Operational aspects of the desulfurization process of energy gases mimics in biotrickling filters ☆

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ABSTRACT

Biological removal of reduced sulfur compounds in energy-rich gases is an increasingly adopted alternative to conventional physicochemical processes, because of economical and environmental benefits. A lab-scale biotrickling filter reactor for the treatment of high-H_2S-loaded gases was developed and previously proven to effectively treat H_2S concentrations up to 12,000 ppm_v at gas contact times between 167 and 180 s. In the present work, a detailed study on selected operational aspects affecting this system was carried out with the objective to optimize performance. The start-up phase was studied at an inlet H_2S concentration of 1000 ppm_v (loading of 28 g H_2S m^{-3} h^{-1}) and inoculation with sludge from a municipal wastewater treatment plant. After reactor startup, the inlet H_2S concentration was doubled and the influence of different key process parameters was tested. Results showed that there was a significant reduction of the removal efficiency at gas contact times below 120 s. Also, mass transfer was found to be the main factor limiting H_2S elimination, whereas performance was not influenced by the bacterial colonization of the packed column after the initial startup. The effect of gas supply shutdowns for up to 5 days was shown to be irrelevant on process performance if the trickling liquid recirculation was kept on. Also, the trickling liquid velocity was investigated and found to influence sulfate production through a better use of the supplied dissolved oxygen. Finally, short-term pH changes revealed that the system was quite insensitive to a pH drop, but was markedly affected by a pH increase, affecting both the biological activity and the removal of H_2S. Altogether, the results presented and discussed herein provide new insight and operational data on H_2S removal from energy gases in biotrickling filters.

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1. Introduction

Energy rich off-gases such as biogas are sometimes not used for electric power generation due to the presence of corrosive compounds, such as reduced sulfur compounds (RSC) (Ross et al., 1996; Tchobanoglous et al., 2003). Among those RSC, hydrogen sulfide (H_2S) is one of the most commonly reported impurities. H_2S concentrations in biogas can range from 0.1 to

extremely high values of 2% v/v (1000−20,000 ppm$_v$), whereas the specifications for the maximum content of H_2S in typical biogas-burning engines are in the range of 0.02−0.05% v/v (200−500 ppm$_v$).

At present, biogas energy recovery is becoming more and more interesting due to increasing environmental and economical constraints associated to fossil fuels. Furthermore, an increasing number of solid and liquid wastes management facilities (biomethanation plants) are being installed with biogas production as the main economical benefit.

So far, biological sulfide removal has usually been applied to odor control (Yang and Allen, 1994; Devinny et al., 1999; Gabriel and Deshusses, 2003; González-Sánchez et al., 2008). However, the growing interest in biological treatment alternatives has lead to an increasing number of studies in the recent years where these techniques are applied to the treatment of highly-loaded off-gases (Buisman et al., 1989; Bailón, 2005; van den Bosch et al., 2007; Fortuny et al., 2008).
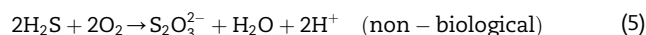
After absorption, treatment and biodegradation of H_2S in bioreactors occur according to the following overall reactions (Kuenen, 1975):

$$H_2S \leftrightarrow HS^- + H^+ \quad (non-biological) \tag{1}$$

$$HS^- + 0.5O_2 \rightarrow S^0 + OH^- \quad (biological) \tag{2}$$

$$HS^- + 2O_2 \rightarrow SO_4^{2-} + H^+ \quad (biological) \tag{3}$$
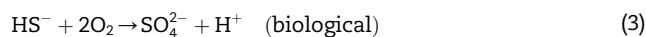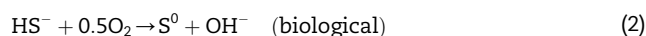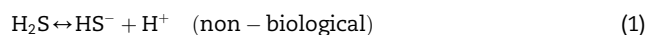
Also, depending on the redox conditions, further oxidation to sulfate can take place if sulfide is limited but elemental sulfur (S^0) is present (Kuenen, 1975):

$$S^0 + 3/2O_2 + H_2O \rightarrow SO_4^{2-} + 2H^+ \quad (biological) \tag{4}$$
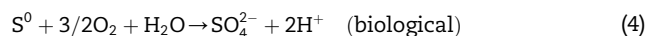
All four reactions above result in pH changes, as do parallel abiotic reactions such as oxidation of sulfide to thiosulfate (Eq. (5)), which in turn can also be biologically oxidized to sulfate (Eq. (6)).

$$2H_2S + 2O_2 \rightarrow S_2O_3^{2-} + H_2O + 2H^+ \quad (non-biological) \tag{5}$$

$$S_2O_3^{2-} + 2O_2 + H_2O \rightarrow 2SO_4^{2-} + 2H^+ \quad (biological) \tag{6}$$

Also, abiotic polysulfide formation and oxidation under alkaline conditions as described by van den Bosch et al. (2007) and González-Sánchez et al. (2008) may occur. These highlight the complex relationships between oxygen availability, pH and sulfide oxidation processes; a better understanding of the effects of these parameters is required for improved system design.

In a preliminary study (Fortuny et al., 2008), the technical feasibility of using a single lab-scale biotrickling filter for the treatment of off-gases containing high concentrations of H_2S was demonstrated. Preliminary results on the system robustness when exposed to short-term perturbations, and the relationship between the choice of packing type and the reactor long-term performance were discussed. Also, the inoculation procedure and start-up phase were studied. Furthermore, Montebello et al. (2010) studied the reactor performance when exposed to increased inlet H_2S

concentrations when validating an integrated analyzer for on-line process monitoring consisting of a Flow Injection Analyzer coupled to a Continuous Flow Analyzer with a previous Gas-Diffusion step (FIA/GD-CFA). The results showed that a slow drop in H_2S removal was caused by progressive sulfide accumulation in the liquid phase. That system was operated at high H_2S loadings (162 g H_2S m^{-3} h^{-1}) and the performance was limited by the biological oxidation of H_2S.

As a follow up, this study was directed toward optimizing the start-up phase using different inoculation methods and an improved reactor design. A second objective was to acquire a deeper knowledge of the influence of key process parameters when operating the system at less extreme conditions (lower H_2S loading rates or inlet concentrations) than those previously tested (Fortuny et al., 2008). Thus, short-term experiments targeting the gas empty bed residence time (EBRT), the trickling liquid velocity (TLV), operating pH and H_2S supply shutdowns were carried out and the response of the bioreactor was determined. Also, the influence of the H_2S loading rate and operating conditions changes on the pH and biological activity were investigated.

2. Materials and methods

2.1. Experimental setup

A lab-scale prototype reactor described in details elsewhere (Fortuny et al., 2010) was used for this study. In short, the biotrickling filter had an inner diameter of 7.1 cm, a packed bed height of 50 cm and a total liquid volume of 2 L. The packing was HD-QPAC® (Lantec Products Inc., Agoura Hills, CA, USA) with a 4 × 4 mm (0.16″ × 0.16″) grid opening cut to tightly fit inside the reactor. Except for the startup period (see Section 2.3), the bioreactor was continuously operated at an inlet H_2S concentration of 2000 ppm$_v$ (corresponding to a loading of 56 g H_2S m^{-3} h^{-1}), an EBRT of 180 s, an average liquid hydraulic retention time (HRT) of 51 ± 6 h and a TLV of 3.8 m h^{-1} (liquid flow of 255 ml min^{-1}). A pH range of 6−6.5 was maintained by automated addition of NaOH 1 M as needed. Aerobic conditions in the liquid phase were ensured by continuous air addition at an O_2/H_2S supplied ratio of 23.6 (v v^{-1}) through a diffuser located in an oxygenation compartment installed in the recycle line (Fortuny et al., 2010). The conditions were only altered during the start-up phase (see Section 2.3) and for short-term exposures to higher loading rates (LR) up to 400 g H_2S m^{-3} h^{-1} and for biomass sampling episodes.

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) as described elsewhere (Fortuny et al., 2010) and a solution of NaHCO$_3$ (21 g L^{-1}) as inorganic carbon source were continuously fed at a rate of 0.8 and 0.4 L day^{-1}, respectively.

2.2. Analytical methods

Continuous monitoring of outlet H_2S concentration was performed using an electrochemical H_2S sensor (Sure-cell, Euro-

Gas Management Services LTD, UK) calibrated up to 300 ± 2 ppm$_v$. In order to measure higher H$_2$S concentrations, a mass flow controller (Bronkhorst, The Netherlands) was used to precisely and continuously dilute the analyte flow with air. Dilution ratios between 1:20 and 1:5 were used.

On-line liquid phase monitoring included pH and oxidation-reduction potential (ORP) (PH 28, Crison Instruments, Spain) and dissolved oxygen (DO) (oxi340i, WTW, Germany) measurements. Also, daily samples of the purge flow were taken for ionic sulfur species and total inorganic carbon (TIC) analysis, using an ICS-1000 Ion Chromatography system with an IonPac AS9-HC column (Dionex Corporation) and a TIC-TOC 1020 analyzer (IO Analytical) respectively. Biomass concentration in the liquid phase was measured as mg N L^{-1} according to van den Bosch et al. (2007). S^0 concentration in the liquid recirculation was also measured according to Goehring and Helbing (1949).

2.3. Inoculation and start-up

Reactor inoculation was carried out using aerobic sludge from a local municipal wastewater treatment plant (MWWTP) diluted 1:1 with MM, thus having a final volatile suspended solids (VSS) concentration of 1.9 g L^{-1}. During the start-up phase the inlet H$_2$S concentration was set to 1000 ppm$_v$ (28 g H$_2$S m^{-3} h^{-1}), the pH setpoint to 6.5–7 in order to match the pH of the original inoculum, and the O$_2$/H$_2$S supplied ratio to 15.7 (v v^{-1}). During the first four days no new MM was supplied, though the NaHCO$_3$ was fed to the reactor to avoid carbon limitation. 10% of the liquid volume needed to be removed twice (on the second and third days) in order to keep the liquid volume constant. Once the start-up phase was over (after 5 days), the operating conditions were set as previously described (see Section 2.1).

2.4. Specific experiments

The maximum elimination capacity (EC) and the effect of reduced EBRTs were assessed 1 and 12 months after reactor

inoculation in order to asses the evolution of the bioreactor treatment capacity over time. The EBRT was decreased stepwise hourly from 180 s down to 30 s through gas flow increases at a constant inlet H$_2$S concentration of 2000 ppm$_v$ and an O$_2$/H$_2$S supplied ratio of 23.6 (v v^{-1}). This corresponds to LR increases from 55 to 334 g H$_2$S m^{-3} h^{-1}. Also, the effect of a stepwise increase of the trickling velocity at a constant EBRT (180 s), LR of 84 g H$_2$S m^{-3} h^{-1} (3000 ppm$_v$), HRT of 10 h and O$_2$/H$_2$S supply ratio of 23.6 (v v^{-1}) was determined. The TLV was increased stepwise from 0.52 to 20 m h^{-1} every 48 h (i.e., about 5 HRT) and the reactor response was monitored.

To test the effect of gas supply shutdowns, the biogas mimic supply was stopped while the air flow, liquid recirculation, the purge and the make-up water flows were all kept constant. Since inorganic carbon in a full-scale system would be normally supplied via the gas, the HCO$_3^-$ supply in the make-up water was also discontinued while the gas supply was stopped.

Finally, short-term, large pH variations were introduced in the system, using either HCl or NaOH 1 M and the pH controller, to assess the impact of pH shocks. Initially, a pH drop down to 2.5 was imposed and kept constant for a period of 34 h prior to resuming normal pH conditions (pH 6–6.5). Afterward, a pH increase up to 9.5 was imposed and maintained for 24 h before returning the pH to its normal setpoint. In both cases, a shorter HRT of 19 ± 1 h was used in order to shorten the reactor response time.

3. Results and discussion

3.1. Inoculation and start-up

After 1 h of operation at 1000 ppm$_v$ inlet concentration, H$_2$S was already detected in the outlet gas stream. This illustrates the low sorption capacity of the system, even when working at constant pH of 7 (Fig. 1). This rapid breakthrough pattern is consistent with the high pKa and relatively unfavorable gas-liquid partition of H$_2$S (pKa$_1$ = 6.9; pKa$_2$ = 12.8;
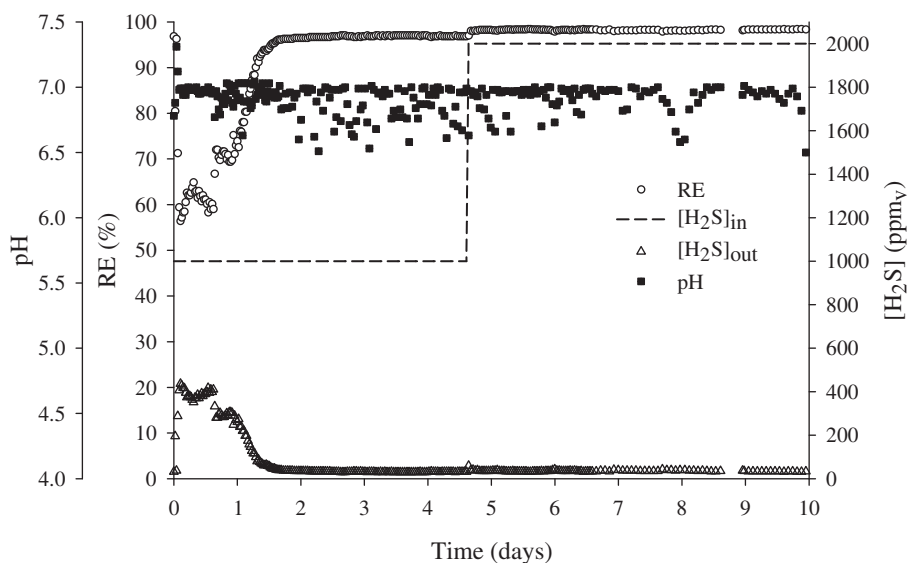

Fig. 1 – On-line monitoring of the pH, H$_2$S inlet and outlet concentrations and removal efficiency (RE) during the start-up phase of the bioreactor.

dimensionless H = 0.39). Even so, some biological activity coupled to absorption of H_2S into the fresh $NaHCO_3$ solution allowed RE to stay within 55–65% during the first day of operation. The average DO concentration was 0.4 mg L^{-1} (data not shown) which could have been limiting, and thus was increased to 2 mg L^{-1} on day 2 by increasing the O_2/H_2S supplied ratio from 15.7 to 23.6 (v v^{-1}). After the first day, the RE progressively increased; H_2S outlet concentrations were below the detection limit of the H_2S sensor (30 ppm_v, corresponding to RE > 97%) already by day 2. In parallel, a progressive shift in the sulfur species composition in the liquid phase, i.e. from primarily reduced S species (H_2S (aq) and HS^-) to more oxidized ones ($S_2O_3^{2-}$ and SO_4^{2-}) occurred due to increasing biological activity as well as to some chemical oxidation (Steudel, 2004). As shown in Fig. 2, there was an initial accumulation and subsequent depletion of thiosulfate and inorganic carbon during the first two days, concurrent with a progressive accumulation of sulfate in the liquid phase. This adds further evidence that hydrogen sulfide sorption and chemical oxidation (Eq. (5)) predominated during the first two days, but were rapidly surpassed by biological oxidation (Eqs. 2, 3 and 6), which became the main mechanism for removal from day 3 onwards. The TIC profile was also in agreement with the above explanation. For the first five days, the carbonate supply was kept constant at 0.9 ± 0.1 g C-NaHCO3 g^{-1} S–H2S with minimum purging of the trickling liquid (see methods). Thus, despite of the increased CO_2 stripping because of the increase of the O_2/H_2S supplied ratio on day 2, the TIC decrease observed after day 2 (Fig. 2) was most likely linked to an increase in the biological uptake due to onset of H_2S removal.

Thus, a very short start-up phase of only 2 days when based on H_2S gas concentrations or about 5 days when considering liquid phase concentrations was obtained. Moreover, even after doubling the LR up to 56 g H_2S m^{-3} h^{-1} (i.e., inlet H_2S of 2000 ppm_v) on day six, the system performance in terms of RE remained high (Fig. 1). A start-up phase of 3–5 days is a much shorter than observed in previous experiments (Fortuny et al., 2008). Such a fast start-up was
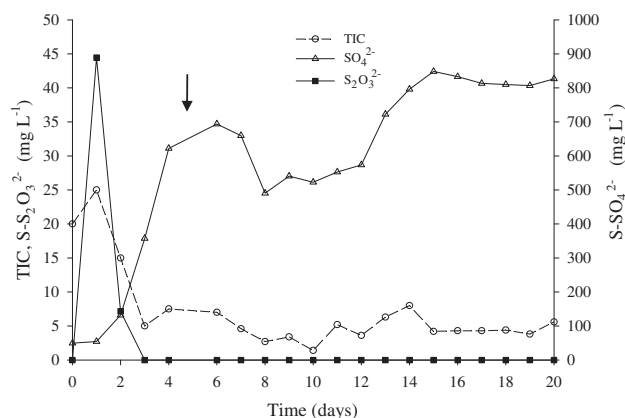
attributed to two main factors. First, the pH control ensured a constant operation at a pH between 6.5 and 7.0 (Fig. 1), which was the same pH as that of the original inoculum. The pH control also avoided any pH increase resulting from the addition of $NaHCO_3$ in the early stages of the system operation, when there was little sulfate production to balance the pH. Second, heavy inoculation with the MWWTP sludge may have played an important role in the startup process. It has been previously described (Prado et al., 2005), that a high biomass concentration, like in MWWTP sludge, may facilitate biofilm formation onto a new packing material.
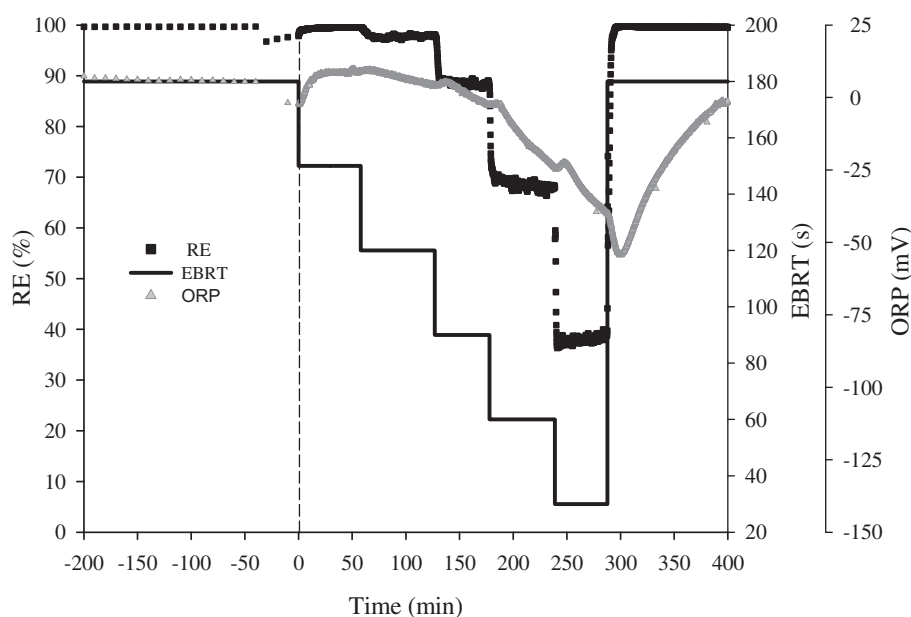
Overall, this results show that specific sulfide oxidizing cultures are not needed in order to start-up a biological sulfide treatment system despite what has been reported by other authors (Koe and Yang, 2000; Sercu et al., 2004; Duan et al., 2006). Sludge from MWWTP works well as an inoculum because of its high microbial diversity (Maestre et al., 2010) and adding a high biomass concentration in the biotrickling filter under suitable conditions ensures that sulfide oxidizing organisms will rapidly establish a thriving community.

3.2. Maximum EC and effect of the EBRT

Fig. 3 shows real time data for the first determination of the maximum EC carried out after one month of operation, while Fig. 4 (run 1) reports the elimination capacities obtained at the end of each step change as a function of the EBRT and the LR. The results show that even after decreasing the EBRT to 120 s (i.e., a LR of 84 g H_2S m^{-3} h^{-1}) the reactor was able to maintain an average RE of 97.7 ± 0.3%. At an EBRT of 90 s, the RE only dropped to 88.6 ± 0.5%. However, when the EBRT was decreased further, there was and important effect on H_2S removal. The RE reached an average value of 39.7 ± 0.9% at an EBRT of 30 s (i.e., a LR of 334 g H_2S m^{-3} h^{-1}).

Examination of Figs. 3 and 4 shows that there was practically no RE reduction at LR up to 84 g H_2S m^{-3} h^{-1} (or EBRT of 120 s). This would allow significant reduction of the EBRT without any effect on H_2S removal at 2000 ppm_v inlet concentration. Another important observation is the rapid recovery after returning the system to its original EBRT of 180 s (at time 288 min). The small ORP drop during the experiment (−50 mV, Fig. 3) provides information on the possible accumulation of sulfide in the liquid. Montebello et al. (2010) showed that ORP values around −50 mV corresponded to very low sulfide liquid concentrations (<1 mg L^{-1}) whereas significant sulfide accumulation caused ORP to drop below −200 mV. Thus, the −50 mV drop suggests that there was not accumulation of sulfide in the liquid phase, indicating that sulfide was oxidized rather than being absorbed. It is worth mentioning that low concentrations of thiosulfate were detected in the liquid phase, but the amount corresponded to less than 1% of the total amount of H_2S removed. Thus, abiotic oxidation was negligible, even during the high loading periods.

The absence of sulfide accumulation during the high-load periods (LR up to 334 g H_2S m^{-3} h^{-1}) indicates that the rate limiting step was mainly mass transfer. This is an interesting finding which contrasts with previous results (Montebello et al., 2010) in which the same reactor became kinetically limited rather than mass-transfer limited when exposed to LR

Fig. 2 – Sulfate, thiosulfate and total inorganic carbon profiles during the first 20 days of operation. Day zero concentrations correspond to the inoculum (MWWTP sludge diluted 1:1 with MM) concentrations. The arrow indicates the beginning of the liquid phase renewal.

Fig. 3 – **Removal efficiency (RE), redox potential (ORP) and empty bed gas residence time (EBRT) during run 1 of the EBRT experiment. The dashed line indicates beginning of experiment.**

above 162 g H$_2$S m^{-3} h^{-1} by only increasing the inlet concentration at a constant EBRT. Therefore, the system becomes kinetically limited when high LR are achieved by an increasing concentration, but is mass transfer limited when high LR are achieved by reducing the EBRT.

A maximum EC of 126 g H$_2$S m^{-3} h^{-1} was achieved (Fig. 4B), which compares favorably to other reported maximum EC (Koe and Yang, 2000; Sercu et al., 2004; Duan et al., 2006). This is remarkable value for a bioreactor that had been operating for only a month. It demonstrates that reactor design, inoculation and operating conditions during startup were close to optimum.

The same determination of EC was repeated after one year of reactor operation (run 2). A 14% increase in the maximum EC was observed, reaching an average value of 144 ± 4 g H$_2$S m^{-3} h^{-1} (Fig. 4B). Since no biological limitation was observed in run 1, the increase in the maximum EC of run 2 must be related to an improved H$_2$S mass transfer. Pollutant transfer occurs through the gas-liquid and gas-biofilm

contact, therefore it is likely that increased bacterial coverage of the packing occurred after a year of operation, which resulted in a greater interfacial surface-to-volume ratio inside the reactor. Another possible contributing factor is that slight accumulation of (bio)solids onto the clean, open-structure of the packing material could cause a slight gas velocity increase, which in turn would increase pollutant mass transfer. The former hypothesis seems more likely than the latter, given the fact that wetting in biotrickling filters is often incomplete (Kim and Deshusses, 2008), which probably extends the time required for complete bacteria colonization of the packing.
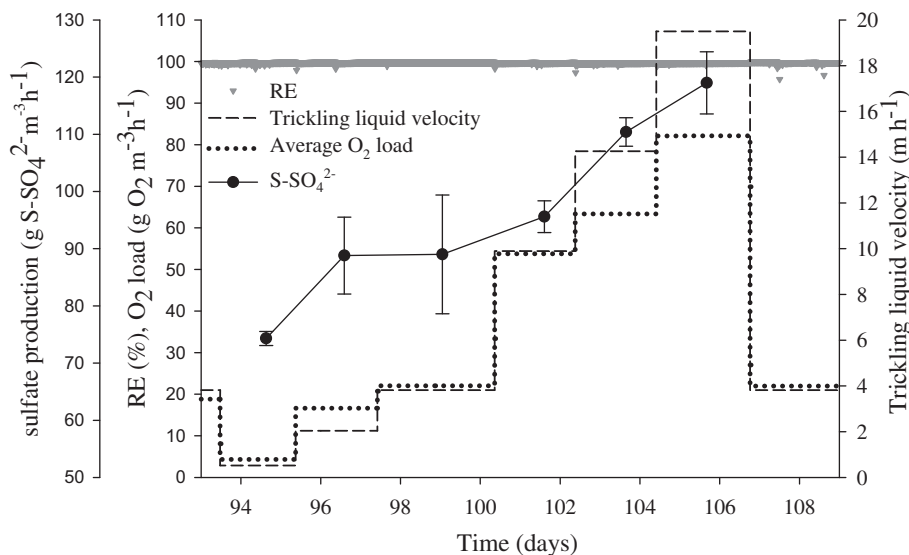
3.3. Effect of the trickling liquid velocity

The TLV is an important parameter for the attachment (and shear) of biomass onto the packing material, for proper gas-liquid mass transfer and for S^0 flushing in case of accumulation. As shown in Fig. 5, no difference in the performance was
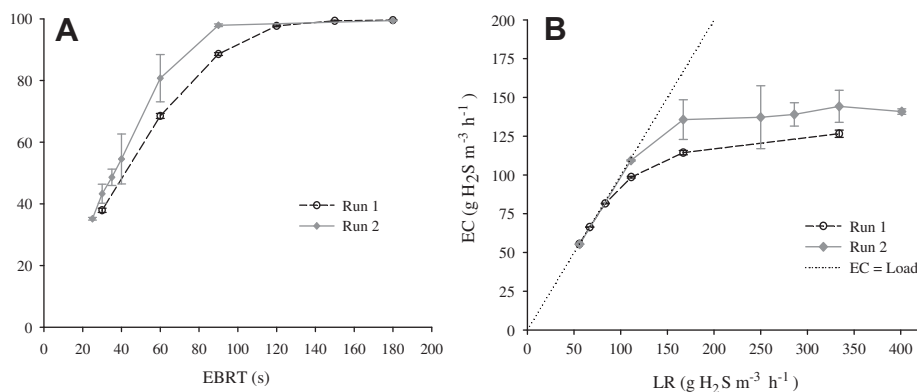
Fig. 4 – **Results for both experimental runs of the EBRT experiment. A) Removal efficiency (RE) versus applied empty bed residence time (EBRT). B) Elimination capacity (EC) versus applied loading rate (LR).**

Fig. 5 – Variation of the trickling liquid velocity (TLV), removal efficiency (RE), sulfate production and oxygen load supplied to the packed bed during the 14 days experiment.

observed when changing the TLV within the tested range (0.51–19 m h^{-1}) at a LR of 84 g H$_2$S m^{-3} h^{-1}. However, one effect of changing the TLV was on oxygen transfer, since changing the TLV altered the liquid retention time in the oxygenation compartment located in the recycle line (Fortuny et al., 2010). Both the DO in the liquid phase (data not shown) and thus the oxygen load supplied to the packed bed (in terms of g DO m^{-3} h^{-1}actually available and supplied via the recirculation liquid) were increased with increases in the TLV (Fig. 5). At TLVs lower than the standard conditions (TLV < 3.8 m h^{-1}), the DO in the recirculation liquid increased up to 4.5 mg L^{-1}, even if the DO load supplied to the packed bed was significantly reduced (79% and 20% reduction for TLV = 0.51 and 2.04 m h^{-1}, respectively, compared to the oxygen load under standard conditions). Conversely, TLVs greater than 3.8 m h^{-1} which led to a DO reduction to an average concentration of 2.5 mg/L, corresponded to an oxygen load increase in proportion to the TLV. Consequently, raising the TLV caused a net increase in the O$_2$ availability and resulted in increased sulfate production (Fig. 5). Montebello et al. (2010) already pointed out to the existence of DO gradients throughout the bed which could be partially reduced by increasing the TLV due to a larger penetration of DO throughout the bed depth when liquid and gas flows operate in counter-current mode. It is relevant to stress that this occurred without any change in the air gas flow rate or oxygen amount supplied to the system and thus, from an operational point of view, such increased sulfate production is an interesting strategy as it could be used to reduce S^0 accumulation without the need for further dilution of the raw gas.

The increase in TLV above typical values for biological systems (1–12 m h^{-1} see Kim and Deshusses, 2008) had been expected to cause a direct effect on (bio)solids shear and wash out. Surprisingly, monitoring of the S^0 and biomass concentrations in the recirculation liquid did not show a relationship between S^0 or biomass concentration and TLV (data not

shown). These results indicate that increasing the TLV, in the short run (hours or days), may not be an efficient measure to scour the S^0 accumulated on the packing material. Once S^0 accumulates, it forms solid aggregates on the packing that are not easily removed. Further research is needed to establish optimum TLV or flushing methods to prevent S^0 accumulation onto the packing.

3.4. Effect of intermittent H$_2$S supply

Starvation periods were implemented to simulate industrial operation with short-term shutdowns. The gas supply was discontinued for 2.5 and 5 days and the response of the reactor was monitored. Only a very small and brief reduction of the RE was detected during the first hours after resuming the gas supply. The maximum RE reduction was 4% after the 2.5-day stop (results not shown) and 7% after the 5-day shutdown (Fig. 6A) and a steady removal of over 99% was reestablished within 4 h.

Shortly after the H$_2$S supply was resumed (day 86.7, Fig. 6A) the ORP dropped to about −150 mV, which indicated a slight sulfide accumulation, in agreement with the transient drop in RE. However, ORP returned to pre-shutdown values (between ± 50 mV) within less than 24 h, indicating absence of dissolved sulfide and presence of oxygen (DO 0.5–2 mg L^{-1}). The ORP pattern after resuming H$_2$S indicated a temporary lag of biological activity followed by a complete recovery. If the culture had been severely affected by the starvation, greater accumulation of sulfide and an ORP drop below −350 mV would have been observed (Montebello et al., 2010).

Interestingly, a sulfur mass balance during the starvation period reveals that actual sulfate concentrations were 30–40% higher than expected from simple dilution by the make-up water (Fig. 6B). Because no dissolved sulfide had accumulated, the excess sulfate concentration measured indicates that biological activity did not completely stop during the
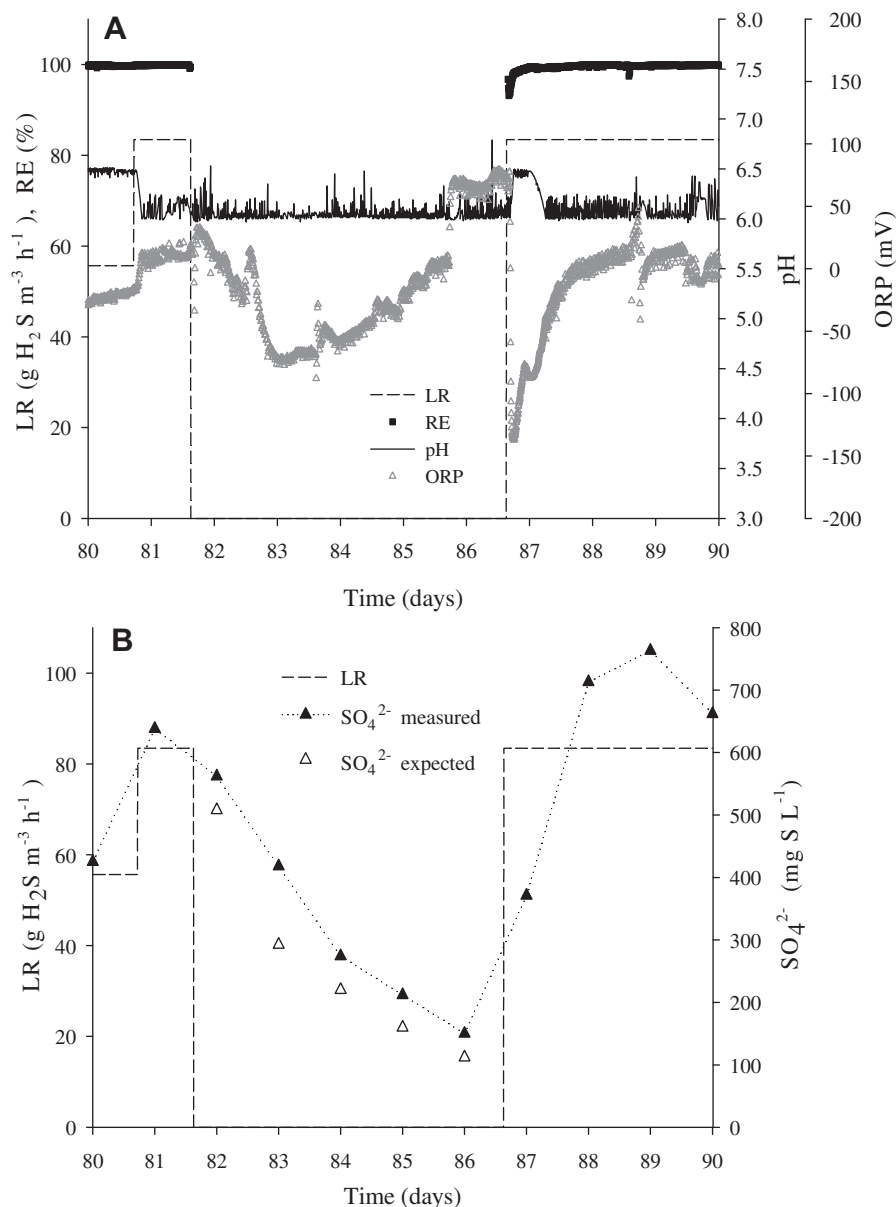
Fig. 6 – Performance of the reactor during and after the 5-day H₂S starvation period. The gas stream was discontinued, but the liquid feed was maintained. A) pH, redox potential (ORP), removal efficiency (RE) and inlet load. B) Inlet load, measured sulfate concentration and expected sulfate concentration (from washout calculation.

starvation period and that oxidation of accumulated S^0 inside the reactor occurred, as previously reported (Fortuny et al., 2010). The source of oxygen for the aerobic oxidation of S^0 was both via the liquid feed, and possibly diffusion of atmospheric O_2 into the biotrickling filter.

These results show that H₂S shutdowns up to 5 days have no, or very little impact on the long-term reactor operation. Proper control of pH during starvation events is likely to be important for prompt recovery. It is also probable that biological oxidation of accumulated biological S^0 during the starvation contributed to the fast recovery of the biotrickling filter, and could possibly allow longer periods of starvation without a greater impact on the reactor performance.

3.5. Effect of short-term pH changes

Complete biological oxidation of sulfide leads to protons production and thus pH changes. However, it is not known to what extent, pH variations need to be controlled to ensure stable bioreactor operation. Since a pH control failure (lack or excess of control actuation) is relatively plausible during industrial operation, the reactor response to large but fast pH variations was studied.

On day 135 the reactor pH was forced to drop to 2.5 for a period of 34 h. Later, after 60 h of operation at normal conditions (i.e., pH 6–6.5), the pH was increased to 9.5 for a 24 h period. As shown in Fig. 7A, the pH drop did not affect the RE of H₂S. However, a sulfur mass balance indicated that
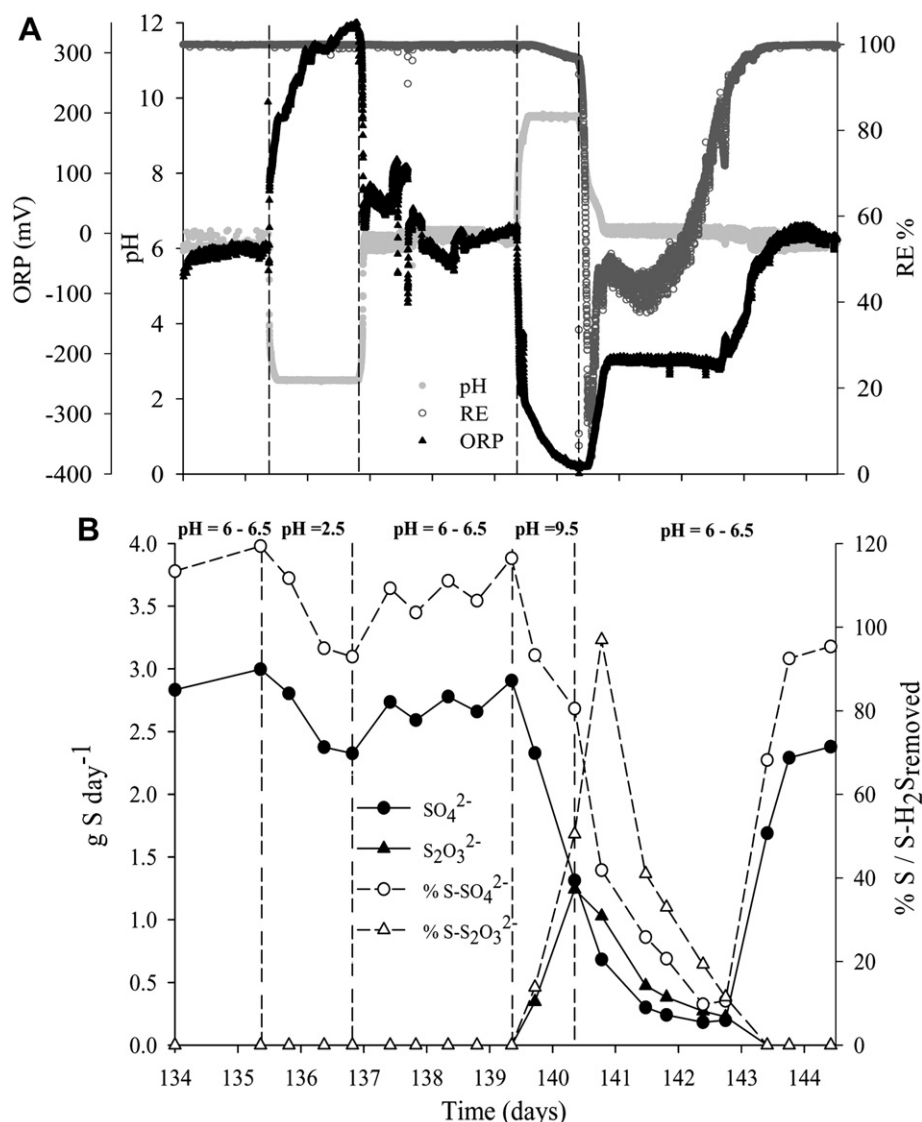
Fig. 7 – Reactor response to pH drop and pH increase episodes. A) Redox potential (ORP), pH and removal efficiency (RE). B) Sulfate and thiosulfate concentration in the liquid phase.

a 25% reduction in the sulfate production occurred after decreasing the pH (Fig. 7B), probably indicating a reduction in the biological activity. A possibility is that under these conditions, sulfide chemical oxidation to thiosulfate, which is unstable at low pH and chemically reacts to produce S^0 contributed to maintain the high RE. This is consistent with the sulfur speciation shown in Fig. 7B, in which neither thiosulfate (chemically converted to S^0) nor other sulfurous ionic species accumulated. Inorganic polysulfides were not measured since they only occur at pH above 6 (Steudel, 2004). Sulfate production increased as soon as the pH was returned to its original value and continued to increase throughout the period at which the pH was kept at 6–6.5 (Fig. 7B). It is worth noticing that sulfate production rates greater than the sulfur load $(S - SO_4^{2-}/S - H_2S_{removed} > 100\%)$ were encountered, probably due to the oxidation of accumulated S^0.

The high pH test was conducted next. Immediately after increasing the pH to 9.5 for 24 h, a sharp drop in the ORP

occurred indicating an accumulation of sulfide (Fig. 7A) while a shift in the sulfur mass balance from sulfate to thiosulfate was observed (Fig. 7B). These reveal that a significant slow-down of the biological activity as well as a shift in the metabolism occurred as a result of the pH change. However, at high pH, both physical absorption of H_2S and chemical oxidation of dissolved sulfide to thiosulfate (van den Bosch et al., 2008) and possibly (poly)sulfide are favored. Therefore, although the biological oxidation was affected, the removal of H_2S only slowly dropped to about 95% at the end of the high pH step. When the pH was returned to 6–6.5, an important transient phase of very low RE (<20%) was observed (Fig. 7A). This was attributed to H_2S stripping and is consistent with the concurrent increase in ORP (i.e., decrease in dissolved sulfide) during this short phase. For the next two days, biological activity was probably severely inhibited and the primary means for H_2S removal was likely sorption and chemical oxidation to thiosulfate. Thiosulfate concentration slowly

decreased because of dilution rather than to biological oxidation since biological oxidation would have led to a sulfate concentration increase. It was not until day 143, i.e., close to 3 days after the perturbation, that biological oxidation to sulfate became again the primary removal means, as shown by the ORP increase (Fig. 7A) and sulfate yields (Fig. 7B). The H_2S RE reached over 99% indicating that the reactor had recovered and was operating normally about 3 days after the pH spike.

This demonstrates that the bioreactor was much more susceptible to high pH exposure than to low pH changes. Such behavior can be explained by the fact that acidification is the natural consequence of sulfide oxidation and, therefore, most sulfide oxidizers are more tolerant to acidic conditions than to alkaline conditions (Brüser et al., 2004; Syed et al., 2006). Also, a low pH results in a decrease of the dissolved sulfurous species concentration (H_2S by stripping and polysulfides and thiosulfate by chemical destabilization), whereas a high pH leads to accumulation of dissolved sulfurous species (sulfides and polysulfides), which can negatively affect the activity of the sulfide degraders.

4.   Conclusions

A detailed study of the operational aspects affecting the biological sweetening of energy gases mimics was carried out in a lab-scale biotrickling filter. Results showed that:

○ Detailed monitoring of the process with on-line H_2S gas, ORP and pH sensors combined with off-line analysis of sulfurous species dissolved in the trickling liquid provided a detailed understanding of the phenomena involved during the treatment of H_2S in the biotrickling filter.

○ Inoculation of the biotrickling filter with MWWTP sludge led to a very fast (3 days) start-up therefore showing that, provided certain conditions, it is not necessary to obtain a specific culture of sulfide oxidizers to inoculate an H_2S degrading system.

○ The EBRT (so reactor volume) can be importantly reduced without significantly affecting the removal of H_2S while treating 2000 ppmv H_2S. However, excessive EBRT reduction lead to an important RE drop due to mass transfer limitation and not due to biological limitation as observed in our previously research when the LR was increased by increasing the H_2S inlet concentration.

○ Gas supply shutdowns for up to 5 days had little effect on the biotrickling filter performance after resuming normal operation. Possibly, controlling pH, addition of make-up water coupled with biological oxidation of S^0 present in the biotrickling filter helped maintain a healthy biological activity during the perturbation.

○ A high TLV is recommended because it favors sulfate production through a better use of the oxygen supplied.

○ A short (34 h) but wide (down to 2.5) pH drop was much less aggressive to the biological activity and overall reactor performance than a short (24 h) but also wide (up to 9.5) pH rise. Even so, the robustness of the system allowed for a full recovery after about 48 h of normal operation.

REFERENCES

Bailón, L., 2005. Development of a biotrickling filter for the removal of H_2S from biogas. In: Proceedings of the II International Congress on techniques for Air Pollution Control. La Coruña, Spain, pp. 143–148.

Brüser, T., Lens, P.N.L., Trüper, H.G., 2004. The biological sulfur cycle. In: Lens, P., Hulshoff Pol, L. (Eds.), Environmental Technologies to Treat Sulfur Pollution. Principles and Engineering. IWA Publishing, London, UK, pp. 47–86.

Buisman, C.J.N., Post, R., Ijspeert, P., Geraats, G., Lettinga, G., 1989. Biotechnological process for sulphide removal with sulphur reclamation. Acta Biotechnologica 9, 255–267.

Devinny, J.S., Deshusses, M.A., Webster, T.S., 1999. Biofiltration for Air Pollution Control. CRC-Lewis Publishers, Boca Raton, Florida, USA.

Duan, H., Koe, LC.C., Yan, R., Chen, X., 2006. Biological treatment of H_2S using pellet activated carbon as a carrier of microorganisms in a biofilter. Water Research 40, 2629–2636.

Fortuny, M., Baeza, J.A., Deshusses, M.A., Gamisans, X., Casas, C., Lafuente, J., Gabriel, D., 2008. Biological sweetening of energy gases mimics in biotrickling filters. Chemosphere 71, 10–17.

Fortuny, M., Guisasola, A., Casas, C., Gamisans, X., Lafuente, J., Gabriel, D., 2010. Oxidation of biologically produced elemental sulfur under neutrophilic conditions. Journal of Chemical Technology and Biotechnology 85 (3), 378–386.

Gabriel, D., Deshusses, M.A., 2003. Retrofitting existing chemical scrubbers to biotrickling filters for H_2S emission control. Proceedings of the National Academy of Sciences of U.S.A 100 (11), 6308–6312.

González-Sánchez, A., Revah, S., Deshusses, M.A., 2008. Alkaline biofiltration of H_2S odors. Environmental Science & Technology 42 (19), 7398–7404.

Goehring, M., Helbing, W., 1949. Journal of Analytical Chemistry V, 129–346.

Kim, S., Deshusses, M.A., 2008. Determination of mass transfer coefficients for packing materials used in biofilters and biotrickling filters for air pollution control - 2: development of mass transfer coefficients correlations. Chemical Engineering Science 63 (4), 856–861.

Koe, L.C.C., Yang, F., 2000. A bioscrubber for hydrogen sulphide removal. Water Science and Technology 41 (6), 141–145.

Kuenen, J.G., 1975. Colourless sulphur bacteria and their role in the sulphur cycle. Plant and Soil 43, 49–76.

Maestre, J.P., Rovira, R., Álvarez Hornos, J., Fortuny, M., Lafuente, J., Gamisans, X., Gabriel, D., 2010. Bacterial community analysis of a gas-phase biotrickiling filter for biogas mimics desulfurization through the rRNA approach. Chemosphere 80, 872–880.

Montebello, A.M., Baeza, M., Lafuente, F.J., Gabriel, D., 2010. Monitoring and performance of a desulphurization

biotrickling filter with an integrated continuous gas/liquid flow analyser. Chemical Engineering Journal 165, 500–507.

Prado, Ó.J., Veiga, M.C., Kennes, C., 2005. Treatment of gas-phase methanol in conventional biofilters packed with lava rock. Water Research 39, 2385–2393.

Ross, C.C., Drake, T.J., Walsh, J.L., 1996. Handbook of Biogas Utilization, second ed. SERBEP, c/o General Bioenergy, Florence, AL.

Sercu, B., Núñez, D., van Lagenhove, H., Aroca, G., Verstraete, W., 2004. Operational and microbiological aspects of a bioaugmented two-stage biotrickling filter removing hydrogen sulfide and dimethyl sulfide. Biotechnology and Bioengineering 90 (2), 259–269.

Steudel, R., 2004. The chemical sulfur cycle. In: Lens, P.N.L., Hulshoff Pol, L. (Eds.), Environmental Technologies to Treat Sulfur Pollution. Principles and engineering. IWA Publishing, London, UK, pp. 1–31.

Syed, M., Soreanu, G., Falletta, P., Béland, M., 2006. Removal of hydrogen sulphide from gas streams using biological processes - a review. Canadian Biosystems Engineering 48, 2.1–2.14.

Tchobanoglous, G., Burton, F.L., Stensel, H.D., 2003. Wastewater Engineering. Treatment and Reuse, fourth ed. McGraw-Hill Companies, New York, NY, USA, pp. 1505–1532.

van den Bosch, P.L.F., van Beusekom, O.C., Buisman, C.J.N., Janssen, A.J.H., 2007. Sulfide oxidation at halo-alkaline conditions in a fed batch bioreactor. Biotechnology and Bioengineering 97 (5), 1053–1063.

van den Bosch, P.L.F., Sorokin, D.Y., Buisman, C.J.N., Janssen, A.J.H., 2008. The effect of pH on thiosulfate formation in a biotechnological process for the removal of hydrogen sulfide from gas streams. Environmental Science and Technology 42 (7), 2637–2642.

Yang, Y., Allen, E.R., 1994. Biofiltration control of hydrogen sulfide.1. Design and operational parameters. Journal of Air and Waste Management 44, 863–868.