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Review Paper

A review on prospects and challenges of biological H_2S removal from biogas with focus on biotrickling filtration and microaerobic desulfurization

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HIGHLIGHTS

- Prospects and challenges of biotrickling filtration and microaerobic desulfurization are discussed.
- Biotrickling filtration is mainly limited by oxygen availability and mass transfer coefficient.
- Providing dissolved oxygen to biotrickling units and using multi-stage filtration improve removal efficiency.
- Under microaeration conditions, H_2S removal mostly occurs at headspace highlighting the importance of optimizing the design of headspaces.
- Microaeration offers lower cost for desulfurization purposes.

GRAPHICAL ABSTRACT

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ABSTRACT

The production of biogas from sulfate-rich materials under anaerobic digestion results in the formation of hydrogen sulfide (H_2S). The recommended level of H_2S in the produced biogas for direct combustion purposes is in the range of 0.02 to 0.05% w/w (200 to 500 ppm), therefore, desulfurization is required to avoid damages to combustion equipment and prevent the formation of sulfur dioxide (SO_2) which is an acid rain precursor. It has been well documented that physical, thermal, and chemical desulfurization approaches suffer from high operation costs as well as waste production needing to be disposed of. Accordingly, a great deal of efforts has been put into biological methods because of being more environmentally friendly and more economically advantageous in comparison with the other techniques. Biotrickling filtration (BTF) and microaerobic desulfurization have shown a high potential for H_2S removal at pilot- and large-scale plants. Despite all the progress made and the promising aspects keeping these methods at the core of interest, there are still challenges to be addressed. The present article attempts to briefly review and discuss the challenges and future prospects of BTF and microaerobic desulfurization.

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Contents

1. Introduction

Biogas produced through anaerobic digestion is a prominent and environmentally friendly source of renewable energy (Khoshnevisan et al., 2018). The produced biogas can be burned directly in combined heat and power plants or can be upgraded and used as transportation fuel. When a substrate used to produce biogas, contains sulfur, the formation of hydrogen sulfide (H_2S) as a biogas component is inevitable (Chaiprapat et al., 2015). H_2S is in fact formed under anaerobic conditions because sulfate (SO_2^{-4}) plays the role of an electron acceptor while organic compounds are biologically degraded. In better words, H_2S is produced by the anaerobic degradation of S-containing compounds (mainly proteins) and the reduction of anionic species (particularly SO_2^{-4}) contained in the feedstock in the digester (Stams et al., 2003; Ramos et al., 2013). Some Sulfate-reducing reactions are presented below (**Eqs. 1-6**) (Haghighatafshar, 2012):

$$4H_2 + SO_4^{2-} + H^+ \rightarrow HS^- + 4H_2O \quad \text{Eq. 1}$$

$$Acetate + SO_4^{2-} \rightarrow HS^- + 2HCO_3^- \quad \text{Eq. 2}$$

$$Propionate + \frac{3}{4}SO_4^{2-} \rightarrow \frac{3}{4}HS^- + Acetate^- + HCO_3^- + \frac{1}{4}H^+ \quad \text{Eq. 3}$$

$$Propionate + \frac{7}{4}SO_4^{2-} + \frac{1}{4}H_2O \rightarrow \frac{7}{4}HS^- + 3HCO^{3-} + \frac{1}{2}H^+ + \frac{1}{4}OH^- \quad \text{Eq. 4}$$

$$\text{Butyrate} \quad \frac{1}{2}SO_4^{2-} \quad o \quad \frac{1}{2}HS \quad 2Acetate \quad \frac{1}{2}H \quad \text{Eq. 5}$$

$$\text{Butyrate} \quad \frac{5}{2}SO_4^{2-} \quad \frac{1}{4}H_2O \quad o \quad \frac{5}{2}HS^- \quad 4HCO_3^- \quad \frac{3}{4}H \quad \frac{1}{4}OH^- \quad \text{Eq. 6}$$

H_2S in the concentrations of 1000-3000 ppm can cause instantaneous death (Wang et al., 2005). This is due to the reaction between H_2S and enzymes in the bloodstream, inhibiting cellular respiration resulting in pulmonary paralysis, sudden collapse, and death (Syed et al., 2006). The combustion of fuels containing H_2S in high concentrations increases the sulfur dioxide (SO_2) emissions which is an acid rain precursor and brings about serious damages to the vegetation and constructions. Moreover, the combustion of these types of fuels results in the corrosion of engines and fast degradation of engine lube oil. The recommended level of H_2S in the produced biogas is in the range of 0.02 to 0.05% (w/w) (200 to 500 ppm) while H_2S-free biogas is more desirable (Rodriguez al., 2014).

Several approaches have been introduced and examined to decontaminate the biogas produced. Physical, thermal, chemical, and biological treatments are the most evaluated methods; each one has its own benefits and drawbacks. Due to the fact that the physical, thermal, and chemical treatments have been shown to be more disadvantageous compared with biological treatments, most researchers have focused on biological gas decontamination. Accordingly, the main objective of the present article is to briefly review the biological desulfurization of biogas with a focus on biotrickling filtration (BTF) and microaerobic desulfurization.

2. Biological biogas desulfurization

Biological biogas desulfurization can be performed either in additional units mainly through using bio-filters and biotrickling filters, or directly in anaerobic digesters, that is, by applying microaerobic conditions during the digestion process (Ramos et al., 2013). Biological treatment of contaminated biogas is a relatively new trend in biogas sweetening and has attracted a great deal of interest. While other gas desulfurization approaches suffer from high operation costs and produce waste needing to be disposed of, this method is economically more advantageous and is more environmentally friendly than the other techniques as well. Biological desulfurization of biogas can proceed at lower temperatures and pressures, as well as with limited or no reagent consumption (Syed et al., 2006). This treatment is also more beneficial when gas stream contains biodegradable or bio-convertible compounds (Devinny et al., 1999; Gabriel and Deshusses, 2003; Tomás et al., 2009).

2.1. Analytical methods

Before describing distinctive desulfurization approaches, the analytical methods by which the treatment processes are evaluated are described. Two equations, i.e., **Equations 7** and **8** are mostly used for evaluating the BTF. The mass of removed H_2S is calculated based on its concentration in the inlet and outlet gas as follows:

$$m_{H_2S} \quad (C_{in} \quad C_{out}) \; uQ \quad \text{Eq.7}$$

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where C_{in} and C_{out} are the mass concentration of H_2S at the inlet and outlet points, respectively, and Q represents the biogas flow rate in $m^3 h^{-1}$. Similarly, the mass of sulfate is calculated:

$$m_{SO_4^{2-}} \quad (C_{SO_4^{2-},out} \quad C_{SO_4^{2-},in}) \; u Q_{L.P} \qquad \text{Eq. 8}$$

where $Q_{L.P}$ is the liquid purge flow rate in $m^3 h^{-1}$. In all scientific papers which have been reviewed, elimination capacity (EC) was one of the considered indices by which the efficiency of the desulfurization process was taken into account. EC is defined as the mass of contaminant degraded per unit volume of packed bed per unit time. EC is calculated as follows (**Eq. 9**):

$$EC \quad (C_{in} \quad C_{out}) \; u \frac{Q}{V} \qquad \text{Eq. 9}$$

where "Q" represents flow rate of biogas entering the desulfurization process filter ($m^3 h^{-1}$), "C_{in}" and "C_{out}" stand for concentrations of inlet and outlet H_2S in gas (g H_2S m^{-3}), and "V" represents empty bed volume (m^3).

H_2S removal efficiency (RE) is another important factor taken into consideration when dealing with desulfurization of biogas. RE is estimated as follows (**Eq. 10**):

$$RE \quad (C_{in} \quad C_{out}) / C_{in} \qquad \text{Eq. 10}$$

where "C_{in}" and "C_{out}" stand for concentrations of inlet and outlet H_2S in gas (g H_2S m^{-3}).

Sulfuric acid (H_2SO_4) recovery is the third most important and relevant index considered. It can be assessed based on the mass of sulfuric acid produced per mass of inlet H_2S on sulfur basis.

2.2. Biotrickling filtration (BTF)

BTF is a subgroup of biological treatment in which H_2S is trapped into some bed materials. In another word, H_2S is solubilized in a humid packed bed inoculated with sulfide-oxidizing bacteria (SOB) as illustrated in **Figure 1**. SOB are aerobic species (more details about SOB and their categories can be seen in Krayzelova et al. (2015)) and are immobilized and grown as biofilm in the presence of O_2 (Noyola et al., 2006). This technology has been tested at industrial-scale and proved to be successful especially at moderate-low H_2S concentrations up to 12,000 ppm (Fortun et al., 2008; Tomàs et al., 2009). However, there are still some problematic issues such as the production of byproducts, i.e., elemental sulfur, and their associated clogging problems, which require further investigations (Burgess et al., 2001; Rodriguez et al., 2014).

The bed materials used in BTF contain immobilized active microbes whose function is to biochemically oxidize H_2S into elemental sulfur (S^0) or sulfuric acid depending on whether partial or complete oxidation is taking place while formation of sulfite and thiosulfate is rarely detected (Gabriel et al., 2013). Different bed materials have been tested by researchers. Fortuny et al. (2008) selected two distinctive bed materials; randomly dumped cubes of open pore polyurethane (PU) foam and polypropylene HD Q-PAC®. Rodriguez et al. (2014) chose glass-fiber reinforced plastic filled with a commercial packing material consisting of polypropylene Pall rings. Chaiprapat et al. (2015) employed coconut husk mixed with cylindrical plastic. Coconut husk was selected because of its rough surface, moisture storage capacity, and inexpensiveness. Cylindrical plastic was used to prevent bed compaction over time.

The biomass-immobilized SOB used for biological sulfide removing purposes are either photoautotrophic or chemolithotrophic. The former uses CO_2 as the terminal electron acceptor, while the latter employs oxygen (aerobic species), nitrate, and nitrite (anaerobic species) as terminal electron acceptors as shown in **Equations 11** and **12** (Tang et al., 2009).

Due to the fact that chemolithotrophic SOB are more advantageous than photoautotrophic, i.e., higher sulfide loading rates, simpler nutritional requirements, and higher sulfide tolerance, they have attracted more interest and attention.

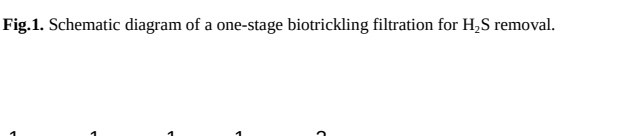

Fig.1. Schematic diagram of a one-stage biotrickling filtration for H_2S removal.

$$\frac{1}{16} H_2S \quad \frac{1}{16} HS \quad \frac{1}{4} O_2 \; o \; \frac{1}{8} SO_4^{2-} \quad \frac{3}{16} H \qquad \text{Eq. 11}$$

$$'G^R \quad 99.57 \frac{kJ}{e \; eq} \; | \; 796.6 \frac{kJ}{mol.sulfide}$$

$$\frac{1}{16} H_2S \quad \frac{1}{16} HS \quad \frac{1}{5} NO_3 \quad \frac{1}{80} H \quad o \; \frac{1}{8} SO_4^{2-} \quad \frac{1}{10} N_2 \quad \frac{1}{10} H_2O \qquad \text{Eq. 12}$$

$$'G^R \quad 93.05 \frac{kJ}{e \; eq} \; | \; 744.4 \frac{kJ}{mol.sulfide}$$

Apart from the microorganisms involved, reactor configuration and operating conditions such as the pH of recirculating liquid, liquid recirculation rate, and empty bed retention time (EBRT) are also important parameters which determine if a partial or complete oxidization occurs. Several studies have been performed to optimize the key parameters in biological-based systems for H_2S abatement such as pH (González-Sánchez and Revah, 2007), the type of packing material (Li et al., 2008), and EBRT (Chaiprapat et al., 2015), among others.

Sulfuric acid could be generated during desulfurization process if a complete oxidation takes place. Therefore, acidic biofiltration is more cost-effective than alkaline BTF due to lower operating cost to maintain pH against the acidifying state. In better words, when the objective is both desulfurization and recovery of sulfuric acid, the preference would be acidic BTF, some research with a main focus on alkaline biofiltration can also be found in the literature though, such as the research conducted by González-Sánchez and Revah (2007).

Since the performance of BTF can be affected by operating conditions, the most important parameters with significant impacts are discussed in the following sections.

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2.2.1. Oxygen availability and mass transfer

Two limiting factors with significant impacts on biofilteration are oxygen availability and mass transfer. This can be attributed to the low solubility of oxygen in water, i.e., 8.24 mg L^{-1} at 25 °C (Colt, 1984). Some attempts have been made to shrink the oxygen mass transfer limitations by evaluating the different types of gas diffusers. Rodriguez et al. (2012) reported that Venturi-based devices offer higher oxygenation capabilities than conventional diffusers or open-end pipe-based devices for intensive gas–liquid mass transfer. If a high supply of oxygen is provided, the biomethane will be so diluted (Chaiprapat et al., 2011). To solve such a problem, Rodriguez et al. (2014) proposed to supply dissolved oxygen (DO) through recirculating a liquid coming in contact with the biogas stream. Under such circumstances, liquid recirculation velocity (q, $m^3 m^{-2} h^{-1}$), i.e., the amount of recirculating liquid applied per unit surface area of the bed materials, is a determinant factor. This approach from one hand reduces CH_4 dilution in biogas, and from the other hand, increases the supply of moisture and nutrients to the SOB inside the reactor, while also removes the microbial metabolic products from the biofilters (Charnnok et al., 2013).

It should be mentioned that BTF was initially performed by recirculating liquid and biogas into reactors through inlet points located at the opposite ends of the reactors. To solve the long travel path of biogas and recirculating liquid, bioreactors have been divided into multiple stages (**Fig. 2**), with each one having their own reactant injection points in order to distribute the reactants more evenly (Metcalf et al., 1980).

Fig.2. Schematic diagram of single-stage and multistage biotrickling filtration.

2.2.2. Impact of empty bed retention time (EBRT) on process performance

By increasing the EBRT, the RE is increased because the gas is provided with a longer period to be absorbed into the liquid film. Chaiprapat et al. (2015) showed that the highest RE for both single BTF (S-BTF) and triple stage BTF (T-BTF) was achieved at the most elevated EBRT tested, i.e., 180s. They reported that, under the above-mentioned condition, the T-BTF with a liquid recirculation velocity of 7.1 $m^3 m^{-2} h^{-1}$ outperformed the other velocity values investigated while the S-BTF with a liquid recirculation velocity of 4.7 $m^3 m^{-2} h^{-1}$ led to the highest RE. Such differences can be explained by the fact that increasing "q" above an optimum level could result in excessive liquid content of the biofilters and consequently reduce media porosity. Generally, the longer EBRT, the higher desulfurization but it requires reactors with larger volumes and consequently higher construction costs.

It should be noted that when reactors are performing at low H_2S concentrations, single and multi-stage BTF produce almost similar results because under such conditions, oxygen mass transfer will not reach the threshold value. In case of higher H_2S concentrations, similar RE cannot be expected (Rodriguez et al., 2014). Based on the literature review performed, it can be inferred that when increasing EBRT is impossible due to reactor volume limitations, maintaining the recirculation velocity at optimum points can help to compensate for lower retention times.

Irrespective of operating reactors equipped with either single stage or multi-stage filtration, increasing EBRT leads to an increased efficiency of sulfuric acid recovery due to higher O_2/H_2S ratios in the bed which is a factor of significant impact on complete oxidation. Chaiprapat et al. (2015) has shown that this ratio highly controls the level of sulfide oxidation. In another words, the higher O_2/H_2S ratio would result in higher acid recovery rates. This phenomenon can be explained by the fact that partial H_2S oxidation requires one-fourth of O_2 needed for complete oxidation (**Eqs. 13** and **14**). This is in line with the findings of Tomàs et al. (2009), who reported that 95% of the solid deposited on the packing materials was elemental sulfur due to low oxygen availability for the microorganisms in the reactor. The main drawback pertaining to the formation of elemental sulfur is the increased pressure drop and eventually the total clogging of the bed.

$$2HS + O_2 \rightarrow 2S^0 + 2OH \qquad \text{Eq. 13}$$
$$\Delta G^0 = -129.50\ kj/mol$$

$$2HS + 4O_2 \rightarrow 2SO_4^{2-} + 2H \qquad \text{Eq. 14}$$
$$\Delta G^0 = -732\ kj/mol$$

One barrier which still limits the complete oxidation is the uneven distribution of O_2/H_2S ratios along the height of the reactors. The difference between O_2/H_2S ratio at the top and bottom of reactors is always meaningful and consequently, reactions cannot be expected to proceed evenly through the whole reactors' height.

Among the different biofiltration systems, the EC of T-BTF stands higher at 175.6 $gH_2S\ m^{-3}\ h^{-1}$ (Chaiprapat et al., 2015) compared with systems in which air is directly mixed with biogas such as HD Q-PAC® (EC:126 $gH_2S\ m^{-3}\ h^{-1}$) (Fortuny et al., 2011), activated carbon biofilters (EC: 125.0 $gH_2S\ m^{-3} h^{-1}$) (Rattanapan et al., 2009), and coconut fiber S-BTF (EC: 113.5 $gH_2S\ m^{-3} h^{-1}$).

2.2.3. Impact of diffuser type on biological removal

As mentioned earlier, diffuser type also plays an important role in the RE achieved throughout BTF. For instance, Rodriguez et al. (2014) in their research study, performed on a full-scale desulfurization plant, compared a conventional diffuser (blower) with a Venturi-based device. They found out that the jet-Venturi offered a lower airflow rate of $5.6 \pm 3.8\ m^3 h^{-1}$ compared with $22.1 \pm 5.7\ m^3 h^{-1}$ by the conventional diffuser. However, in spite of its lower airflow rate, the jet-Venturi offered a higher DO concentration (i.e., 2.8 ± 1.4 *vs.* 1.4 ± 1.1 mg L^{-1}). Due to the better mass transfer efficiency, the oxygen transferred/oxygen supplied during the operation with the jet-Venturi was 26.7% compared with as little as 1.4% using the blower with in turn resulted in 17.3% higher H_2S conversion to sulfate.

2.2.4. Clogging detection and wash-out strategies

The formation of elemental sulfur gradually increases the pressure drop and eventually clogs the filters. The pressure drop between the biogas inlet to the reactors and the clean biogas stored in the storage tanks can be used as an indicator to reflect the clogging problem in a system under investigation. One way to solve the clogging problem is to shut down filtration systems to withdraw the accumulated solids from packing materials. Fortuny et al. (2010) was inspired by the stoichiometric equation (**Eq. 15**) presented by Kuenen (1975) and proposed a new strategy to wash out the accumulated elemental sulfur. This strategy has been developed based on the idea that the same microorganisms that degrade H_2S are also capable of degrading the elemental sulfur into sulfate.

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$$S^0 + \frac{3}{2}O_2 + H_2O \rightarrow SO_4^{2-} + 2H^+ \quad \text{Eq. 15}$$

Tichý et al. (1994) showed that biological elemental sulfur has a hydrophilic behavior – forming ionic bonds with other molecules –, which is a key factor for biological elemental sulfur removal. This is due to the fact that the microorganisms need to adhere to elemental sulfur to oxidize it to sulfate. Fortuny et al. (2010) reported a total biological elemental sulfur wash-out of 57% in the sixth day of operation. In another study reported by Rodriguez et al. (2014), the same strategy was examined and a total wash-out of 40.3% was reported. They also reported that the maximum elemental sulfur consumption rate (10.65 kg S^0 d^{-1}) was noticed during the early days after stopping the feeding process in order to initiate the wash-out process. However, the consumption rate decreased by time reaching 2.21 kg S^0 d^{-1}. The descending trend of the wash-out value compared with what reported by Fortuny et al. (2010) was attributed to the operating problems related to the equipment, i.e., some parts of the BTF were frozen (severe winter conditions) during the elemental sulfur oxidation test (Rodriguez et al., 2014). Using acidic BTF, Montebello et al. (2014) reported an 80% removal of the accumulated sulfur under high loads of H_2S.

2.2.5. Influence of liquid velocity and flow pattern on oxygen transfer

The introduction of biogas and trickling liquid into BTFs can be performed either in co-current or counter-current patterns. As mentioned earlier, the efficiency of process and consequently the final product of desulfurization process depend on the O_2/H_2S ratio. Therefore, flow pattern can significantly affect the gas conditioning process. When the flow pattern is counter-current, the DO and biogas inlets are located at the opposite points of the desulfurization unit. This means that a lower oxygen concentration would be available at the biogas inlet, resulting in partial desulfurization. In spite of this shortcoming, counter-current configuration has been predominantly used in BTF units (Fortuny et al., 2011; Montebello et al., 2012; Rodriguez et al., 2014). A co-current pattern may suggest a more favorable O_2/H_2S concentration. Therefore, a number of studies have been performed using this flow pattern by taking into account influential variables with significant impacts on BTF performance for removing different contaminants such as xylene and trichloroethene (Trejo-Aguilar et al., 2005; Popat and Deshusses, 2010).

López et al. (2016a) compared the performance of co-current and counter-current flow patterns for improving oxygen transport in an aerobic BTF system for biogas desulfurization. Employing an aerobic BTF packed with plastic Pall rings, they concluded that in the co-current configuration, the majority of H_2S removal took place in the first reactor bed. Their results showed that at different recirculating velocities (4.4 - 14.5 $m^3 m^{-2} h^{-1}$) for a given sulfur loading rate, the overall RE of the system was relatively constant. However, in the first reactor bed, RE varied depending of sulfur loading rate. More specifically, the lowest and the highest sulfur loading rates led to Res of 95.4% and 77.9%, respectively. They claimed that under the co-current pattern investigated, the highest EC ever reported was achieved, i.e., 643.4 gS-H_2S $m^{-3} h^{-1}$ (López et al., 2016a)

In another study carried out by Almenglo et al. (2016a), the effect of gas-liquid flow pattern on desulfurization process and oxygen transfer was investigated in a pilot-scale BTF. What made this study different from the work of López et al. (2016b) laid in the use of nitrate as electron acceptor instead of oxygen. They found no significant difference between co- and counter-current configurations in terms of mass transfer coefficients. Their results showed that the highest EC was obtained under counter-current condition, 140 gS $m^{-3} h^{-1}$.

2.2.6. Effect of pH on BTF performance

Although BTF benefits from slightly acidic conditions, drops in pH to very low values resulting from the formation of sulfuric acid would decrease the process performance. In low pH values, the solubility of H_2S decreases which in turn slows down the H_2S mass transfer to the circulating media. In better words, the lower H_2S mass transfer, the lower desulfurization performance. Moreover, under strict acidic conditions, the activity of microorganisms is inhibited (Chitwood et al., 1999; Jin et al., 2005). Two different strategies can be used to control the pH of the medium; 1- replacing low pH medium with fresh medium or 2- employing buffering agents such as calcium carbonate, dolomite, or oyster shells. **Table 1** compared some BTFs in terms of medium pH and pH adjustment methods. Jin et al. (2005) evaluated the effect of pH on H_2S removal. They reported that the RE remained high, above 95%, between pH 4 and 7, and then dropped slightly to 94 and 87% at pH values of 3 and 2, respectively. Accordingly, they concluded that biotrickling filter could also be operated at pH values ranging from 2 to 4 without much performance deterioration. Under such acidic conditions, a simple water washing would be sufficient to remove hydrogen ions as fast as they form.

2.2.7. Effects of temperature and packing materials on BTF performance

The impact of temperature on BTF performance has not been deeply investigated yet. The performance of BTF is mostly confined by the low mass transfer rate of air/oxygen into the liquid media. The Henry coefficient determines how fast the mass transfer occurs. By increasing the temperature, this coefficient decreases while simultaneously the diffusion coefficient is improved (Kennes and Veiga, 2013). The increased diffusion coefficient leads to facilitatied mass transfer inside the bioreactors. These two effects are completely opposite and may neutralize the effect of each other. Optimizing the temperature of liquid media can be further investigated as a key parameter to improve BTF performance.

Packing (bed) materials also play a pivotal role in BTF because SOB are stabilized inside bed materials, thereby, the reactions between DO and H_2S occur in this part of the filters. Different sorts of packing materials have been reportedly tested for H_2S removal inside biotrickling filters. Large specific area, high porosity, high chemical stability and structural strength, low weight, suitable surface for bacterial attachment and growth, and low cost are among the important features a good packing material should have in order to meet the requirements. **Table 2** tabulates some of the relevant packing materials used at lab-, pilot-, and full-scale BTF. As can be observed in **Table 2**, random dump plastic packings such as Pall rings have been frequently employed by different researchers owing to the fact that they are easy to handle, cheap, and porous but suffer from poor biofilm establishment on their surface (Kazenski and Kinney, 2000). Moreover, compared with some other types of packing materials, they have lower

Table 1.
Operating conditions and the medium pH of some biotrickling filtration (BTF) reactors to remove H_2S from biogas.

pH adjustment method	Medium source	Medium pH	Reference
Fresh pH-adjusted medium	Anaerobic digester effluent	Swing between 4 and 0.5	Chaiprapat et al. (2015)
Alkaline nutrient	Treated water from the wastewater treatment plant enriched with nutrients	Kept between 6.8 to 7.4	Almenglo et al. (2016)
Fresh medium	-	-	Rodriguez et al. (2012)
$NaHCO_3$	Mineral medium enriched by nutrients	Swing between 6.78 and 2	Jin et al. (2005)
NaOH	Mineral medium and a solution of $NaHCO_3$	Kept between 6 to 6.5	López et al. (2016a)
NaOH/HCl	-	Kept between 6.5 to 7	López et al. (2016b)
NaOH	Mineral medium and a solution of $NaHCO_3$	Kept between 6 to 6.5	Fortuny et al. (2011)

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Table 2.
Some of the relevant packing materials used at lab-, pilot- and full-scale BTF.

Specific surface area (m^2 m^{-3})	Packing material	Reference
354	Polypropylene Pall rings	López et al. (2016b)
-	Open-pore polyurethane foam	Almenglo et al. (2016a)
600	Open-pore polyurethane foam	Almenglo et al. (2016b)
209	Polypropylene Pall rings	Rodriguez et al. (2014)
859	High-density polyethylene	Vikromvarasiri and Pisutpaisal (2016)
350	Polypropylene Pall rings	Jin et al. (2005)
134	Coconut husk	Chaiprapat et al. (2015)
600	Open-pore polyurethane foam	Fortuny et al. (2008)
620	3D-printed honeycomb-monolith	Qiu and Deshusses (2017)

specific surface area, which limits achieving a high EC.

Open-pore polyurethane foams are relatively new packing materials with a high specific surface. Cox and Deshusses (2001) reported an improved performance with polyurethane foam cubes over other types of packings, especially at high gas flow rates with low H_2S concentrations. They mentioned that the open structure and high porosity maintained the pressure drop at low levels even at relatively high gas velocities. Moreover, their large specific surface area proved beneficial with respect to mass transfer limitation observed at low H_2S concentrations.

2.3. Microaeration desulfurization

A new trend in desulfurization process, which has gained growing interest, is the microaeration approach. This method is also called "microaerobic" (Ramos et al., 2012; Ramos and Fdz-Polanco, 2013; Ramos et al., 2013; Ramos et al., 2014b and c), ''limited aeration'' (Zhou et al., 2007; Zitomer and Shrout, 2000), or even ''microoxygenation'' (Polanco et al., 2009; Díaz et al., 2011a and b; Díaz and Fdz-Polanco, 2012) and has particularly succeeded at full-scale during the anaerobic digestion of sludge in wastewater treatment plants (Jeníček et al., 2017). Although not a strict rule, the term "microaeration" is used when air is injected into anaerobic digesters. In contrast, when pure oxygen is dosed into the reactors, the term "microoxygenation" is preferred (Díaz and Fdz-Polanco, 2012; Krayzelova et al., 2015). From now on, the term "microaeration" will be used to generally refer to the process regardless air or oxygen is used. Hence, microaeration desulfurization refers to the process in which a small amount of air or oxygen is injected into anaerobic digesters to grow SOB, so that S^0 is formed as a result of desulfurization process (Díaz et al., 2010; Kobayashi et al., 2012). Due to the fact that desulfurization of the biogas is performed inside biogas digesters, periodic cleaning is inevitable to prevent clogging problems and avoids any decreases in the H_2S removal efficiency. This periodic maintenance adds additional costs to the whole operational cost (Díaz and Fdz-Polanco, 2012).

It needs to be highlighted that the microaeration can be performed either in the liquid or gaseous phases while the biogas or liquid is recirculated. **Figure 3** illustrates two different dosing points; dosing to liquid phase with liquid recirculation (**Fig. 3A**) and dosing to the gaseous phase with biogas recirculation (**Fig. 3B**). However, dosing points and recirculating methods are independent. Among different combinations, dosing air in the headspace with liquid recirculation is most frequently used (Muñoz et al., 2015). As mentioned earlier, desulfurization can occur directly into the main digester or in a separate microaerobic compartment. Under the latter condition, the higher utilization of air/oxygen would be possible while the accumulation of elemental sulfur in the headspace could be avoided.

Several factors have been introduced as influential parameters on the performance and efficiency of the process. The amount of air/oxygen, air/oxygen flow rate, dosing point, location of oxidation process, reactor configuration, biogas residence time, and temperature can be mentioned as key parameters in microaerobic desulfurization. These parameters are discussed below.

A

B

Fig.3. The scheme of possible aeration methods; (A) to liquid phase and (B) to gaseous phase.

2.3.1. Air/oxygen dosage

The use of different air/oxygen dosages has been reported in the literature ranging from 0.03 to 218 L O_2 L^{-1} feed. The $O_2/H_2S_{supplied}$ and $O_2/H_2S_{consumed}$ ratios can be employed to evaluate the performance of the process. The correlation between the $O_2/H_2S_{consumed}$ and the $O_2/H_2S_{supplied}$ is interpreted as variations in SO_4^{2-}/S^0. van den Ende and van Gemerden (1993) reported that at oxygen concentrations below 0.1 mg L^{-1}, elemental sulfur is the major end-product. Although complete oxidation has been observed even at low ratios of $O_2/H_2S_{supplied}$, the elevated $O_2/H_2S_{supplied}$ would result in an increased production of sulfate up to 70% as reported by Fortuny et al. (2008). Ramos et al. (2013) showed that there is a positive correlation between the $O_2/H_2S_{supplied}$ and the $O_2/H_2S_{consumed}$ ratios. They also demonstrated that a higher $O_2/H_2S_{supplied}$ did not necessarily mean an increased efficiency of O_2 utilization inside the microaerobic desulphurization units (MDU). The highest O_2 utilization efficiency will be achieved if the $O_2/H_2S_{supplied}$ and the $O_2/H_2S_{consumed}$ ratios increase simultaneously.

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While most researchers have focused on O_2 concentration as a parameter which determines to what extent the biological oxidation of sulfur takes place, Klok et al. (2013) introduced sulfide concentration as a determinant factor for sulfide biological oxidation. Based on their results, sulfide at concentrations from 0 to 0.15 mmol L^{-1} and 0.3 to 1.0 mmol L^{-1} increased and decreased the biological oxidation of sulfide, respectively. The biological oxidation increased again when the sulfide concentration was in the range of 1.0 to 5.0 mmol L^{-1}. Díaz et al. (2011a) determined the optimal O_2 rate at low and high H_2S concentrations while the oxygen was dosed into the reactor headspace. The optimal O_2 rate and RE were found to be at 6.4 NL O_2 Nm^{-3} biogas and 96%, respectively, when treating biogas with low H_2S concentrations, i.e., 0.33% (v/v). The counterpart values for biogas with high H_2S concentrations, i.e., 3.38% (v/v), were achieved at 118 NL O_2 Nm^{-3} biogas and 99%. They also reported that the ratio of O_2 rate/biogas production rate would be a proper parameter to control the O_2 dose in the digester. In another study performed by Ramos et al. (2014a), a pilot anaerobic sludge digester with an HRT of 22–24 d was evaluated. The H_2S concentration in the biogas varied between 0.21 and 0.38% (v/v). They observed that at 0.25–0.30 NL O_2 L^{-1} feed, the biogas was entirely desulfurized, and its O_2 content remained below 1.03% (v/v).

As mentioned ealier, both air and oxygen can be injected into reactors to promote microaeration conditions. Although being less expensive than oxygen, the use of air can dilute the calorific value of the biogas due to its nitrogen content. This has been confirmed by the findings of a number of research works indicating similar removal efficiencies using both oxygen and air, while also recording slightly lowered methane concentration in the biogas using air (Díaz et al., 2011a; Guerrero et al., 2015). However, the diluted biogas can still be used in combustion engines (Porpatham et al., 2008).

2.3.2. Dosing point

One of the most important key parameters when biogas undergoes microaeration desulfurization process, is the injection point of the oxygen/air. Oxygen can be injected into either the liquid phase of MDUs or into the headspace (middle/top) of the reactors. The amount of air needed per given amount of hydrogen sulfide will be minimized if the injection point is the headspace. This is due to the fact that the reaction between oxygen and H_2S could occur directly (Díaz et al., 2011a; Ramos et al., 2012). By injecting air into the headspace, lower contamination of biogas by nitrogen – as air composition – will occur due to the lower amount of aeration. Moreover, the higher amount of air/oxygen can result in diluted biogas which decreases the product quality. Contrary, when the air/oxygen is bubbled into the liquid phase, a fraction of oxygen is used to oxidize the degradable organic compounds leading to some losses of oxygen. Under such circumstances, higher amounts of air/oxygen need to be dosed into the reactor which would result in an increased possibility of biogas contamination and dilution as discussed earlier In order to determine the proper dosage of air/oxygen injected into the reactor, a ratio in relation to the biogas production (O_2 rate/biogas rate) has been proposed by Muñoz et al. (2015). They argued that a 0.3-3% O_2 rate in relation to biogas production rate is suitable for microaeration. (Krayzelova et al., 2014). Recently, a silicone-based biomembrane has been proposed by Pokorna-Krayzelova et al. (2017a) allowing an efficient H_2S removal under microaerobic conditions while minimizing biogas contamination with oxygen and nitrogen.

Ramos et al. (2013) in their research study on microaerobic desulfurization evaluated three injection points where the H_2S-contaminated biogas as well as oxygen was dosed into an MDU. Although a substantial reduction in RE and O_2 transfer was expected by the authors when they injected O_2 into the headspace compared with the liquid phase, no significant differences were observed in terms of RE. Therefore, they concluded that the overall performance of the MDU was independent of the injection point.

It is worth mentioning that when air/oxygen is injected into the liquid phase, sulfide concentration in the liquid decreases as reported by Krayzelova et al. (2014) and Van der Zee et al. (2007). This brings about the positive effect of decreased sulfide toxicity towards methanogens. Regardless of dosing point, most researchers unanimously reported that sulfide oxidation predominantly took place on the walls of the headspace (Kobayashi et al., 2012; Rodriguez et al., 2012), there are a few reports indicating partial or even no accumulation of elemental sulfur on the walls of the headspace though (Díaz et al., 2011a; Ramos et al., 2014c).

In general, the headspace is a "poorly designed biofilter", which explains the long biogas residence time (BRT) required to achieve high REs. Ramos et al. (2014a) found out that by increasing reactor headspace from 0.3 to 25 L the desulfurization process was improved significantly. They concluded that SOB could well grow on the extended area of the walls of the reactor headspace and that the microbial mat formed on this area acted as a biofilter, which is a key point of the process. It is worth mention that large-scale biogas reactors usually include large headspaces to store biogas and this is considered as an advantage for the implementation of such biofilters capable of providing enough BRT to reach acceptable REs.

2.3.3. Biogas residence time (BRT)

Sufficient residence time is another key factor for a successful microaerobic desulfurization. As presented in **Table 3**, a BRT bigger that 5 h secures REs up to 90%. Schneider et al. (2002) and Rodríguez et al. (2012) achieved REs of 88% and 72%, respectively, when a BRT of about 2.5 h was tested. Kobayashi et al. (2012) demonstrated that a BRT of 1.4 h would result in a low RE of 68%. Contrary to the above-mentioned reports, Ramos et al. (2013) demonstrated a successful RE of 96% under variable BRTs ranging from 59 to 97 min. Such a successful H_2S removal was achieved while both the biogas H_2S content and the inlet concentration of H_2S were oscillating.

Table 3.
The role of residence time on H_2S removal efficiency.

Biogas residence time (h)	Removal efficiency (%)	Reference
2.5	88	Schneider et al. (2002)
5–8	99	Polanco et al. (2009)
5.3	99	Díaz et al. (2010)
6.6	97.5	Díaz et al. (2010)
6.3	98	Díaz et al. (2011a)
2.4	72	Rodríguez et al. (2012)
1.4	68	Kobayashi et al. (2012)
6	90	Ramos and Fdz-Polanco (2013)
8	99	Ramos and Fdz-Polanco (2014)
10	99	Ramos et al. (2014b)

2.3.4. Temperature and reactor configuration

Temperature and its fluctuations could affect the process in different ways. Generally, higher removal efficiencies are observed at higher temperatures but any deteriorations in the system performance followed a temperature drop cannot be unequivocally associated with this temperature drop. Ramos et al. (2013) concluded that changes in temperature influenced the SOB and a lower correlation between the $O_2/H_2S_{supplied}$ ratio and the $O_2/H_2S_{consumed}$ ratio was noticed when the process temperature was decreased from 34 to 29 °C. It should be highlighted that generally temperature cannot be a limiting factor because under practical conditions temperature is fixed.

Based on the existing literature, the type of the reactor in which the desulfurization process takes place does not have significant impacts on the process performance. In better words, the success of the process mostly depends on the above-discussed factors rather than the type of the reactor used. As shown in **Table 4**, the process performance is independent of the reactor type. Direct microaerobic desulfurization can be performed in different reactor designs including up-flow anaerobic sludge blanket (UASB) reactors, expanded granular sludge bed (EGSB) reactors, fluidized bed reactors (FBR), continuous stirred-tank reactors (CSTR), and plug-flow reactors (PFR). Separate MDU (SMDU) can also be designed and used for desulfurization purposes. In this context, anaerobic baffled reactors (ABR) with a final compartment for microaeration have been designed and tested by several researchers (Fox and Venkatasubbiah, 1996; Bekmezci et al., 2011). Each approach has its own benefits. For instance, better performance of the organic matter removal has been reported using the

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Table 4.
Type of reactor, reactive used, and removal efficiency obtained under microaeration desulfurization.

Type of reactor	Reactive used	Removal efficiency (%)	Reference
CSTR[1]	Air	99	Tang et al. (2003)
UAF[2] & SMDU[3]	O_2	99	Khanal and Huang (2006)
FBR[4]	Air	82	Van der Zee et al. (2007)
ND*	Air	92	Jenicek et al. (2008)
CSTR	O_2	99	Polanco et al. (2009)
CSTR	Air	99	Jenicek et al. (2010)
CSTR	Air	68	Kobayashi et al. (2012)
FBR containing GAC[5]	O_2	72	Rodríguez et al. (2012)
UASB[6]	Air	73	Krayzelova et al. (2014)
UASB	Air	99	Pokorna-Krayzelova et al. (2017b)
PFD[7]	Air	99	Mulbry et al. (2017)
SCR[8]	O_2	99	Ruan et al. (2017)
EGSB[9]	Air	80	Chen et al. (2017)

[1] Continuous stirred-tank reactor
[2] Up-flow anaerobic filter
[3] Separate microeaeration desulfurization unit
[4] Fluidized bed reactor
[5] Granular activated carbon
[6] Up-flow anaerobic sludge blanket
[7] Plug-flow reactor
[8] Semi-continuous reactor
[9] Expanded granular sludge bed
* ND: not determined.

direct method due to reduction in sulfide inhibition to methanogens (Zhou et al., 2007). In the case of SMDU, higher amount of oxygen can be dosed into the unit while the other important benefit is that S^0 formed can be easily removed without affecting the core reactor (Ramos et al., 2013).

Although the type of reactor has little impact on the desulfurization process as mentioned earlier, some researchers have shown that some changes made in the common reactors could help to achieve better performances. For instance, the use of natural zeolite in a microaerobic procedure performed in a UASB reactor enhanced the granulation process and process startup, i.e., a time decrease of 50%, as well as reactor performance compared with that of the UASB reactor without zeolite (Fernández et al., 2007; Montalvo et al., 2014). Despite the fact that the performance of the UASB reactor with zeolite as well as the microaeration were affected by hydraulic retention time and volumetric organic loads, it was proved that the system was sufficiently reliable to remove hydrogen sulfide from biogas.

3. Conclusions

The performance of BTF is mainly limited by oxygen availability and mass transfer coefficient. SOB are aerobic species that grow inside the bed material as a biofilm in the presence of O_2. Although some researchers showed improvements in oxygen mass transfer by replacing conventional diffusers or open-end pipe-based devices with Venturi-based devices, recent studies have focused on providing DO to desulfurization units. The DO is supplied through recirculating liquid coming in contact with the biogas stream. The main advantage of this approach is reduced CH_4 dilution in biogas as well as increased supply of moisture and nutrients to the microorganisms. The performance of BTFs with DO recirculation was also improved when multi-stage filtration replaced single-stage filtration. In all types of BTFs, increased EBRT results in better REs. Recirculating velocity would be a limiting factor when single-stage BTFs are used and velocities higher than 4.7 $m^3m^{-2}h^{-1}$ would result in reduced media porosity and consequently lower REs. Co-current flow pattern of recirculating liquid and biogas is another promising approach to improve the EC due to more favorable O_2/H_2S concentration ratio but this approach is limited by the higher H_2S removal taking place in the first reactor bed.

Microaeration inside anaerobic reactors improves the degradation of organic materials and participates in biological desulfurization. Since the aeration takes place inside the main reactor, the amount of dosed air/oxygen is the most influential parameter. The highest O_2 utilization efficiency could be achieved if the $O_2/H_2S_{supplied}$ and the $O_2/H_2S_{consumed}$ ratios increase simultaneously. Under microaeration conditions, desulfurization process mostly occur at the headspace (or on the gas–liquid interphase). The amount of air needed per given amount of hydrogen sulfide will be minimized if the injection point is the headspace. This decreased aeration also prevents the contamination of biogas by nitrogen.

When comparing two systems, biotrickling filters can reliably reach lower H_2S concentrations than microaeration if low H_2S concentrations in biogas are required. Biotrickling filters are precisely designed to remove H_2S while enough headspace is not usually provided for microaeration. This generally results in acceptable REs by using biotrickling filters leading to very low H_2S concentrations while the biogas obtained using microaeration requires some additional ”polishing”. From the economic point of view, the cost associated with aerobic and anoxic BTF has been estimated at 0.013 to 0.016 € m^{-3} of biogas treated, while the cost of microaeration stands at 0.0037 and 0.0026 € m^{-3} of biogas treated, when air and pure oxygen was dosed into the reactors, respectively. This shows that microaeration offers lower cost for desulfurization purposes.

Future works on microaerobic desulfurization may probably shift towards microaeration process control where there is not still a global agreement on control parameters. Additionally, optimizing the design of the headspaces is a field of study for microaeration. Currently, the process takes advantage of headspaces to desulfurize and adjust the relevant parameters discussed to maximize RE. However, inconsistent results could also be found in the published literature because headspaces were not specifically designed for these purposes.

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