High H_2S concentrations abatement in a biotrickling filter: start-up at controlled pH and effect of the EBRT and O_2/H_2S supply ratio

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ABSTRACT

In this study, a biotrickling filter reactor was set up and used to treat high concentrations of gaseous H_2S. Inoculation was carried out at an inlet H_2S concentration of 1,000 ppm_v (27.8 g H_2S m^{-3} h^{-1}) and sludge from a municipal wastewater treatment plant (MWWTP) was used as inoculum. After 3 days, removal efficiency (RE) above 98 % was achieved even after the loading rate (LR) was increased up to 55.6 g H_2S m^{-3} h^{-1} (2,000 ppm_v). Operation at such LR, with an empty bed residence time (EBRT) of 180 s and controlled pH of 6.5-7 was carried out during 3 months. The start-up phase, the effect of decreasing EBRTs at constant inlet concentration and the composition of the process end-products in relation to the supplied O_2/H_2S ratio were studied. Also, a carbon mass balance under steady state conditions was calculated.

1 INTRODUCTION

There are multiple industrial processes which produce biogas as a by-product of their main objective, but still it is a common practice only to use it as a heat-power source or just to burn it at the torch. This is mainly because secondary components present in biogas make it technically difficult and economically expensive to use it for electric

251

power production. Among them, hydrogen sulfide (H_2S), a corrosive, toxic and odorous gas, typically representing from 0.1 to 2 % (vv^{-1}) of the biogas (Janssen *et al.*, 1998), has a major role since concentrations below 500 ppm_v (0.05 % vv^{-1}) are usually required for biogas burning engines.

However, biogas energy recovery is becoming more and more interesting due to the increasing environmental and economical problems associated to fossil fuels and because an increasing number of solid and liquid waste management facilities are being installed with biogas energy recovery as the main economic benefit.

So far, most commonly applied technologies are adsorption and absorption processes, but their high operating costs represent an important drawback and, thus, other less expensive alternatives are being developed.

Biological techniques have proven to be a suitable, environmental-friendly alternative for low H_2S concentrations treatment (Devinny *et al.*, 1999; Yang and Allen, 1994; Gabriel and Deshusses, 2003), although few references can be found dealing with biological treatment of high concentrations of H_2S in biotrickling filters (Fortuny *et al.*, 2006; Bailón, 2005).

Biological H_2S abatement is based on biological sulphur metabolism, being the main reactions involved (Kuenen, 1975):

$$2 \ HS^- + O_2 \rightarrow 2 \ S^0 + OH^-$$
$$2 \ HS^- + 4 \ O_2 \rightarrow 2 \ SO_4^{2-} + 2 \ H^+$$
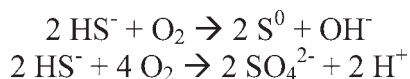
In a previous study, H_2S concentrations up to 10,000 ppm_v were proven to be successfully treated in a biotrickling filter with an empty bed retention time of 180 s. However, some operational problems such as liquid pH variation, carbon limitation and sulphur accumulation due to very low O_2/H_2S supplied ratios hindered reactor performance and life span, and probably contributed to a very long start-up phase of about 25 days (Fortuny *et al.*, 2006).

Thus, the purpose of this study was to obtain a better knowledge of the H_2S biological oxidation process, through a deeper insight in some of the operational parameters such as the EBRT and the process end-products speciation in relation to the amount of supplied oxygen. Also, a different approach for the reactor start-up was investigated.

2 MATERIALS AND METHODS

2.1 EXPERIMENTAL SETUP

In this work, an experimental reactor based on a conventional biotrickling filter with a separated oxygen supply system was used. (Fig. 1). HD-QPAC® (Lantec Products
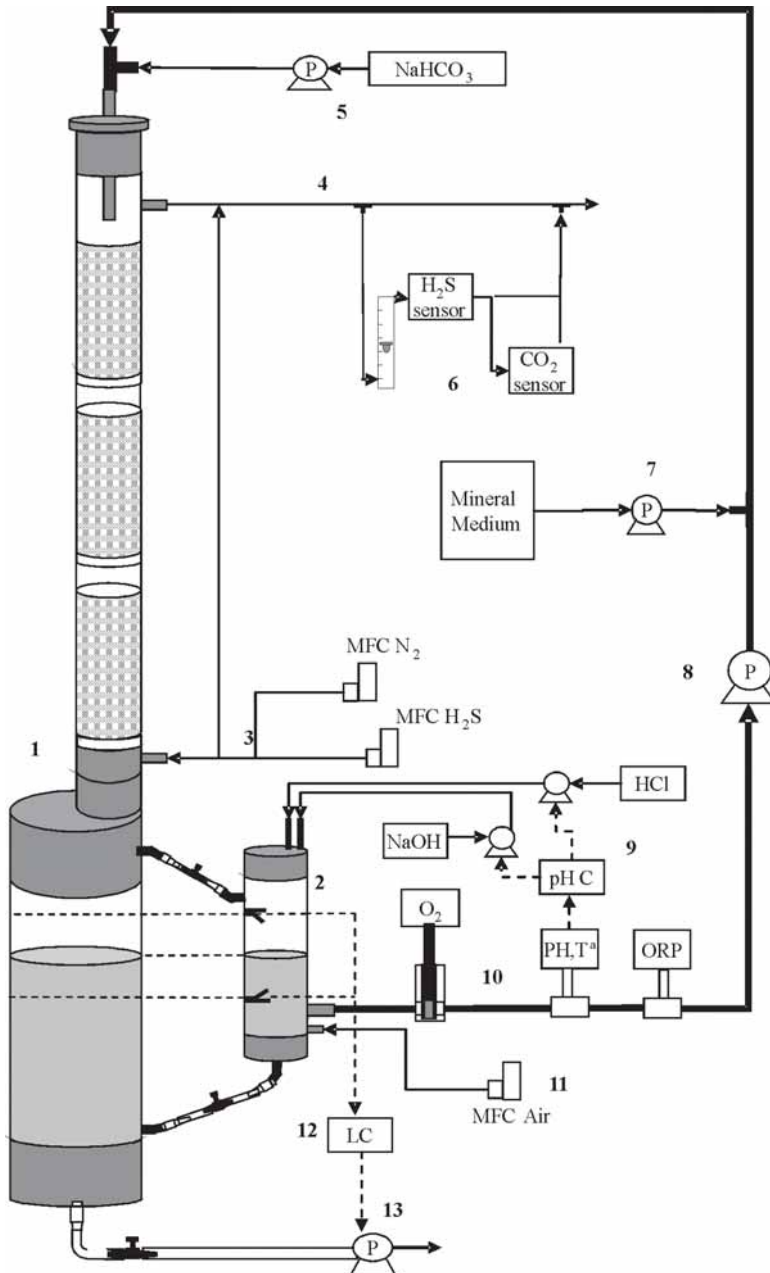
Figure 1. Schematic of the lab-scale setup. 1: Main reactor; 2: Air supply reactor; 3: Gas inlet; 4: Gas outlet; 5: HCO$_3^-$ supply; 6: Gas monitoring; 7: MM supply; 8: Recirculation pump; 9: pH control; 10: Liquid monitoring; 11: Air supply; 12: Level control; 13: Liquid purge.

Inc., CA, USA) with a 4×4 mm (0.16" $\times$ 0.16") grid opening cut to tightly fit inside the reactor was used as packing material since its regular and open structure had proved to better suit the system requirements in previous research (Fortuny *et al.*, 2006). Operation was continuously carried out for a period of three months at EBRT of 180 s, an average liquid retention time (LRT) of 54 ± 7 h , an inlet concentration of 2,000 ppm_v (55.6 g H_2S m^{-3} h^{-1}) and a liquid recirculation velocity (LRV) of 3.6 m h^{-1} (241 ml min^{-1}).

Metered amounts of H_2S, N_2 and air using digital mass flow controllers (Bronkhorst, The Netherlands) were used to simulate a controlled biogas inflow.

Mineral medium (MM) containing (g L^{-1}): NH_4Cl, 1; KH_2PO_4, 0.12; K_2HPO_4, 0.15; $CaCl_2$, 0.02; $MgSO_4 \cdot 7H_2O$, 0.2; trace elements, 1 ml L^{-1}, and $NaHCO_3$ as inorganic carbon source were continuously fed.

Liquid phase was continuously renewed by automated timing of the MM supply, bicarbonate supply and the liquid purge, using 3 different peristaltic pumps (Fig. 1).

2.2 ANALYTICAL METHODS

Continuous monitoring of outlet H_2S and CO_2 gas phase concentrations was performed using an electrochemical H_2S sensor (Sure-cell, Euro-Gas Management Services LTD, UK) and a Carbocap® Carbon Dioxide Probe GMP343 (Vaisala, Helsinki, Finland).

On-line liquid phase monitoring included pH, oxidation-reduction potential (ORP) and dissolved oxygen (DO) measurements. A pH control by HCl or NaOH addition and a level control by liquid purge regulation was also installed.

Also, daily samples of liquid outlet were taken for inorganic carbon (TIC) and sulphur ionic species analysis using a TOC 1020 analyzer (IO Analytical) and an ICS-1000 Ion Chromatography system with an IonPac AS9-HC column (Dionex Corporation), respectively.

Measurement of dissolved sulfide species (H_2S, HS^-, S^{2-}) was also carried out by flow injection analysis (Delgado *et al.*, 2006).

2.3 REACTOR INOCULATION AND START-UP

Reactor inoculation was carried out using aerobic sludge from a MWWTP. A sludge volatile suspended solids (VSS) concentration of 1.9 g L^{-1} and an inlet H_2S concentration of 1000 ppm_v (27.8 g H_2S m^{-3} h^{-1}) were used.

During the first four days no new MM was supplied excepting $NaHCO_3$ to ensure no carbon limitation. During that time, 10 % of the liquid phase volume was twice removed (second and third days) in order to keep the reactor volume constant.

3 RESULTS AND DISCUSSION

3.1 INOCULATION AND START-UP

After one hour of operation at 1,000 ppm$_v$ inlet concentration, significant amounts of H$_2$S were already detected in the outlet gas phase, therefore showing a low sorption capacity of the system, even working at constant pH = 7 (Fig. 2). However, the RE did not drop under 60 % during the first day, operating at very low DO and ORP values, and raised up to 70 % the second day after an oxygen supply increase. From then on, a progressive removal efficiency increase leading to outlet concentrations under the H$_2$S setup detection limit (thus having RE over 97 %, Fig. 2b) was observed, whilst the DO decreased and the ORP increased (Fig. 2a). Increasing ORP and decreasing DO measurements probably indicated a progressive change in the sulphur-species liquid-phase composition, i.e. from dominating H$_2$S$_{(aq)}$ and HS$^-$ to SO$_4^{2-}$ (Lens and Hulshoff, 2000), due to an increasing biological oxygen consumption.
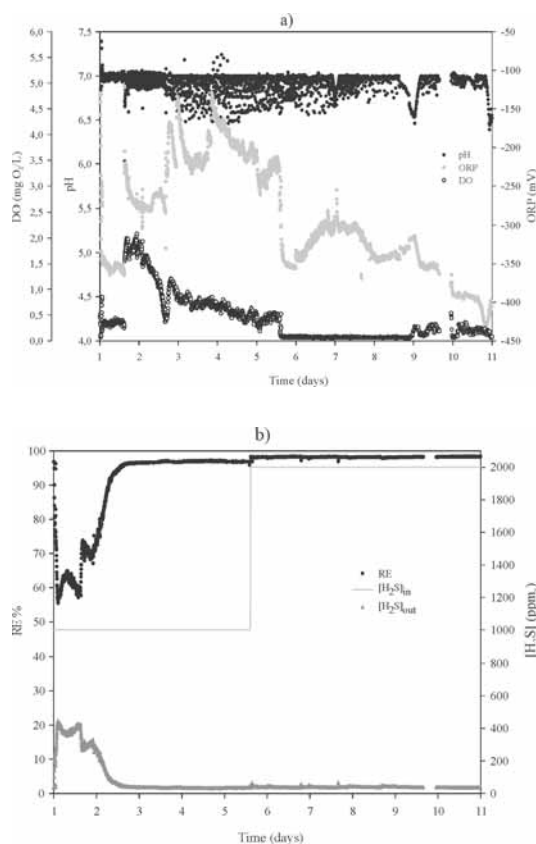

Figure 2. a): pH, ORP and DO during start-up. b): RE, [H$_2$S]$_{in}$ and [H$_2$S]$_{out}$ during start-up.

Accordingly, an initial accumulation and subsequent depletion of thiosulfate and inorganic carbonate during the first two days and a progressive accumulation of sulfate and phosphate were detected in the liquid phase (Fig. 3). Hence, it seems that an initial sorption process could have been supported by a low biological sulfide oxidation activity from the inoculum biomass. Favourable operating conditions from the very beginning contributed to a fast start-up, since operating pH was kept constant at the same original inoculum pH. In addition, favourable room temperature and excess inorganic carbonate were ensured.
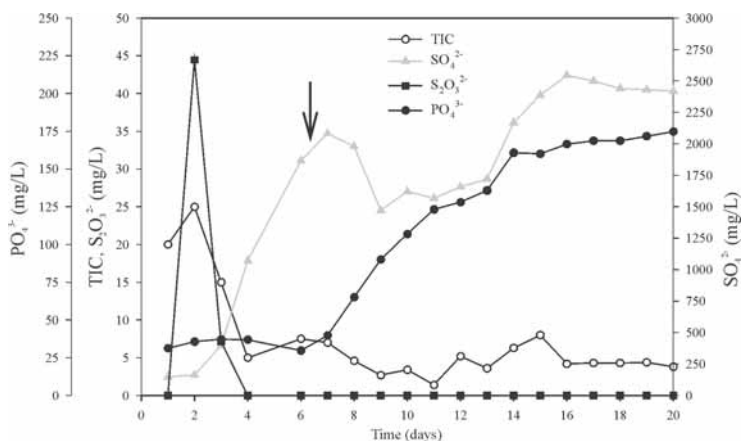

Figure 3. Liquid phase ionic composition. Arrow indicates beginning of liquid renewal.

However, the thiosulfate trend indicates that the second and third days of operation, after increasing the oxygen supply, the chemical oxidation of sulfide to thiosulfate under low biological sulfide activity (Janssen *et al.*, 1995) was the dominating process, subsequently being substituted by an already favoured biological oxidation to sulfate from the third day on. Inorganic carbonate and phosphate measurements were also in agreement. At a constant carbonate supply (0.71 ± 0.08 g C-$NaHCO_3$ g^{-1} S-H_2S) the initial accumulation was consumed from the second day on, even if until the sixth day no liquid phase renewal was applied. Also, probably an initially growing biomass population would have had more phosphate requirements, thus leading to a phosphate accumulation trend up to the 15th -20th day after starting operation.

Thus, a very short start-up phase of only 3 to 5 days was observed. Moreover, even after increasing the LR up to 55.6 g H_2S m^{-3} h^{-1} (2,000 ppm_v) the sixth day of operation, the system performance in terms of RE did not showed any appreciable drop; on the contrary, increased accordingly (Fig. 2).

This is a much shorter time than the observed in similar previous studies (Fortuny *et al.*, 2006). Such a fast start-up has been attributed to two main topics. On the one hand, the pH control ensured a constant operation at a pH between 6.5 and 7.0 (Fig. 2, a), the same original inoculum pH. Also, the pH control initially avoided the pH increase which would have been caused by the constant addition of NaHCO$_3$ at an early stage of the system operation, with not enough sulfate production to balance the pH. Actually, the possibility to constantly add bicarbonate without altering the pH was a very positive aspect that contributed to a fast start-up since no carbon limitation could be guaranteed.

On the other hand, the WWTP sludge used as inoculum may have played an important role in the process. Most probably the high biomass concentration facilitated the biofilm formation onto the new packing material (Prado *et al.*, 2005) and enough sulfide oxidizing biomass ensured a fast adaptation to the new substrate therefore facilitating the start-up phase.

Overall, this results show that it is not always worth spending time, energy and money obtaining a specific culture in order to start-up a biological treatment system, as it has usually been reported (Fortuny *et al.*, 2006; Veiga and Kennes, 2001; Duan *et al.*, 2006). Sludge from MWWTP can perfectly work as inoculum since its high biomass variety and concentration ensure some kind of sulfide oxidising population that will be favoured under appropriate growing conditions inside the biological reactor.

3.2 SYSTEM PERFORMANCE UNDER DIFFERENT O$_2$/H$_2$S LOADING RATES

As it has been previously reported (Buisman *et al.*, 1989; Janssen *et al.*, 1995; Fortuny *et al.*, 2006), biological oxidation of sulfide leads to sulfate or sulfur formation, depending on the oxygen availability. Janssen *et al.*, (1995) showed that probably both reactions can be performed by the same metabolic type of micro-organism and that the oxidation end-product can be selected just by changing the amount of supplied oxygen.

In this study, operating at O$_2$/H$_2$S supply ratios from 1.6 to 23.6 (vv^{-1}) allowed obtaining a relationship between this parameter and the percentage of H$_2$S oxidised to sulfate (Fig. 4).

This is a useful information to take into account for a reactor scale-up or for other similar systems (as long as equal or very similar O$_2$ gas-liquid mass transfer can be assumed). WWTP and waste management facilities usually deal with biogas effluents with H$_2$S concentrations typically in the range of a few thousands ppm$_v$ (Syed *et al.*, 2006) and sulphur production can be an important problem if it is not controlled.

With such information, if the reactor's design allows it, only varying the air flow rate accordingly to an on-line H$_2$S concentration measurement, it may be possible to choose which or what amount of each possible end product should be obtained (SO$_4^{2-}$ or S^0). On the other hand, if elemental sulfur generation is a problem, depending on the O$_2$/H$_2$S supplied ratio it will be possible to estimate the amount of produced sulfur over time and thus anticipate possible operational problems.

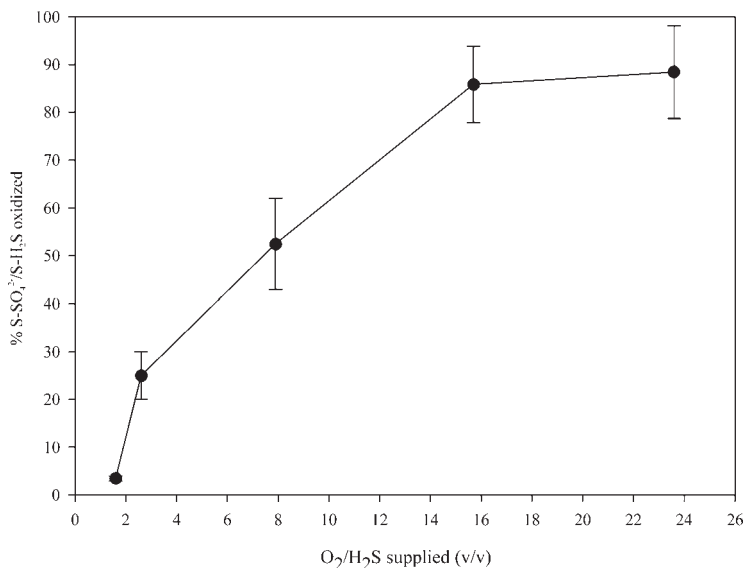Figure 4. % H_2S oxidized as SO_4^{2-} at different O_2/H_2S supplied ratios.

Also, unnecessary amounts of supplied air to the biogas flow could be saved, thus avoiding operational adjustments (for the correct burning mixture) to the burning engines and possible explosion risks at very high air supply.

3.3 SYSTEM MAXIMUM ELIMINATION CAPACITY ASSESSMENT

After one month operation at a constant LR of 55.6 g H_2S m^{-3} h^{-1} and EBRT of 180 s, an experiment to evaluate the effect of decreasing EBRTs at a constant inlet concentration (2,000 ppm$_v$) and constant O_2/H_2S supply ratio (23.6 v v^{-1}) was performed.

As shown in Fig. 5a, the system was able to operate with RE above 95 % up to an EBRT of 120 s (LR = 83.5 g H_2S m^{-3} h^{-1}) and with 90 % RE at an EBRT of 90 s. Thus, up to LR of about 80 g H_2S m^{-3} h^{-1} there is no mass transfer limitation at such operating conditions, which would allow reducing the EBRT almost 60 s without any effect on the system performance.

According to the fast performance recovery after applying again an EBRT of 180 s, it can be concluded that only mass transfer limitation was hindering the reactor performance and no significant sulfide accumulation occurred in the liquid phase during the high loaded periods. Also, if sulfide had accumulated, an important drop on the ORP would have been observed and ORP did not drop below values of -50 mV.

Thus, at that time, a maximum elimination capacity (EC) of 125.6 g H_2S m^{-3} h^{-1} was achieved.
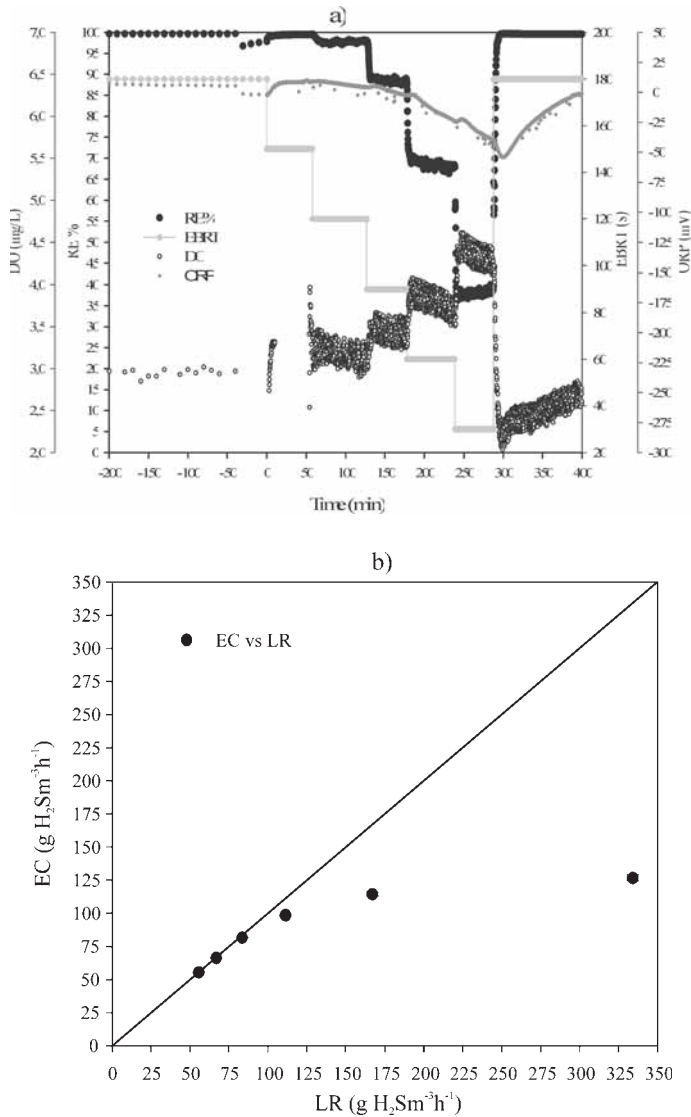
Figure 5. a) RE, ORP, DO and EBRT vs. time. B) EC vs. LR

However, not only biological oxidation contributed to the sulfide oxidation during the high loading periods, since during three days after the experiment (LRT= 54 ± 7 h) small concentrations of thiosulfate (representing less than 1 % of the total amount of degraded H$_2$S) were detected in the liquid phase (results not shown). This probably means that chemical oxidation of sulfide occurred again.

3.4 CARBON AND SULFUR MASS BALANCES

During the whole operation period, a constant ratio of 0.71 ± 0.08 g C-NaHCO$_3$ g^{-1} S-H$_2$S was supplied since previous research had shown it was necessary to guarantee a C/S supplied ratio of 0.3-0.4 g g^{-1} in order to avoid carbon limitation.

Thus, at constant operating conditions corresponding to: inlet H$_2$S concentration = 2000 ppm$_v$; O$_2$/H$_2$S supplied ratio = 23.6 v v^{-1} (leading to 90 % hydrogen sulfide oxidized to sulfate) and at pH 6.55 ± 0.05, a carbon mass balance was calculated according to the following expression:

$$[C]_{NaHCO_3} \times Q_C + [CO_2]_G \times F_{G_{in}} = [CO_2]_G \times F_{G_{out}} + [C]_P \times Q_P$$

Where: $[C]_{NaHCO_3}$: carbonate concentration, mg C L^{-1};

Q_C : carbonate inflow, L min^{-1}

$[CO_2]_G$: gas phase carbon concentration, mg C L^{-1};

$F_{G_{in}}$: air flow in, L min^{-1}

$F_{G_{out}}$: total gas flow out, L min^{-1};

Q_P : liquid purge flow, L min^{-1};

$[C]_P$: total dissolved C in the liquid purge, mg C L^{-1};

According to the balance, a 92 % of the total supplied carbon was detected either as dissolved carbon or CO$_2$. The other 8 %, representing 259 mg C day^{-1}, may be attributed to biomass growth and extracellular polymer substances.

4 CONCLUSIONS

A biotrickling filter based system was used to successfully treat up to 2,000 ppm$_v$ of H$_2$S (55.6 g H$_2$Sm^{-3}h^{-1}) with steady-state RE over 99 % and complete oxidation to sulfate.

Inoculation with MWWTP sludge led to a very fast start-up phase that needed only 3 days to reach RE over 98 %, therefore showing that it is not always needed to obtain a specific culture of sulfide oxidizing bacteria to inoculate an H$_2$S degrading system. The biomass diversity of a MWWTP's sludge, under favourable and stable growing conditions, among which a pH control may play a major role, can become an optimum and easy-to-obtain inoculum.

Operation at different O$_2$/H$_2$S supply ratios allowed obtaining a relationship between this parameter and the percentage of degraded sulfide as sulfate, therefore being able to select the process end-product only by varying the amount of air supplied.

Finally, an experiment to evaluate the effect of decreasing EBRT at constant inlet concentration showed that the system's EBRT could be decreased up to 120 s without a notable loss of performance. Lower EBRT (higher LR) led to an important RE drop, which was caused by mass transfer limitation instead of biological limitation. No sulfide accumulation was observed although it was not completely biologically degraded. Chemical oxidation occurred since thiosulfate was afterwards detected.

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