Biotrickling filters for biogas sweetening: oxygen transfer improvement for a reliable operation

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Abstract:

An industrial-scale biotrickling filter for the removal of high concentrations of H_2S is described in this work. The system has been operating at H_2S inlet concentrations between 1000 and 3000 ppm_v at acidic conditions. A decrease of pH from 2.6 to 1.8 did not affect the biological activity inside the biofilter while reducing the water make-up consumption up to 75%. The current oxygen supply system, based on direct injection of air to the liquid phase, has demonstrated to be inefficient for a long term operation leading to elemental sulfur accumulation in the packing material (i.e. promoting clogging episodes). The present study demonstrates it is possible to partially remove (40.3%) the deposited elemental sulfur by bio-oxidation when biogas is not fed. In normal operation conditions, the implementation of an aeration system based on jet-venturi devices has shown quite promising results in terms of oxygen transfer efficiency and robustness. Such improvement of oxygen transfer was translated in a better conversion of H_2S to sulfate, which increased around 17%, prolonging the lifespan operation at low pressure drop.

1.Introduction

The use of renewable and alternative energy sources is an effort to reduce the greenhouse gas emissions and global warming. In this sense, the biogas produced in the anaerobic digestion in both municipal solid wastes (MSW) and wastewater treatment plants (WWTP) is a prominent, renewable energy source. Burning biogas in a combined heat and power (CHP) plant is an interesting option to reduce the emissions and the operational cost of a WWTP. However, prior to biogas burning it is necessary to remove the hydrogen sulfide (H_2S) produced during anaerobic digestion process. This will eventually avoid facility corrosion, unnecessary production of byproducts, and SO_2 emissions. The specifications for the maximum content of H_2S for CHP are in the range of 0.02–0.05% v/v (200–500 ppm_v). The biogas generated in anaerobic digestion facilities in WWTPs contains average concentrations of H_2S in the range from 0.1 to 0.5% vol. (1,000-5,000 ppm_v) (Walsh *et al.* 1998).

Biological removal of H_2S in biotrickling filters (BTF) has been successfully tested in applications at moderate-low pollutant loads containing H_2S concentrations up to 12,000 ppm_v (Fortuny *et al.* 2008). The technology has proved to be a good alternative to the more expensive physical-chemical systems (Kim and Deshusses 2005). In recent years, the use of the biofiltration technology for the removal of H_2S at high concentrations have been developed and tested at industrial-scale (Tomás *et al.* 2009). However some issues concerning the production of by-products such as elemental sulfur, which has been related to clogging episodes, hinders the robustness and reliability of the technology. In the previous studies of Tomás *et al.* (2009), performed in the same BTF at similar operation conditions, an elementary analysis denoted that the 95% of the solid deposited on the packing material was elemental sulfur. The biological oxidation of H_2S follows two possible reactions according to equations 1 and 2 (Madigan *et al.* 2009):

$$HS^{-} + 0.5\ O_2\ (aq) \rightarrow S^{o} + OH^{-} \qquad \Delta G^{0'}=-209.4\ \text{KJ reaction}^{-1} \qquad (1)$$

$$HS^{-} + 2\ O_2\ (aq) \rightarrow SO_4^{2-} + H^{+} \qquad \Delta G^{0'}=-798.2\ \text{KJ reaction}^{-1} \qquad (2)$$

Depending on the oxygen availability for the microorganisms in the bioreactor, the final product of the oxidation can be either sulfate (high O_2/H_2S ratio in the biofilm) or elemental sulfur (low O_2/H_2S ratio). If the oxygen is less than the stoichiometric requirement the elemental sulfur formation is enhanced (Buisman *et al.* 1991). Then, elemental sulfur accumulates in the packing material, increasing the pressure drop or even causing the total clogging of the bed (Fortuny *et al.* 2008). Since the solubility of oxygen in water is 80 times less than that for the hydrogen sulfide, large quantities of oxygen (or air) are necessary to ensure the biological removal of H_2S to sulfate. For this reason, the capacity of the system for oxygen transfer from air to water is a key parameter in the correct operation of BTFs, without forgetting other maintenance aspects such as periodic carrier material washings and the use of appropriate water distribution systems.

Several studies can be found in the literature about the optimization of several parameters in biological-based systems for H_2S abatement such as pH (Gonzalez-Sanchez and Revah 2007), the type of packing material (Li *et al.* 2008), empty bed residence time and the influence of inoculation among others. Conversely, the way to supply oxygen to the system has not received much attention, despite this is a critical parameter for long-term operation and reactor stability.

Another equivalent strategy for H_2S removal in biogas is the anoxic treatment using nitrate as final electron acceptor (instead of oxygen). On the one hand, the limitation of oxygen transfer is avoided and, besides, hydrogen sulfide from biogas and nitrate from the liquid effluent can be treated simultaneously. In this sense, Montebello *et al.* (2012) compared the efficiency of aerobic and anoxic treatment of methylmercaptan and hydrogen sulfide; both systems offered a reasonable response in terms of efficiency (Montebello *et al.* 2012). On the other hand, a large amount of nitrate can be required for the anoxic removal of hydrogen sulfide. Therefore, if this is not produced in the plant, the operational cost can increase significantly by the consumption of chemicals.

At industrial scale, oxygen (or air) is often supplied directly to the H_2S loaded stream prior to the entrance at the BTF. Thus, large amounts of air are required to provide the oxygen necessary for the complete biological oxidation to sulfate. The operational cost associated to the blower operation coupled to the biogas dilution may hinder process viability due to the poor mass transfer efficiency between gas and liquid phases.

Recent studies on oxygen transfer improvement have shown the suitability of venturi-based devices for intensive gas-liquid mass transport (Rodriguez *et al.* 2012). Jet-venturi systems offer higher oxygenation capabilities than conventional diffuser- or open-end pipe based devices. According to that, the objective of this study was to assess the improvement on the oxygen transfer from air to water in an industrial BTF for biogas sweetening.

2. Materials and methods

2.1.BTF description

The BTF is located in the Manresa-Sant Joan de Vilatorrada (Barcelona, Spain) WWTP and has been intermittently operating since 2007. The design of the BTF was based on previous studies performed in a lab-scale pilot plant (Fortuny *et al.* 2008). The BTF was made with glass-fiber reinforced plastic. In order to optimize the gas contact time, the BFT was divided into four equal modules with an internal baffle and two levels of sprinklers for each side. This forces the biogas to flow first upflow in parallel mode through the first two modules, and then downflow in a counter-current mode in the next two modules. The bed volume is 5.15 m^3 with a commercial packing material consisting of polypropylene Pall rings with 209 m^2 m^{-3} specific surface area. A blower (JSA ferran, Model 40-S) connected to a submerged perforated tube in the sump of the BTF was used for air supply. This configuration provided an O_2 transferred /O_2 supplied ratio of 1.4% (the method used to calculate this ratio can be found in Rodriguez *et al.*, 2012). Some design and operational parameters of the BTF are shown in Table 1. Details of the reactor construction can be found elsewhere (Tomás *et al.* 2009).

The identity of the oxidizing bacteria responsible of the hydrogen sulfide degradation in the BTF was not studied. Since the studied system is a full scale plant, it is quite difficult to justify a shutdown procedure just for biomass sampling purpose. Some studies in the literature working at similar conditions as those tested in this study, (e.g. Duan *et al.* (2006)) determined that the dominant specie is *Acidithiobacillus thiooxidans*. Also, in their review paper, Syed *et al.* (2006) reported as dominant species, when operating at similar pH as in the present study and in aerobic conditions, *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans*.”

2.2. BTF background and troubleshooting

The BTF treated biogas flowrates between 1000 and 3000 m^3 biogas day^{-1}, which corresponded with the total biogas produced at the facility. Biogas production fluctuations were related to the environmental conditions and operational issues (e.g. foam formation) of the anaerobic digesters. The composition of the biogas in the anaerobic digestion facility of the WWTP of Manresa- Sant Joan de Vilatorrada is approximately 69% methane, 29% CO_2, 1% N_2 and variable concentrations of H_2S from 1500 to 3000 ppm_v.

During the period 2007-2010 the BTF was operated at a biogas pressure of 0.1-0.5 bars. However, in 2010 the biogas storage system was changed in order to optimize the operation of the plant. The improvement consisted in storing the H_2S laden biogas in tanks 2 and 3 (Figure 1) with a maximum working pressure of 2 bars. Since the designed maximum pressure of the BTF is 0.6 bars, a pressure regulating valve was installed at the inlet of the BTF to ensure a pressure ranging from 0.45-0.52 bar. The biogas treated is stored in tank 1 at a maximum pressure of 0.5 bars prior to be burned in either the boiler or the CHP plant. The burning device used depends on the heat demands of the digesters. For instance, the CHP cannot produce the necessary heat for the operation of the anaerobic digesters in winter due to the low biogas productions (800-1200 m^3 day^{-1}). In this scenario, burning the biogas in the boiler unit is necessary. In consequence, less strict biogas sweetening requirements are needed. In 2010 the control system of BTF was integrated into the Supervisory Control and Data Acquisition (SCADA) of the WWTP, allowing a better monitoring of the system.

pH, percent volume of methane and pressure inside the BTF are controlled automatically for optimal BTF operation. The pH set-point was set at 1.8, being this value adjusted by means of the addition of make-up water (effluent from the WWTP containing average values of 5 mg BOD_5 L^{-1}, 7 mg TKN L^{-1} and 7 mg P_{total} L^{-1}). The water addition and/or purge system was also linked to the liquid level inside the BTF through a three-level contactor. The leachate was sent at the inlet of the WWTP through the plant sewage system

The percent volume of methane is an important safety variable in the system, since methane is explosive in the range from 5-15% volume in air. A safety switch allowed stopping the air supply system if the methane percentage was below 50%.

The pressure in the system was automatically controlled with a pressure regulating valve. However, some operating problems such as clogging of the bed, pressure changes upstream and downstream of the BTF or low biogas production can affect the pressure inside the BTF. For this reason it was necessary to control the blower operation as a function of the pressure in the BTF. If the BTF pressure is higher than 0.52 bar then the blower is stopped to avoid high-pressures in the system. The blower is also stopped if the BTF pressure is lower than 0.2 bar to avoid the possibility of creating explosive mixtures within the bioreactor. However, it is worth noticing that the amount of air supplied at the BTF was never controlled as a function of the oxygen requirements of the process (biogas flowrate or H_2S inlet concentration), which had an important impact on reactor performance as further discussed in next sections.

2.3. BTF monitoring

The reactor monitoring included continuous measuring of the pressure inside the tank (Desin, TPR 18), dissolved oxygen (DO) (Hach lange, LDO), pH (Crison, Model 5330), biogas flow (Endress Hauser, Proline t-mass 65), air flow (Georg Fischer, Model SK11) and percent volume of methane (Prevensigas). H_2S concentration was acquired daily with an electrochemical sensor (Sixth Sense, Surecell-H_2S-L) equipped with a dilution system. Liquid flow rate (for bottom and top sprinklers), liquid level in the tank, reactor temperature and water consumption were measured manually. Besides, the aqueous phase was also monitored for anionic species by ionic chromatography (Dionex Corporation, Model IonPac AS9-HC).

3. Results and discussion

3.1. Effect of operating pH

The inoculation of the BTF was carried out several times during the lifetime of the reactor due to different shutdowns and operational troubleshooting. Since the use of activated sludge from WWTPs has been shown to be suitable alternative for the inoculation of sulphide removing biotrickling filters at low- and high-loads of H_2S (Fortuny *et al.* 2008; Gabriel and Deshusses, 2003), activated sludge from the Manresa WWTP was used, which was diluted with industrial water. The target volatile suspended solids (VSS) concentration in the 2.25 m^3 sump liquid was 1.5-2 g VSS l^{-1}. The diluted inoculum was recirculated for 24 hours without make-up water addition nor biogas feed. After this immobilization biomass period the biogas feed was started, without make-up water addition, to avoid biomass loss in the liquid purge. Only when the H_2S removal efficiency was above 90% the pH control was activated. Results reported herein correspond to an operational period starting on July 12, 2011. Thereafter, the BTF was operated during 118 days with a pH of 2.6 and on November 8, 2011, the pH set-point was changed to 1.8 to assess the effects of reduced water make-up consumption.

Table 2 shows some average values of both operational periods at different pH. Some important standard deviations were encountered in some variables such as biogas flowrate or inlet and outlet H_2S concentrations due to the inherent dynamic nature of industrial sites which are subject to day to day operational changes. However, it has been observed that when the BTF was subject to shutdown periods shorter than 15 days related with problems in the biogas line, punctual malfunctioning of the blower or other operational problems, the biological process presented a RE close to 100% in less than 24 hours after operation resumption (data not shown). In agreement with the results obtained by Fortuny *et al.* (2011) a recovery of % RE = 99 of the BTF after a short shut-down was in 4 hours (Fortuny *et al.* 2011). Also, Liu *et al.* (2013) reported a recovery time of 2 days after a shutdown of 5 days (Liu *et al.* 2013).

Despite the highest H_2S load was treated during the operation at pH 1.8, the highest average elimination capacity was observed in this period. The H_2S conversion to sulfate is an indicator of the correct operation of the BTF. Since no thiosulfate and/or H_2S were detected in the liquid phase, the conversion % to sulfate allows calculating the amount of elemental sulfur produced. The better RE results and conversion percentage to sulfate during the second operational period was directly related to the higher DO concentrations in this period.

During the operation at pH 2.6 the average water consumption was around 19.5 ± 6.1 m^3 day^{-1}, and the decrease of pH operation in 0.8 points induced a saving of 15 m^3 day^{-1} of water. Consumption of water in the WWTP was not a problem, but it could be a limiting issue when considering the BTF-based technology in other types of industry.

Overall, the reactor performed well in both operational periods. However, a significant better performance was found at the lowest pH in terms of RE, EC, water consumption and H_2S conversion to sulfate. Interestingly, the sulfate concentration found at the lowest pH was much higher than that reported by other authors to produce some inhibition Jin *et al.* (2005). They operated a BTF with polypropylene Pall rings treating inlet H_2S concentrations in a range from 0-190 ppm_v either at pH 4-7 (RE was 95%) and at pH 2-3 (RE was 87%). Authors found that the biological activity of microorganisms was inhibited due to the low pH and high sulfate content (at pH = 2 the sulfate content in the water was 1900 mg l^{-1}). Also, other authors (Kim and Deshusses 2005) that operated at pH 1.8-2.5 and at pH=1.0-2.0 (Duan *et al.* 2006) concluded that it is possible to work at such low pH conditions and defined a low-pH limitation at pH below 1.

3.2. Operation with a conventional (blower) oxygen supply system

To understand the problems associated with dissolved oxygen limitation, the low-pH operating period (November 8, 2011 to January 23, 2012) has been selected. Figure 2 shows the biogas flowrate treated, the elimination capacity (EC), the sulfate content in the purge line and the removal efficiency (% RE). Biogas production variability (900 to 2700 $m^3 day^{-1}$) in the WWTP is observed in Figure 2, which corresponded to the usual behavior of the anaerobic digesters due to the many factors that affect the production of biogas (temperature stability and foaming among others). Since the sulfate content in the make-up water was around 200 mg SO_4^{2-} l^{-1}, the sulfate content in the purge was mostly due to H_2S complete oxidation production, which correlated well with the amount of biogas treated.

The lowest RE (63.73 %) was found on day 76 of operation (H_2S concentration at the outlet of 818 ppm_v) corresponding to an EC of 29.02 g H_2S m^{-3} h^{-1}, which was related with the decrease in the biogas production. Under this scenario, the control system that prevents for a low methane percentage stopped the blower. Then, the process becomes oxygen limited. The maximum punctual H_2S ECs were found on days 45 and 55 (corresponding to an inlet load of 115 and 119 g H_2S m^{-3} h^{-1} respectively) with EC of

108 and 110 g H_2S m^{-3} h^{-1}, and a RE of 99 and 98 % respectively. These results are similar to those found by Rattanapan *et al.* (2009), maximum EC of 125 g H_2S m^{-3} $h^{-1}$and IL of 149 g H_2S m^{-3} h^{-1} and by Fortuny *et al.* (2011), EC_{max} of 144 g H_2S m^{-3} h^{-1} and IL of 170 g H_2S m^{-3} h^{-1}.

The operation with the blower has shown to be poorly reliable and very sensitive to pressure changes in the BTF. Despite the removal efficiencies obtained were acceptable, the fluctuations observed in the air supply system suggests the possibility of uncompleted H_2S oxidation.

3.3. Elemental sulfur accumulation and washing out strategy

The elemental sulfur accumulation was calculated with a mass balance in the BTF. Since sulfur might be found in different states, and in order to avoid possible errors in the mass balance, the presence of thiosulfates and sulfites were evaluated in the liquid phase. The presence of these anions in the liquid purge and/or recirculation line was below the detection limit throughout the present study. The amount of hydrogen sulfide that was not converted into sulfate was assumed to be elemental sulfur. Out of it, an undetermined fraction accumulated in the packed bed of the BTF.

Figure 3 shows the cumulative elemental sulfur produced and the inlet load throughout the 76 days of operation at pH 1.8. The vertical line indicates the day that the biogas flowrate was stopped. During the operation, it is remarkable that in day 42 the air fed to the BTF decreased from 24.90 to 13.39 m^3 h^{-1} due to a blower equipment change. This reduction of the air supplied to the BTF caused a dramatic increase of the elemental sulfur produced. In the study published by Alcántara *et al.* 2004 it is demonstrated that the amount of supplied oxygen is the key factor for elemental sulfur and/or sulfate formation (Alcántara *et al.* 2004). In fact the ratio load/oxygen supply is the main factor affecting the byproducts formation (Fortuny *et al.* 2008). Between days 62 and 66 the decrease of elemental sulfur production was related to the decreases of biogas production (and, again, related to H_2S loading rate). The average % conversion to elemental sulfur was 49 % (with average O_2/H_2S ratio of 6), which is higher than 37% reported by Fortuny *et al.* (2010) during an artificially forced sulfur accumulation period in a similar lab-scale BTF O_2/H_2S supplied ratios in the range 23.6-1.5, EBRT = 180 s, and TLV = 3.8 m h^{-1}). Such conversion percentage implies a total generation of 364 kg of elemental sulfur in the BTF during 76 days of operation. From the pressure drop detected between the biogas inlet to the reactor and the clean biogas storage tank, it was assumed that the system was almost clogged. At this point the BTF was shut-down in order to withdraw the accumulated solids from the packing material. However, an unclogging strategy was tested according to Fortuny *et al.* (2010). They tested the oxidation of biologically produced elemental sulfur under neutrophilic conditions as a wash out strategy based on the principle that the same microorganisms that degrade H_2S are capable of degrading the elemental sulfur into sulfate according to equation 3 (Kuenen 1975) .

$$S^o + 3/2O_2 + H_2O \rightarrow SO_4^{2-} + 2H^+ \quad \Delta G^0 = -587.1 \text{ KJ reaction}^{-1} \qquad (3)$$

In the present case, the wash out procedure was performed at acidic pH (1.8) by stopping the biogas feed while keeping the aeration and the recirculation active. The air flow rate during the wash out was 13.05 ± 4.1 m^3 h^{-1}, corresponding to an average dissolved oxygen concentration of 7 mg l^{-1} in the recirculated liquid phase. The lowest elemental sulfur oxidation during two first days suggesting some sort of acclimation period. As can be observed in Figure 3 a maximum elemental sulfur consumption rate of 10.65 Kg S° day^{-1} was observed in the early days after the feed stop. Later on, the elemental sulfur consumption decreased to 2.21 Kg Sº day^{-1} on day 19 of the biological wash out procedure. Such decrease in the S consumption rate was related with the availability of elemental sulfur (Fortuny *et al.* 2010). Tichý *et al.* (1994) studied the degradation of elemental sulfur, biological and not biological, showing that biological elemental sulfur has a hydrophilic behavior. This is a key factor for biological removal since the microorganism needs adhesion at the sulfur surface to oxidize the elemental sulfur to sulfate.

The total wash out of elemental sulfur was 40.3% by day 21 of the biological wash out step, which is lower than 57% previously reported by Fortuny et al (2010) in the sixth day of wash out. Probably this lower value was related to operational problems in the equipment, as some parts of the BTF were frozen (severe winter conditions) during the elemental sulfur oxidation test.

3.4. Modifications in the BTF to improve the oxygen transfer

As shown above, the BTF had a serious oxygen transfer limitation with the conventional oxygen supply system. Thus, the objective of the modification was to solve the mass transfer problems with the implementation of a jet-venturi device for supplying the necessary oxygen for the complete hydrogen sulfide oxidation to sulfate. However, implementation of a jet-venturi device in the water recirculation line of the BTF implied to also install an additional pump due to the large water flow rate needed to produce the Venturi effect in the jet-Venturi unit. Figure 4 (a) shows the conventional system based on a blower connected to a perforated pipe in the sump of the BTF while figure 4 (b) shows the new system based on the jet-venturi device.

The following modifications were made in the BTF to optimize the oxygen transfer from the air to the water phase. First, an additional centrifugal water pump (Inbeat, MPN 50-32-160) equipped with an inverter (Marem Aplicacions i Serveis SL, Nord SK500E) was added to supply the driving force for air suction with the jet-venturi. Also, a new flow meter (Georg Fischer, Type 335) and a jet-venturi of 2 ” (Venturi Pumps, type 484 water jet exhauster) were added. An O_2 gas sensor (Ortat, ExTox 0-25% KE) was installed in the outlet pipe which was the measuring device of a control loop for controlling the amount of air supplied to the BTF. A programmable logic controller (B&R Automation, model X20CP1483-1) was used to setup the control loop. First, a simple on/off control strategy was established which turns the pump on or off when the % volume of oxygen in the outlet pipe is below or above 2%, respectively. This set point of 2% ensured that the biological process has the necessary amount of oxygen and prevented and controlled the biogas dilution with excessive air as occurred with the conventional air supply system.

Table 3 shows a comparison of the performance of the BTF during the period between November 8, 2011, and January 23, 2012, with the conventional air supply system; and the period between June 6, 2012, and June 21, 2012, with the jet-venturi already installed. It must be highlighted that the latter period corresponds to the first period of operation with the improved aeration system after a short 4-days period of forced BTF stop to perform the modifications. Thus, optimum performance was somehow not encountered yet and results might be influenced by such bias. As shown in Table 3, operating conditions such as pH and make-up water supply (and correspondingly the hydraulic residence time) were maintained.

Interestingly, the air flow rate supplied with the jet-venturi was reduced by a factor of 5. However, the RE and EC were maintained. Despite such lowest air flow, the DO concentration increased due the best mass transfer efficiency when the jet-venturi was used. The oxygen transferred/oxygen supplied with the Jet-venturi was 26.7 % compared with the 1.4 % during the operation using the blower. Such improved efficiency was in agreement with the observations made by Rodríguez *et al.* (2012) with similar aeration devices tested at lab-scale.

Such improved oxygen transfer was translated in a better conversion of H_2S to sulfate, which increased around 17%. Additional limitations were probably occurring simultaneously as indicated by the remaining DO in the recirculation line. Probably, startup from a clean, recently inoculated packed bed would further improve the results in the long-run of the BTF. An additional benefit was encountered in terms of the reduced variability (3%) of the methane % at the exit of the BTF with the Jet-venturi compared with the blower operation (12 %), which implies a best operation of the CHP unit.

4. Conclusions

An industrial-scale BTF was capable to remove with almost 100% RE the hydrogen sulfide in concentrations ranging from 1000 to 3000 ppm_v at drastic acidic pH conditions. The conventional blower-based aeration systems has been demonstrated ineffective in terms of oxygen transfer and, consequently, promotes the excessive accumulation of elemental sulfur in the packing material.

The wash out strategy of elemental sulfur, with water and air addition and without the biogas feed, is an effective method to partially remove the elemental sulfur. This wash out procedure can be done during maintenance shutdowns scheduled for the CHP maintenance.

The implementation of a jet-venturi device for oxygen supply at the biological process is an important improvement through a better gas-liquid oxygen mass transfer. Further monitoring of the new BTF configuration is needed to assess the long term operation improvement.

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6. References

Alcántara, S., A. Velasco, A. Munoz, J. Cid, S. Revah and E. Razo-Flores. 2004. Hydrogen sulfide oxidation by a microbial consortium in a recirculation reactor system: Sulfur formation under oxygen limitation and removal of phenols. Environmental Science and Technology 38:918–923.

Buisman, C. J. N., P. I. Jspeert, A. Hof, A. J. H. Janssen, R. T. Hagen and G. Lettinga. 1991. Kinetic parameters of a mixed culture oxidizing sulfide and sulfur with oxygen. Biotechnology and Bioengineering 38:813-820.

Duan, H., L. C. C. Koe, R. Yan and X. Chen. 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., A. Guisasola, C. Casas, X. Gamisans, J. Lafuente and D. Gabriel. 2010. Oxidation of biologically produced elemental sulfur under neutrophilic conditions. Journal of Chemical Technology and Biotechnology 85:378-386.

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

Fortuny, M., X. Gamisans, M. A. Deshusses, J. Lafuente, C. Casas and D. Gabriel. 2011. Operational aspects of the desulfurization process of energy gases mimics in biotrickling filters. Water Research 45:5665-5674.

Gabriel, D. and M. A. Deshusses. 2003. Performance of a full-scale biotrickling filter treating H_2S at a gas contact time of 1.6 to 2.2 seconds. Environmental Progress 22:111-118.

Gonzalez-Sanchez, A., and S. Revah. 2007. The effect of chemical oxidation on the biological sulfide oxidation by an alkaliphilic sulfoxidizing bacterial consortium. Enzyme and Microbial Technology 40:292-298.

Jin, Y. M., M. C. Veiga and C. Kennes. 2005. Autotrophic deodorization of hydrogen sulfide in a biotrickling filter. Journal of Chemical Technology and Biotechnology 80:998-1004.

Kim, S. and M. A. Deshusses. 2005. Understanding the limits of H2S degrading biotrickling filters using a differential biotrickling filter. Chemical Engineering Journal 113:119-126.

Kuenen, J. G. 1975. Colourless sulfur bacteria and their role in the sulfur cycle. Biomedical and Life Sciences 43:49-76.

Li, Z., T. Sun, N. Zhu, X. Cao and J. Jia. 2008. Comparative study of using different materials as bacterial carriers to treat hydrogen sulfide. Applied Microbiology and Biotechnology 81:579-588.

Liu, C., J. Liu, J. Li, H. He, S. Peng, C. Li and Y. Chen. 2013. Removal of H2S by co-immobilized bacteria and fungi biocatalysts in a bio-trickling filter. Process Safety and Environmental Protection 91:145-152.

Madigan, M. T., J. M. Martinko, and J. Parker. 2009. Brock Biology of microorganisms. 12th ed. edition, San Francisco, USA.

Montebello, A. M., M. Fernández, F. Almenglo, M. Ramírez, D. Cantero, M. Baeza and D. Gabriel. 2012. Simultaneous methylmercaptan and hydrogen sulfide removal in the desulfurization of biogas in aerobic and anoxic biotrickling filters. Chemical Engineering Journal 200–202: 237-246

Rattanapan, C., P. Boonsawang, and D. Kantachote. 2009. Removal of H2S in down-flow GAC biofiltration using sulfide oxidizing bacteria from concentrated latex wastewater. Bioresource Technology 100:125-130.

Rodriguez, G., A. D. Dorado, A. Bonsfills, R. Sanahuja, D. Gabriel, and X. Gamisans. 2012. Optimization of oxygen transfer through venturi-based systems applied to the biological sweetening of biogas. Journal of Chemical Technology and Biotechnology 87:854–860.

Syed M., G. Soreanu, P. Faetta and M. Béand. 2006. Removal of hydrogen sulfide from gas streams using biological processes – A review. Canadian Biosystems Engineering 48: 2.1-2.14.

Tichý, R., A. Janssen, J. T. C. Grotenhuis, G. Lettinga, and W. H. Rulkens. 1994. Possibilities for using biologically-produced sulphur for cultivation of Thiobacilli with respect to bioleaching processes. Bioresource Technology 48:221-227.

Tomás, M., M. Fortuny, C. Lao, G. D, J. Lafuente, and X. Gamisans. 2009. Technical and economical study of a full-scale biotrickling filter for H2S removal from biogas. Water Practice and Technology 4:26-33.

Walsh, J., C. Ross, M. Smith, S. Harper, and W. Wilkins. 1998. Handbook of biogas utilization. The Environment, Health, and Safety Divsion, Georgia, USA.

FIGURE CAPTIONS

Figure 1: Location of the biotrickling filter within the anaerobic digestion facility at the WWTP of Manresa-Sant Joan de Vilatorrada (Spain).

Figure 1 description: Anaerobic digestion facility and heating system schematic.

Figure 2: Biogas flowrate (●), H_2S elimination capacity (□), sulfate concentration in the purge (▲) and removal efficiency (% RE) (○) along the operation period from November 8, 2011 to January 23, 2012.

Figure 3: Elemental sulfur accumulation (▲), H_2S inlet load (IL) (●) during November 8, 2011 to January 23, 2012 operation period and cleaning operation (after discontinued line)

Figure 4 (a): Conventional system for air supply to the BTF. 1= Biogas inlet, 2=Make-up water inlet, 3=Outlet air, 4=Blower, 5= Liquid purge, 6= Recirculation water pump and 7=Biogas outlet. LS=Level sensor, pH=pH probe, DO=Dissolved oxygen probe, PS=Pressure sensor and MS= sensor of % volume of methane in the gas phase.

Figure 4 (b): Jet-venturi-based system for air supply to the BTF. 1= Biogas inlet, 2=Make-up water inlet, 3=Jet-Venturi device, 4= Water pump for the jet-venturi, 5= Liquid purge, 6= Recirculation water pump and 7=Biogas outlet. LS=Level sensor, pH=pH probe, DO=Dissolved oxygen probe, PS=Pressure sensor, O2S=sensor of % volume of oxygen in the gas phase and MS= sensor of % volume of methane in the gas phase.

TABLE CAPTIONS

Table 1: Design an operational parameters of the BTF

Table 2: Average values during the two last operations.

Table 3: Average values during operations with blower and with Jet-venturi