S}</td>
<td>Concentration of elemental sulfur in the biofilm phase, g m^-3</td>
</tr>
<tr>
<td>C_{B,TS}</td>
<td>Concentration of thiosulfate in the biofilm phase, g m^-3</td>
</tr>
<tr>
<td>C_{B,DO}</td>
<td>Concentration of dissolved oxygen in the biofilm phase, g m^-3</td>
</tr>
<tr>
<td>C_{g,O_2}^{AC}</td>
<td>Oxygen inlet concentration in the aeration column, g m^-3</td>
</tr>
<tr>
<td>C_{g,O_2}^{out}</td>
<td>Oxygen outlet concentration in the aeration column, g m^-3</td>
</tr>
<tr>
<td>C_{g,i}^{nvs}</td>
<td>Concentrations of component i in the bulk gas in layer nvs, g m^-3</td>
</tr>
<tr>
<td>C_{L,i}^{in}</td>
<td>Concentration of compound i in the mineral medium, g m^-3</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
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<td>----------</td>
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<tr>
<td>$C_{L,i}^{nvs}$</td>
<td>Concentrations of component $i$ in the bulk liquid in layer $nvs$, g m(^{-3})</td>
</tr>
<tr>
<td>$C_{L,i}^P$</td>
<td>Concentration of compound $i$ in the purge flow, g m(^{-3})</td>
</tr>
<tr>
<td>$C_{L,i}^{RE}$</td>
<td>Concentration of compound $i$ in the recirculation flow, g m(^{-3})</td>
</tr>
<tr>
<td>$C_{L,SO_4}^{-2}$</td>
<td>Concentration of sulfate in the liquid phase, g m(^{-3})</td>
</tr>
<tr>
<td>$D_i$</td>
<td>Diffusivity of component $i$ in water, m(^2) h(^{-1})</td>
</tr>
<tr>
<td>$EBRT$</td>
<td>Empty Bed Residence Time, s</td>
</tr>
<tr>
<td>$F_{L,in}$</td>
<td>Fresh liquid mineral medium flow rate, m(^3) h(^{-1})</td>
</tr>
<tr>
<td>$F_{L,P}$</td>
<td>Liquid purge flow rate, m(^3) h(^{-1})</td>
</tr>
<tr>
<td>$F_L$</td>
<td>Liquid flow rate, m(^3) h(^{-1})</td>
</tr>
<tr>
<td>$F_T$</td>
<td>Total (biogas + air) gas flow rate, m(^3) h(^{-1})</td>
</tr>
<tr>
<td>$HRT$</td>
<td>Hydraulic retention time, h</td>
</tr>
<tr>
<td>$H_i$</td>
<td>Gas-liquid dimensionless Henry coefficient for component $I_i$</td>
</tr>
<tr>
<td>$K_{L,O_2,AC}$</td>
<td>Gas-liquid global mass transfer coefficient for O(_2) in the aeration column, h(^{-1})</td>
</tr>
<tr>
<td>$K_{L,i}$</td>
<td>Gas-liquid global mass transfer coefficient of component $i$, h(^{-1})</td>
</tr>
<tr>
<td>$K_{max}$</td>
<td>Maximum intracellular S(^0) stored to biomass, g S g(^{-1/3}) VSS</td>
</tr>
<tr>
<td>$K$</td>
<td>Substrate switch constant, g S m(^{-3})</td>
</tr>
<tr>
<td>$K_{TS}$</td>
<td>Affinity constant for S(_2)O(_3)^{2-} consumption, g S m(^{-3})</td>
</tr>
<tr>
<td>$k_{SS}$</td>
<td>Affinity constants for sulfide, g S m(^{-3})</td>
</tr>
<tr>
<td>$k_{is}$</td>
<td>Sulfide inhibition constant, g S m(^{-3})</td>
</tr>
<tr>
<td>$k_o$</td>
<td>Affinity constants for oxygen, g DO m(^{-3})</td>
</tr>
<tr>
<td>$k$</td>
<td>Kinetic constant for S(_2)O(_3)^{2-} production under biotic conditions, h(^{-1})</td>
</tr>
<tr>
<td>$m_S^0$</td>
<td>Cumulative mass of elemental sulfur, g</td>
</tr>
<tr>
<td>$r_{Bj}$</td>
<td>Rate equation for each biological process considered, g m(^{-3}) h(^{-1})</td>
</tr>
<tr>
<td>$TLV$</td>
<td>Trickling Liquid Velocity, m h(^{-1})</td>
</tr>
<tr>
<td>$V_{bed}$</td>
<td>Packed bed volume, m(^3)</td>
</tr>
</tbody>
</table>
1. \( V_{g, nvs} \) Empty volume of the packed bed of layer \( nvs \) m\(^3\)

2. \( V_{L, nvs} \) Liquid volume of layer \( nvs \), m\(^3\)

3. \( V_{L, D} \) Volume of liquid in the sump of the BTF, m\(^3\)

4. \( V_{L, AC} \) Liquid volume of the aeration column, m\(^3\)

5. \( V_{g, AC} \) Gas phase volume of the aeration column, m\(^3\)

6. \( Y_{X/S} \) Biomass growth yield using \( S^0 \), g VSS g\(^{-1}\) S

7. \( Y_{X/SS} \) Biomass growth yield using \( S^{2-} \), g VSS g\(^{-1}\) S

8. \( Y_{X/TS} \) Biomass growth yield using \( S_2O_3^{2-} \), g VSS g\(^{-1}\) S

9. \( X \) Biomass concentration, g X m\(^{-3}\)

10. \( v_{ij} \) Stoichiometric coefficient for compound \( i \) in process rate \( j \)

11. Greek letters

12. \( \alpha \) Kinetic constant for elemental sulfur accumulation, -

13. \( \varepsilon_g \) Gas phase porosity, -

14. \( \varepsilon \) Packed bed porosity, -

15. \( \delta_L \) Thickness of the water layer, m

16. \( \delta_{B-nb} \) Thickness of one biofilm subdivision, m

17. \( \varphi \) Dynamic hold-up, -

18. \( \beta \) Kinetic constant for thiosulfate, -

19. \( \mu_{max,1} \) Specific growth rates for SOB over \( S^{2-} \), h\(^{-1}\)

20. \( \mu_{max,2} \) Specific growth rates for SOB over \( S^0 \), h\(^{-1}\) g X \(^{1/3}\) g S\(^{-1/3}\)

21. \( \mu_{max,3} \) Specific growth rates for SOB over \( S_2O_3^{2-} \), h\(^{-1}\)

22. Superscripts
**Acknowledgements**

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**References**


of a H2S desulfurizing biotrickling filter with random packing material., Chemosphere.

93 (2013) 2675–82.


[33] A.M. Montebello, M. Fernández, F. Almenglo, M. Ramírez, D. Cantero, M. Baeza, D.


Table 1. Experimental conditions for the simulated periods

<table>
<thead>
<tr>
<th>Period</th>
<th>[H$_2$S] (ppm$_v$)</th>
<th>LR (g S-H$_2$S m$^{-3}$ h$^{-1}$)</th>
<th>O$_2$/H$_2$S (% v v$^{-1}$)</th>
<th>Period simulated (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1: Calibration and sensitivity analysis</td>
<td>2000</td>
<td>56.3</td>
<td>42.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4000</td>
<td>112.9</td>
<td>21.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6000</td>
<td>169.6</td>
<td>14.0</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>8000</td>
<td>226.6</td>
<td>10.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10000</td>
<td>283.8</td>
<td>8.4</td>
<td></td>
</tr>
<tr>
<td>2: Stationary Validation</td>
<td>2000</td>
<td>56.3</td>
<td>42.2</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>2758$^a$</td>
<td>78.9</td>
<td>35.8</td>
<td></td>
</tr>
<tr>
<td>3: Dynamic Validation</td>
<td>5000$^b$</td>
<td>141.1</td>
<td>84.4</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>1000$^c$</td>
<td>28.1</td>
<td>16.8</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Average concentration
$^b$Maximum concentration
$^c$Minimum concentration
Table 2. Process stoichiometry for the aerobic sulfide, thiosulfate and elemental sulfur oxidation by S-oxidizing biomass.

<table>
<thead>
<tr>
<th>Process</th>
<th>Compounds</th>
<th>Sulfide</th>
<th>Thiosulfate</th>
<th>Sulfur</th>
<th>Sulfate</th>
<th>Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Growth on sulfide</td>
<td></td>
<td>$\frac{1}{Y_{X/SS}}$</td>
<td>$\frac{1}{Y_{X/SS}}$</td>
<td>$0.42^{*}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Growth on elemental sulfur</td>
<td></td>
<td>$\frac{1}{Y_{X/S}}$</td>
<td>$\frac{1}{Y_{X/S}}$</td>
<td>$1.22^{*}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. Growth on thiosulfate</td>
<td></td>
<td>$\frac{1}{Y_{X/TS}}$</td>
<td>$\frac{2}{Y_{X/TS}}$</td>
<td>$1.65^{*}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. Thiosulfate production</td>
<td></td>
<td>1</td>
<td>-2</td>
<td></td>
<td>-1.5</td>
<td></td>
</tr>
</tbody>
</table>

*Mora et al. [21]
Table 3. Process kinetics for the aerobic sulfide, thiosulfate and elemental sulfur oxidation by S-oxidizing biomass

<table>
<thead>
<tr>
<th>Process</th>
<th>Process rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Growth on sulfide</td>
<td>$\mu_{\text{max},1} \cdot \left( \frac{C_{B,SS}}{k_{SS} + C_{B,SS} + \frac{C_{B,SS}^2}{k_\text{is}}} \right) \cdot \left( 1 - \left( \frac{C_{B,SS}^*}{K_{\text{max}}} \right)^{\alpha} \right) \cdot \left( \frac{C_{B,DO}}{C_{B,DO} + k_0} \right) \cdot X$</td>
</tr>
<tr>
<td>2. Growth on elemental sulfur</td>
<td>$\mu_{\text{max},2} \cdot \left( \frac{C_{B,SS}}{X} \right)^{2/3} \cdot \left( \frac{K}{C_{B,SS} + K} \right) \cdot \left( \frac{C_{B,DO}}{C_{B,DO} + k_0} \right) \cdot X$</td>
</tr>
<tr>
<td>3. Growth on thiosulfate</td>
<td>$\mu_{\text{max},3} \cdot \left( \frac{C_{B,TS}}{C_{B,TS} + K_{TS}} \right) \cdot \left( \frac{K}{C_{B,SS} + K} \right) \cdot \left( \frac{C_{B,DO}}{C_{B,DO} + k_0} \right) \cdot X$</td>
</tr>
<tr>
<td>4. Thiosulfate production</td>
<td>$k \cdot C_{B,SS}^\beta$</td>
</tr>
</tbody>
</table>
Table 4. Sensitivity results for key BTF model parameters assessed at an inlet H₂S concentration of 10000 ppmv.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Units</th>
<th>RE (%)</th>
<th>$m_s^0$ (g-S)</th>
<th>$C_{LSO4}^{2-}$ (g-S L⁻¹)</th>
<th>RE (%)</th>
<th>$m_s^0$ (g-S)</th>
<th>$C_{LSO4}^{2-}$ (g-S L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific interfacial area</td>
<td>a</td>
<td>m² m⁻³</td>
<td>0,79</td>
<td>0,00</td>
<td>1,09</td>
<td>1,51</td>
<td>0,31</td>
<td>0,90</td>
</tr>
<tr>
<td>O₂ mass transfer coefficient</td>
<td>$K_{L,O₂}$</td>
<td>m h⁻¹</td>
<td>0,45</td>
<td>-0,30</td>
<td>0,68</td>
<td>1,20</td>
<td>-0,19</td>
<td>0,53</td>
</tr>
<tr>
<td>O₂ Diffusivity</td>
<td>$D_{O₂}$</td>
<td>m² h⁻¹</td>
<td>0,40</td>
<td>-0,10</td>
<td>0,33</td>
<td>1,02</td>
<td>-0,05</td>
<td>0,25</td>
</tr>
<tr>
<td>Specific growth rate over sulfur</td>
<td>$μ_{max,2}$</td>
<td>h⁻¹</td>
<td>-0,40</td>
<td>-0,22</td>
<td>0,27</td>
<td>-0,48</td>
<td>0,04</td>
<td>0,51</td>
</tr>
<tr>
<td>H₂S Henry's constant</td>
<td>$H_{H₂S}$</td>
<td>dimensionless</td>
<td>-0,30</td>
<td>-0,46</td>
<td>0,24</td>
<td>-0,08</td>
<td>-0,50</td>
<td>0,25</td>
</tr>
<tr>
<td>Biofilm layer thickness</td>
<td>$δ_B$</td>
<td>μm</td>
<td>-0,05</td>
<td>0,05</td>
<td>0,13</td>
<td>1,42</td>
<td>0,04</td>
<td>0,13</td>
</tr>
<tr>
<td>Biomass concentration</td>
<td>X</td>
<td>g X m⁻³</td>
<td>0,06</td>
<td>0,12</td>
<td>0,11</td>
<td>1,31</td>
<td>0,12</td>
<td>0,11</td>
</tr>
<tr>
<td>Substrate switch</td>
<td>$K_{max}$</td>
<td>g S g X⁻¹</td>
<td>0,11</td>
<td>0,18</td>
<td>0,04</td>
<td>1,21</td>
<td>0,21</td>
<td>0,01</td>
</tr>
<tr>
<td>H₂S mass transfer coefficient</td>
<td>$K_{L,H₂S}$</td>
<td>m h⁻¹</td>
<td>-0,10</td>
<td>0,21</td>
<td>-0,04</td>
<td>-0,04</td>
<td>0,25</td>
<td>-0,07</td>
</tr>
<tr>
<td>O₂ half-saturation constant</td>
<td>$k_o$</td>
<td>g DO m⁻³</td>
<td>0,14</td>
<td>0,08</td>
<td>-0,08</td>
<td>0,11</td>
<td>0,08</td>
<td>-0,09</td>
</tr>
<tr>
<td>Liquid layer thickness</td>
<td>$δ_L$</td>
<td>μm</td>
<td>-0,50</td>
<td>0,02</td>
<td>-0,25</td>
<td>-0,37</td>
<td>0,04</td>
<td>-0,31</td>
</tr>
<tr>
<td>O₂ Henry's constant</td>
<td>$H_{O₂}$</td>
<td>dimensionless</td>
<td>-1,41</td>
<td>0,22</td>
<td>-0,76</td>
<td>-0,72</td>
<td>0,55</td>
<td>-1,23</td>
</tr>
</tbody>
</table>
Table 5. Summary of main parameters of the BTF model for biogas desulfurization

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass concentration</td>
<td>$X$</td>
<td>$139.7 \times 10^3$</td>
<td>g X m$^{-3}$</td>
<td>Calibrated</td>
</tr>
<tr>
<td>Biofilm layer thickness</td>
<td>$\delta_B$</td>
<td>200</td>
<td>$\mu$m</td>
<td>Calibrated</td>
</tr>
<tr>
<td>Liquid layer thickness</td>
<td>$\delta_L$</td>
<td>10</td>
<td>$\mu$m</td>
<td>Calibrated</td>
</tr>
<tr>
<td>Specific growth rate for sulfur</td>
<td>$\mu_{max,2}$</td>
<td>$2.17 \times 10^{-2}$</td>
<td>h$^{-1}$</td>
<td>Calibrated</td>
</tr>
<tr>
<td>$H_2S$ Global mass transfer coefficient</td>
<td>$K_{L,H_2S}$</td>
<td>0.23</td>
<td>m h$^{-1}$</td>
<td>Calibrated</td>
</tr>
<tr>
<td>$O_2$ Global mass transfer coefficient in the BTF</td>
<td>$K_{L,O_2}$</td>
<td>0.38</td>
<td>m h$^{-1}$</td>
<td>[34]</td>
</tr>
<tr>
<td>$O_2$ mass transfer coefficient in the Aeration column</td>
<td>$K_{L,O_2,AC}$</td>
<td>0.4</td>
<td>h$^{-1}$</td>
<td>Experimentally determined</td>
</tr>
<tr>
<td>Liquid hold-up</td>
<td>$\varphi$</td>
<td>$3.57 \times 10^{-2}$</td>
<td>dimensionless</td>
<td>Experimentally determined</td>
</tr>
<tr>
<td>Specific interfacial area</td>
<td>$a$</td>
<td>354.33</td>
<td>m$^2$ m$^{-3}$</td>
<td>Packing material</td>
</tr>
<tr>
<td>Packing material porosity</td>
<td>$\varepsilon$</td>
<td>0.85</td>
<td>dimensionless</td>
<td>manufacturer</td>
</tr>
<tr>
<td>$H_2S$ diffusivity</td>
<td>$D_{H_2S}$</td>
<td>$5.80 \times 10^{-6}$</td>
<td>m$^2$ h$^{-1}$</td>
<td>[35]</td>
</tr>
<tr>
<td>$O_2$ diffusivity</td>
<td>$D_{O_2}$</td>
<td>$9.00 \times 10^{-6}$</td>
<td>m$^2$ h$^{-1}$</td>
<td>[35]</td>
</tr>
<tr>
<td>$SO_4^{2-}$ diffusivity</td>
<td>$D_{SO_4^{2-}}$</td>
<td>$3.80 \times 10^{-3}$</td>
<td>m$^2$ h$^{-1}$</td>
<td>[35]</td>
</tr>
<tr>
<td>$H_2S$ Henry’s constant</td>
<td>$H_{H_2S}$</td>
<td>0.42</td>
<td>dimensionless</td>
<td>[36]</td>
</tr>
<tr>
<td>$O_2$ Henry’s constant</td>
<td>$H_{O_2}$</td>
<td>32.80</td>
<td>dimensionless</td>
<td>[36]</td>
</tr>
</tbody>
</table>
Table 6. Summary of main biokinetic parameters of the BTF model for biogas desulfurization calibrated by Mora et al. [21] through respirometry for the biotrickling filter modeled herein.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific growth rate for sulfide</td>
<td>( \mu_{\text{max},1} )</td>
<td>0.41</td>
<td>h(^{-1})</td>
</tr>
<tr>
<td>Specific growth rate for sulfide</td>
<td>( \mu_{\text{max},3} )</td>
<td>0.012</td>
<td>h(^{-1})</td>
</tr>
<tr>
<td>Sulfide affinity constant</td>
<td>( k_{SS} )</td>
<td>0.32</td>
<td>g S m(^{-3})</td>
</tr>
<tr>
<td>Sulfide inhibition constant</td>
<td>( k_{is} )</td>
<td>42.4</td>
<td>g S m(^{-3})</td>
</tr>
<tr>
<td>Oxygen affinity constant</td>
<td>( k_{o} )</td>
<td>0.11</td>
<td>g DO m(^{-3})</td>
</tr>
<tr>
<td>maximum intracellular elemental sulfur stored in the biomass</td>
<td>( K_{\text{max}} )</td>
<td>0.252</td>
<td>g S g(^{-1/3}) VSS</td>
</tr>
<tr>
<td>Thiosulfate affinity constant</td>
<td>( K_{TS} )</td>
<td>0.0023</td>
<td>g S m(^{-3})</td>
</tr>
<tr>
<td>Kinetic constant for thiosulfate</td>
<td>( k )</td>
<td>6.35</td>
<td>h(^{-1})</td>
</tr>
<tr>
<td>Substrate switch constant</td>
<td>( K )</td>
<td>0.014</td>
<td>g S m(^{-3})</td>
</tr>
<tr>
<td>Kinetic constant for thiosulfate</td>
<td>( \beta )</td>
<td>0.530</td>
<td>dimensionless</td>
</tr>
<tr>
<td>Kinetic constant</td>
<td>( \alpha )</td>
<td>1.71</td>
<td>dimensionless</td>
</tr>
</tbody>
</table>
Figure 1

Click here to download high resolution image
Figure 4
Click here to download high resolution image
Figure 5

[Assuming the diagram shows two graphs: A and B. The X-axis represents time (h) ranging from 0 to 1000, and the Y-axis represents concentration (mg L$^{-1}$) for each graph.

Graph A: The data points show a downward trend with time, indicating a decrease in concentration over time. The line connects the data points smoothly, showing a gradual decline.

Graph B: The data points are scattered around a horizontal line, indicating little change in concentration over time. The line is a general trend line that appears to be flat, suggesting stability in the concentration.
]
FIGURE CAPTIONS

Fig. 1. Schematic of the A) BTF discretization in \( n_v \)s vertical layers and in \( n_b \) subdivisions of the biofilm, B) schematic of the main phenomena considered in the model, C) co-current biotrickling filter setup, and D) biological mechanisms for \( \text{H}_2\text{S} \) oxidation. In Figure 1C numbers correspond to (1) the biogas inlet, (2) air inlet, (3) aeration column, (4) exhaust air from the oxygenation column, (5) main reactor, (6) biogas outlet from the BTF, (7) BTF liquid outlet, (8) liquid recycling pump, (9) liquid purge, (10) mineral medium and bicarbonate inlet. In Figure 1D numbers correspond to (1) partial sulfide oxidation to elemental sulfur (2) thiosulfate production from polysulfide pathway (3) biological oxidation of thiosulfate and intracellular elemental sulfur.

Fig. 2. Variable \( \text{H}_2\text{S} \)-LR profile used for dynamic validation of the BTF model.

Fig. 3. Experimental and predicted \( \text{H}_2\text{S} \) concentration during period 1 after model calibration. A) experimental and simulated \( \text{H}_2\text{S} \) concentration profiles at different BTF bed heights. B) experimental and simulated \( \text{H}_2\text{S} \) concentration along the BTF height. Fig. 3A: Inlet \( \text{H}_2\text{S} \) concentration (solid line), experimental and simulated data from the 1\(^{st}\) bed (▲ and medium dashed line), the 2\(^{nd}\) bed (◊ and dashed-dot line), and the 3\(^{rd}\) bed (● and short dashed line). Fig. 3B: Experimental and simulated data at a LR of 56.3 g S-H\(_2\)S m\(^{-3}\) h\(^{-1}\) (○ and solid line), 112.9 g S-H\(_2\)S m\(^{-3}\) h\(^{-1}\) (△ and short dashed line), 169.6 g S-H\(_2\)S m\(^{-3}\) h\(^{-1}\) (■ and medium dashed line), 226.6 g S-H\(_2\)S m\(^{-3}\) h\(^{-1}\) (● and dot line), and 283.8 g S-H\(_2\)S m\(^{-3}\) h\(^{-1}\) (● and dashed dot line).

Fig. 4. \( \text{H}_2\text{S} \) inlet concentration (dashed line) and experimental (symbols) and predicted profiles (solid lines) of cumulative mass of (A) elemental sulfur and (B) sulfate during model calibration.

Fig. 5. Experimental (symbols) and model predictions (solid lines) during the stationary feeding period: (A) cumulative mass of sulfur and (B) sulfate concentration.

Fig. 6. Sulfate concentration comparison between experimental data (symbol) and model predictions (solid line) during dynamic validation.
Supplementary Material
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