

## Modelling biotrickling filters to minimize elemental sulfur accumulation during biogas desulfurization under aerobic conditions

L.R. López<sup>1</sup>, A.D. Dorado<sup>2</sup>, M. Mora<sup>1</sup>, Ll. Prades<sup>2</sup>, X. Gamisans<sup>2</sup>, J. Lafuente<sup>1</sup>, D. Gabriel<sup>1</sup>

<sup>1</sup> Universitat Autònoma de Barcelona, Department of Chemical Engineering, Escola d'Enginyeria, 08193 Belleterra, Spain.

<sup>2</sup> Universitat Politècnica de Catalunya, Department of Mining Engineering and Natural Resources, Bases de Manresa 61-73, 08240 Manresa, Spain.

e-mail: luisrafael.lopez@uab.cat

### Abstract

A mathematical dynamic model describing biological removal of high loads of H<sub>2</sub>S from biogas streams through a biotrickling filter (BTF) was developed, calibrated and validated to a range of specific experimental conditions of a lab-scale BTF. This model takes into account the main processes occurring in the three phases of the desulfurizing BTF (gas, liquid and biofilm phase) in a co-current configuration flow mode. This model attempts to describe accurately intermediate products obtained from H<sub>2</sub>S oxidation using kinetic models, previously developed using respirometric techniques with biomass samples obtained from the same BTF set up used here. Previous to the model parameters calibration, a sensitivity analysis was performed in order to focus the parameters estimation on those parameters that showed a highest influence on modelling results over the main process variables. To calibrate the model, an objective function considering the difference between the experimental and the predicted data was minimized. Experimental data for model calibration corresponded to a period of 5 days of operation of the BTF under stepwise increasing H<sub>2</sub>S concentrations between 2000 and 10000 ppm<sub>v</sub>. Once the model was calibrated, model was validated by simulating a period of 2 months of operation of the BTF at an average concentration of 2000 ppm<sub>v</sub>. Validation was successfully achieved since the model also described the reactor performance during a pseudo steady-state period.

### Keywords

Energy recovery; biogas desulfurization; biotrickling filter; modelling; co-current; sensitivity analysis

## INTRODUCTION

In the last decades, a strong global demand of crude oil, spare oil production capacity, and continuing political instability in certain oil producing regions has been the main causes of crude oil dramatically rise despite of its price. Considering this last scenario and the urgent need to act over greenhouse gas emissions in order to stop global warming and all those negative consequences that this situation is actually leading, the using of less, cleaner and locally produced energy is needed, including energy recovery from waste (Pöschl et al. 2010). In this context, biogas production by anaerobic digestion of organic wastes is the key to meet these targets (Mæng et al. 1999). Biogas is an energy rich-effluent that can be used directly for heating and electricity generation, and as substitute for fossil fuel applications, as transport fuel (FNR et al. 2012). A prior pre-treatment to remove biogas impurities such as reduced sulfur compounds (RSC) is required for energy recovery from biogas (Ross et al. 1996, Tchobanoglous et al. 2003). Biogas desulfurization performed through biotrickling filters (BTFs) is one of the most efficient biological alternatives (Fortuny et al. 2008, Montebello et al. 2014) to physical-chemical desulfurization treatments (Woodcock and Gottlieb 2007). Equations 1 to 2 are commonly used to describe hydrogen sulfide (H<sub>2</sub>S) desulfurization process in BTFs, where the H<sub>2</sub>S contained in biogas is converted to elemental sulfur and further to sulfate (SO<sub>4</sub><sup>2-</sup>) by S-oxidizing bacteria.



In some cases, partial sulfide oxidation to elemental sulfur but also to thiosulfate can be observed, and therefore different oxidation mechanisms can describe the desulfurization process (Mora et al. 2014). However, the industrial application of this emerging biological-based technology is slow and there are still some technical aspects to be improved. The main drawback related with the industrial application of desulfurizing BTFs is bed clogging caused by elemental sulfur accumulation (Rodriguez et al. 2013). This situation occurs when high loads of H<sub>2</sub>S are treated under limiting dissolved oxygen concentrations (Fortuny et al. 2008, Rodriguez et al. 2014). Efforts to improve and optimize the BTF performance can be experimentally done (Rodriguez et al. 2014, López et al. Submitted 2014), or alternatively simulating different operational scenarios, such as H<sub>2</sub>S loading rate (LR) increments due to H<sub>2</sub>S inlet concentration or to sudden biogas volumetric flow rate increment, and after study the response of the BTF under the simulated conditions. The aim of this work is to develop, calibrate and

validate a dynamic model of an aerobic BTF for H<sub>2</sub>S removal from biogas streams. The BTF model attempts to describe, besides the gas phase dynamics, intermediate products obtained from H<sub>2</sub>S oxidation using a kinetic model previously developed by Mora et al. (2014) determined by respirometric techniques with biomass samples obtained from the BTF set up used here. Multiple works in literature have focused on modelling for odour control (Li et al. 2002, Deshusses et al. 2003) where only the gas phase dynamics was simulated. Considering the modelling of intermediate products of the biological reaction it is crucial in biogas desulfurization, since the operability of the reactor at industrial scale depends on the sulfate production capacity (pCSO<sub>4</sub><sup>2-</sup>). Low pCSO<sub>4</sub><sup>2-</sup> can lead to an excessively elemental sulfur formation that consequently carries significant increase of pressure drop inside BTF bed (Andreassen et al. 2012), leading to considerable reduction of BTF operational life and process security. In addition, a BTF model is essential to develop control strategies and towards process optimization by improving the oxygen (O<sub>2</sub>) gas-liquid mass transfer phase to favour the complete oxidation of H<sub>2</sub>S to SO<sub>4</sub><sup>2-</sup>.

## MATERIALS AND METHODS

### Differential Biotrickling filter equipment

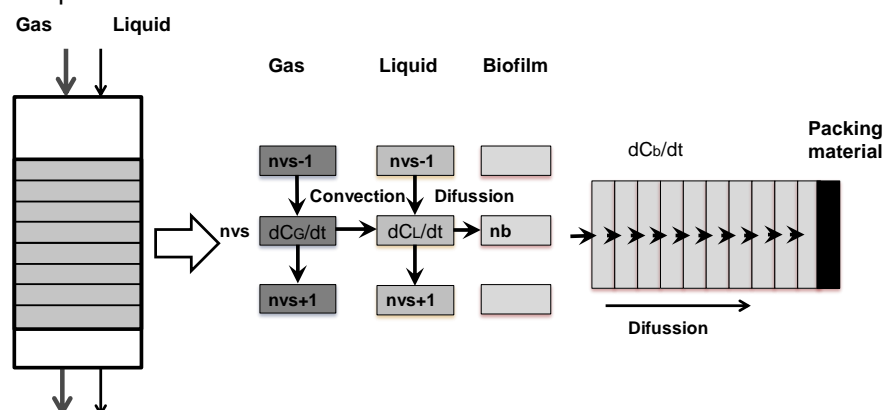
Experimental data used for the calibration and validation of the model was obtained from the lab scale BTF set up during operation under different H<sub>2</sub>S-LR according to table 1. Detailed information of the BTF inoculation, set up dimensions and analytical methods can be found elsewhere (López et al. Submitted 2014). Model parameters calibration was performed using data obtained during stepwise LR increments from 56.3 to 283.8 g S-H<sub>2</sub>S m<sup>-3</sup> h<sup>-1</sup> as a consequence of H<sub>2</sub>S inlet concentration increase. Further information of experimental conditions and results of this experiment can be found elsewhere (López et al. Submitted 2014). For model validation, different operational conditions corresponding to a pseudo steady-state period of 58 days were simulated.

**Table 1. Experimental conditions for periods simulated**

| Period         | [H <sub>2</sub> S]<br>(ppm <sub>v</sub> ) | [H <sub>2</sub> S] LR<br>(g S-H <sub>2</sub> S m <sup>-3</sup> h <sup>-1</sup> ) | O <sub>2</sub> /H <sub>2</sub> S<br>(% v v <sup>-1</sup> ) | Previous<br>operation<br>(days) | Period<br>simulated<br>(days) |
|----------------|---|--|--|---------------------------------|-------------------------------|
| 1: Calibration | 2000                                      | 56.3   | 42.2   | 114                             | 5                             |
|                | 4000                                      | 112.9  | 21.0   |                                 |                               |
|                | 6000                                      | 169.6  | 14.0   |                                 |                               |
|                | 8000                                      | 226.6  | 10.5   |                                 |                               |
|                | 10000                                     | 283.8  | 8.4  |                                 |                               |
| 2: Validation  | 2000                                      | 56.3   | 42.2   | 56                              | 58                            |

## MODEL DEVELOPMENT

In this work, a mathematical dynamic model describing biological removal of high loads of H<sub>2</sub>S from biogas streams through a BTF (Rodriguez et al. 2013) was firstly adapted to the specific setup. A three phase model (gas, liquid and biofilm) was considered to model the reactor dynamics when the reactor is operated under co-current flow pattern configuration (figure 1). The model attempts to describe accurately intermediate products obtained from H<sub>2</sub>S oxidation using kinetic models developed by Mora et al. (2014) using respirometric techniques with biomass samples obtained from the same BTF set up used here.



**Figure 1.** BTF discretization in nvs vertical layers and in nb layers for each biofilm layer.

In order to describe the main processes taking place in the desulfurizing BTF, some assumptions were made, most of them often assumed in BTF models in literature (Li et al. 2002, Kim and Deshusses et al. 2003, Devigny and Ramesh et al. 2005): **(1)** The whole biofilm is completely covered by liquid. **(2)** The adsorption capacity of the plastic packing material is neglected. **(3)** The packing material is entirely covered by a uniform layer of biofilm, which have a uniform thickness. **(4)** Biomass in the biofilm consists of active biomass responsible for substrate removal and no biomass growth is considered, therefore its distribution and density is considered to be uniform along the BTF packed bed. **(5)** Gas-Liquid mass transport is described by a gas-liquid mass transfer coefficient ( $k_L$ ). **(6)** According to the Henry's theory, gas-liquid interfaces are at equilibrium. **(7)** Plug-flow mode without axial or radial dispersion was considered to describe the circulation of the gas flow through the BTF bed. **(8)** The mass flux through each finite division of the BTF bed is simulated as a single continuous stirred tank reactor (CSTR), therefore the complete BTF bed is simulated as a sequence of CSTR's. All species and phases (gas, liquid, biofilm and packed support) were considered in each of the divisions. **(9)** Diffusion of the species through the biofilm is described by Fick's law. Some particular considerations based on Mora et al. (2014) were made for the biodegradation kinetic model **(10)** It considers that  $H_2S$  is partially oxidized to elemental sulfur but also to sulphite, which in presence of sulfide reacts to subsequently form thiosulfate. Then once sulfide is completely depleted, elemental sulfur, that was intracellularly stored, and thiosulfate are oxidized to sulfate, the end product of the reaction. **(11)**  $H_2S$  biodegradation kinetic is described by a Haldane equation, since substrate inhibition caused by sulfide over sulfide oxidation is considered. Also accumulation of intracellular elemental sulfur was considered in the kinetic model. **(12)** Dissolved oxygen and thiosulfate limitation were described by a multi-substrate Monod-type kinetic. **(13)** Elemental sulfur biodegradation kinetic is described by a non-competitive inhibition term in order to describe the substrate switch. Furthermore elemental sulfur biodegradation kinetics was described using a shrinking particle model analogous to that used for biological consumption of other solid substrates such as Poly-hydroxy-butyrate (PHB). Further information related to model equations and variable nomenclature can be founded elsewhere in González-Sánchez et al (2014). Detailed information of the reaction mechanisms and of the kinetic reaction rates can be found elsewhere in Mora et al. (2014).

#### Reaction rates:

$$R_{B,SS} = \left(\frac{1}{Y_{XSS}}\right) \cdot \mu_{max,1} \cdot \left(\frac{C_{B,SS}}{k_{SS} + C_{B,SS} + \frac{C_{B,SS}^2}{k_{IS}}}\right) \cdot \left(1 - \left(\frac{C_{B,S}}{X}\right)^\alpha\right) \cdot \left(\frac{C_{B,OD}}{C_{B,OD} + k_O}\right) \cdot X \quad (3)$$

$$R_{B,S} = \left(\frac{1}{Y_{XS}}\right) \cdot \mu_{max,2} \cdot \left(\frac{C_{B,S}}{X}\right)^{2/3} \cdot \left(\frac{K}{C_{B,SS} + K}\right) \cdot \left(\frac{C_{B,OD}}{C_{B,OD} + k_O}\right) \cdot X \quad (4)$$

$$R_{B,TS} = \left(\frac{1}{Y_{XTS}}\right) \cdot \mu_{max,3} \cdot \left(\frac{C_{B,TS}}{C_{B,TS} + K_{TS}}\right) \cdot \left(\frac{K}{C_{B,SS} + K}\right) \cdot \left(\frac{C_{B,OD}}{C_{B,OD} + k_O}\right) \cdot X \quad (5)$$

$$R_{B,TS} = k \cdot C_B^b \quad (6)$$

Where the subindexes SS refers to sulfide, S refers to elemental sulfur and TS refers to thiosulfate.

## RESULTS AND DISCUSSION

### Sensitivity analysis

Before model calibration, a sensitivity analysis was performed in order to determine the parameters that showed a highest influence on model outputs over the main process variables. Typical operational parameters on biofiltration such as the  $H_2S$  Removal Efficiency (RE), the accumulated mass of sulfur ( $m_S^0$ ) and the sulfate concentration in the liquid phase ( $C_{L,SO_4^{2-}}$ ) were the variables selected to perform the sensitivity analysis. Model parameters were varied 0.9 and 1.1 times the reference value. The conditions selected to perform the sensitivity analysis were those corresponding to period 1 (table 1). Sensitivity analysis results (data not shown) correspond to those at an  $H_2S$  inlet concentration of 10000 ppm<sub>v</sub>. Similar results were obtained for the rest of step wise concentration steps (results not shown). As stated in Deshusses et al. 2003, model parameters fall in the following categories: physical-chemical properties and systems specific (dimensions), biokinetic, and mass transfer parameters. The sensitivity analysis showed that biokinetic and mass transfer parameters were the most sensitive, which are often the most difficult to determine experimentally (Munz et al. 2009, Mora et al. 2014) and usually obtained from a mathematical approach (Iliuta et al. 2005, Dorado et al. 2015).

Results obtained from the sensitivity analysis reflects that the RE is strictly influenced by the specific growth rate for sulfur ( $\mu_{max,2}$ ). Since the equation that predicts the consumption of elemental sulfur considers the effect of the accumulation of intracellular sulfur, therefore those variables related

to the formation or consumption of elemental sulfur are model sensitive as well. On the other hand, the most sensitive parameters related to  $m_S^0$  are those parameters related to its formation, *i.e.*  $H_2S$  and  $O_2$  mass transfer parameters and physical-chemical properties and parameters related to its consumption ( $\mu_{max,2}$ ). Finally, the most sensitive parameters over  $C_{L,SO_4^{2-}}$  are these parameters related to  $O_2$  properties (physical-chemical and mass transfer properties) and parameters related to  $m_S^0$ . This result is in concordance with the biokinetic mechanism of formation of sulfate, which depends on the accumulation of intracellular sulfur. Furthermore, results obtained highlight the importance of  $O_2$  over the formation of sulfate, the end product of the biological desulfurization reaction. Excluding those parameters that can be determined using correlations ( $K_{L,O_2}$ ) or that can be found in literature ( $D_{O_2}$ ,  $H_{H_2S}$ ,  $K_{max}$ ,  $k_O$ ,  $H_{O_2}$ ), five parameters were selected for curve-fitting estimation during model calibration: biomass ( $\delta_B$ ) and liquid layer thickness ( $\delta_L$ ), specific growth rate for sulfur ( $\mu_{max,2}$ ), biomass concentration ( $X$ ) and  $H_2S$  mass transfer coefficient ( $K_{L,H_2S}$ ). The number of parameters was selected according to the number of variables experimentally measured ( $H_2S$  gas concentration profile along the bed height, sulfate concentration and mass of elemental sulfur accumulated)

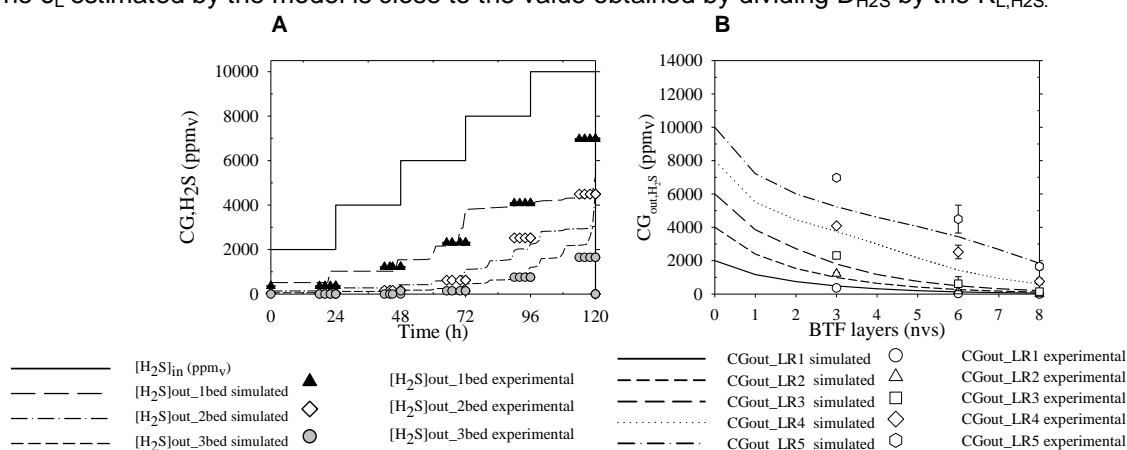
### Model parameters estimation

Model parameters during calibration were estimated 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 RE and  $C_{L,SO_4^{2-}}$  to consider both the gas-phase and the liquid-phase dynamics, respectively. Since experimentally  $m_S^0$  is not anatically measured, see Lopez et al. (submitted 2014) for further details,  $m_S^0$  was not included in the objective function. A summary of the main parameters estimated of the BTF model is shown in Table 2, while figure 2 and figure 3 shows the comparison of model predictions using the parameters estimated and the experimental data corresponding to the calibration period (table 1).

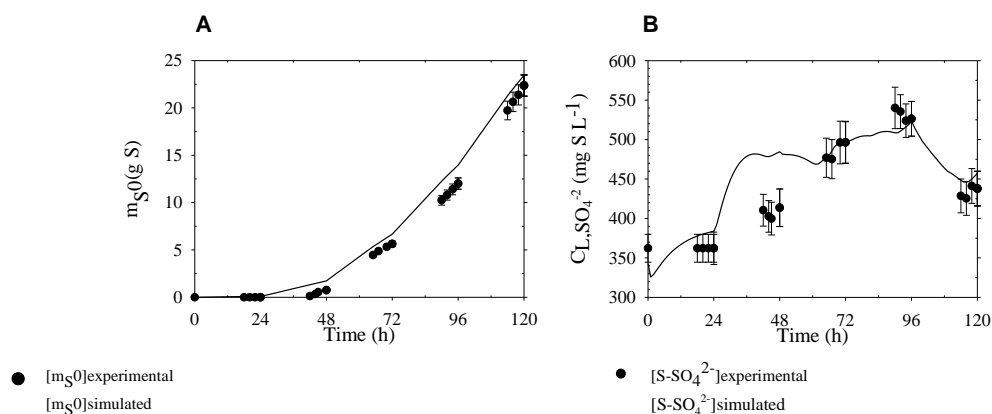
**Table 2. Summary of main parameters of the BTF model for biogas desulfurization**

| Parameter                        | Symbol        | Value                | Units  |
|----------------------------------|---------------|----------------------|--|
| Biomass concentration            | $X$           | 3166                 | $g_{\text{biofilm}} L^{-1}_{\text{biofilm}}$ |
| $H_2S$ mass transfer coefficient | $K_{L,H_2S}$  | 2.31                 | $m h^{-1}$                                   |
| Specific growth rate for sulfur  | $\mu_{max,2}$ | $3.31 \cdot 10^{-2}$ | $mg X^{1/3} mg S^{-1/3} h^{-1}$              |
| Biofilm layer thickness          | $\delta_B$    | 200                  | $\mu m$                                      |
| Liquid layer thickness           | $\delta_L$    | 10.07                | $\mu m$                                      |

The biomass concentration ( $X$ ) estimated by the model (table 2) is in coherence with the visual observations on the BTF, with SEM pictures (data not showed) and with reported data for  $H_2S$  degrading BTFs (Li et al. 2002). The  $K_{L,H_2S}$  is in concordance with the  $K_{L,O_2}$  value which both are related by the square root of the diffusivity values of each species.  $\mu_{max,2}$  lies in the range of values described in Mora et al. 2014. The  $\delta_B$  denotes that the biofilm is thick enough compared to common  $H_2S$ -degrading biofilms, which is important in order to perform the removal of high  $H_2S$  loads in biogas. The  $\delta_L$  estimated by the model is close to the value obtained by dividing  $D_{H_2S}$  by the  $K_{L,H_2S}$ .



**Figure 2.** Results of the calibration of the BTF model with experimental data related to the gas phase. A) Experimental and simulated  $H_2S$  gas concentration profiles for different BTF bed heights. B) experimental and simulated  $H_2S$  gas concentration along the BTF height during period 1.



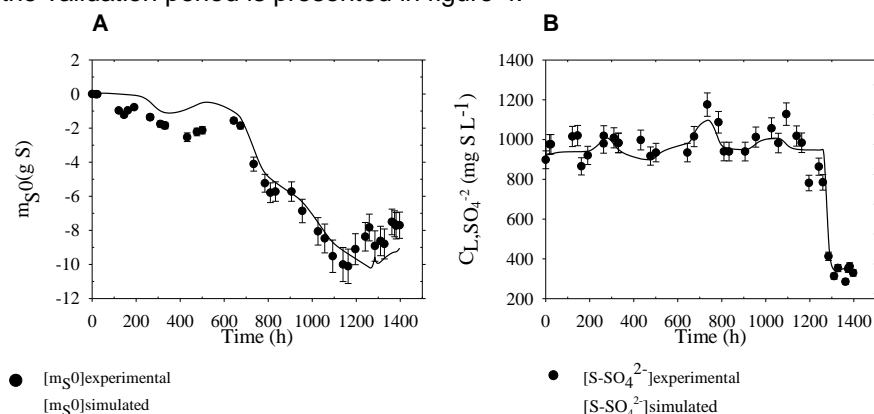
**Figure 3.** Results of the calibration of the BTF model with experimental data related to solid phase (elemental sulfur) and liquid phase. A) experimental and simulated elemental sulfur accumulated during period 1 (see table 1). B) experimental and simulated sulfate concentration during period 1.

In figure 2 and 3 experimental results and model predictions of the effect of a LR increase due to H<sub>2</sub>S inlet concentration increase on the BTF are presented. From figure 2 A) shows that inlet H<sub>2</sub>S concentrations lower than 6000 ppm<sub>v</sub> lead to outlet concentrations below the detection limit, which was properly predicted by the model, even for the measures at different BTF bed heights (Figure 2A and 2B). When the inlet concentration raised from 6000 ppm<sub>v</sub> to 10000 ppm<sub>v</sub>, a RE loss occurs in the reactor, mainly due to the accumulation of elemental sulfur inside the bed (Figure 3A). According to elemental sulfur consumption reaction (Equation 4) and model estimations, a higher mass of elemental sulfur accumulated leads to a lower RE of the reactor.

Regarding to the  $C_{L,SO_4^{2-}}$  (figure 3B), the simulated profile fits properly the experimental data for the complete period, although during the step concentration of 4000 ppm<sub>v</sub> the simulated  $C_{L,SO_4^{2-}}$  was a 15% higher than the experimental measure. Such difference may be due to a biological delay time of the BTF to start to produce sulfate, since such first step increment up to 4000 ppm<sub>v</sub> was the first produced in the reactor after a long pseudo steady-state operation at 2000 ppm<sub>v</sub>.

### Model Validation

After calibration, the response of the model was evaluated in a different experimental period from that used for calibration. 58 days of pseudo steady-state conditions were used to validate the model, corresponding to period 2 in table 1. BTF performance during period 2 was always close to the optimal, since a 100% of RE and sulfate production capacity ( $pCSO_4^{2-}$ ) was obtained. Model simulation of the validation period is presented in figure 4.



**Figure 4.** BTF model response during validation period: accumulated mass of sulfur time evolution profile (A) and sulfate concentration time evolution profile (B).

From figure 4 the predicted profiles and experimental data for  $m_S^0$  and  $C_{L,SO_4^{2-}}$  are shown. It can be seen that despite of experimental data variability, model predictions showed an excellent agreement with experimental data. Model was able to accurately reproduce the elemental sulfur decumulation

along the period as well as the BTF behaviour after a change in the HRT on day 58 (1296h of operation) from 30 h to 9 h, in which the  $C_{L,SO_4^{2-}}$  was decreased due to wash out.

### CONCLUSIONS

A dynamic model for a BTF for biogas desulfurization in aerobic conditions was developed and successfully calibrated and validated, allowing a proper description of different operational scenarios from LR increments due to  $H_2S$  concentration increases in the biogas stream or hydrodynamical changes such as HRT changes. Furthermore the behaviour of the different phases (gas, liquid and elemental sulfur) involved in the biogas desulfurization were correctly simulated. The development of the BTF model will allow 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  $H_2S$  and avoid the formation of elemental sulfur in the BTF bed, since an excessive accumulation of elemental sulfur can significantly diminish the reactor performance (RE and  $pCSO_4^2$ ). Therefore control strategies must be based on the improvement of the oxygen transfer to the liquid phase towards process optimization.

### AKNOWLEDGMENTS

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