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H_2S removal from biogas using bioreactors: a review

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Abstract
This review aims to provide an overview of the bioprocesses used for the removal of H_2S from biogas. The ability of aerobic and anoxic bioreactors (biotrickling filters, bioscrubbers, and a combination of chemical scrubbers and bioreactors) to perform the degradation of H_2S is considered. For each operating mode (aerobic and anoxic), the bioprocesses are presented, the operating conditions affecting performance are summarized, the state of the art of research studies is described and commercial applications are given. At laboratory-scale, whatever their operating mode, biological processes are effective for biogas cleaning and provide the same performance. The clogging of the packed bed due to the deposit of elemental sulfur S^0 and biomass accumulation clearly represents the main drawback of bioprocesses. Although elimination capacities (EC) determined at laboratory-scale can be very high, EC should not be higher than 90 g m^{-3} h^{-1} at industrial-scale in order to limit clogging effects. For aerobic processes, the need to control the oxygen mass transfer accurately remains a key issue for their development at full-scale. As a result, the aerobic processes alone are probably not the most suitable bioprocesses for the treatment of biogas highly loaded with H_2S. For anaerobic bioprocesses using nitrate as an electron acceptor, the scale-up of the laboratory process to a full-size plant remains a challenge. However, the use of wastewater from treatment plants, which constitutes a cheap source of nitrates, represents an interesting opportunity for the development of innovative bioprocesses enabling the simultaneous removal of H_2S and nitrates.
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Keywords: Aerobic; Anoxic; Bioreactor; Biogas; Hydrogen sulfide.

1. Introduction

Biogas is a result of the anaerobic digestion of organic substances by a consortium of microorganisms through a series of metabolic stages (hydrolysis, acidogenesis, acetogenesis and methanogenesis). Biogas is a renewable energy consisting mainly of methane (CH_4) and carbon dioxide (CO_2) (Table 1). Other gases such as nitrogen (N_2), water vapor (H_2O), ammonia (NH_3), hydrogen sulfide (H_2S) and other sulfur compounds are also found. According to the production site considered (landfills, wastewater treatment plants WWTP, plants treating industrial or food waste), biogas may also contain siloxanes, halogenated hydrocarbons and volatile organic compounds (VOCs). In order to be used as a source of energy (biomethane) generating heat and electricity, biogas must be cleaned (H_2S and siloxane removal) and upgraded (CO_2 removal). H_2S in biogas usually ranges from 50 to 5,000 ppmv but can reach up to 20,000 ppmv (2% v/v) in some cases. It is a colorless, flammable, malodorous (rotten eggs) and toxic gas. The main issues due to the presence of high H_2S concentrations in biogas are (i) its corrosive action, which damages engines, and (ii) the production of sulfur oxides (SO_x) due to H_2S combustion, whose emissions

can be subject to regulations (moreover, SO_2 has a poisoning effect on fuel cell catalysts). As a result, H_2S concentration in biogas must be reduced to levels where damage of combustion processes and SO_x emissions are limited. Various techniques are available to clean biogas and recent reviews have provided a comprehensive survey of the physicochemical processes used [1, 2]. In the present paper, the objective is to review the biological techniques currently used to remove H_2S from biogas.

Table 1. Biogas composition [3]

	Organic waste	Sewage	Landfill
Methane CH_4 (% vol)	60 - 70	55 - 65	45 - 55
Carbon dioxide CO_2 (% vol)	30 - 40	35 - 45	30 - 40
Nitrogen N_2 (% vol)	< 1	< 1	5 - 15
Hydrogen sulfide H_2S (ppmv)	10 - 2,000	10 - 40	50 - 300

Bioreactors (biofilters, biotrickling filters and bioscrubbers), which operate at ambient temperature and at atmospheric pressure, have become common processes for H_2S treatment in air. Several references provide a comprehensive survey of these bioreactors for air treatment and give the advantages and limitations of each one [4-10]. Today, bioreactors are acknowledged as effective, economical and environmentally friendly processes [11], which can thus be adapted to treat H_2S in biogas.

Bioreactors are usually classified according to the state of the liquid phase (stationary or flowing) and of the microorganisms (immobilized or suspended). For air treatment, the principles of operation of the three main bioreactors (biofilters, biotrickling filters and bioscrubbers), generally similar but with some differences, can be summarized as follows.

Biofilters contain microorganisms immobilized in the form of a biofilm fixed on a packed bed composed of material such as peat, soil, compost, and synthetic substances, or combinations of these (Figure 1). Various microbial communities exist on natural materials, but biomass from activated sludge can be added or selected species can be inoculated. H_2S biofiltration requires the following mechanisms: (i) transfer of H_2S from the gas phase to the aqueous phase, (ii) diffusion to the biofilm, (iii) adsorption by the biofilm and the packing material, and (iv) biodegradation by the biofilm. In the presence of oxygen, the biodegradation converts H_2S to biomass, CO_2, H_2O, metabolic by-products, and S^0 and SO_4^{2-}. Each mechanism is extensively described in a specialized book [5]. Several parameters affect biofilter performance: temperature, moisture, pH, nutrients, oxygen levels, gas velocity (or Empty Bed Residence Time EBRT), and pressure drops. The influence of each of these parameters is described hereafter. The temperature of the packed bed is mainly governed by the difference in temperature between the inlet gas and the outdoor air, but the heat generated by the exothermic biological reactions must also be taken into account. The optimal bed temperature is around 35-37 °C but most biofilters operate at temperatures ranging from 20 to 45 °C [9]. The optimum moisture of the packed bed is around 40-60% [5, 11]. Excessive moisture (up to saturated medium) increases considerably the pressure drops and can lead to the formation of anaerobic zones, whereas significant drop removal efficiency is observed at low moisture levels. Concerning the pH conditions, the optimal value is between 6 and 8, but H_2S can also be oxidized at acidic pH. Carbon, energy and nutrients (nitrogen, potassium, phosphorous and trace elements) are required for microbial growth. For inorganic and synthetic materials, an extra nutrient supply is needed, whereas organic packing materials, such as compost, have the advantage of containing these nutrients. However, over the course of time, these nutrients are progressively depleted. In a long-term bioreactor operation, the increase in pressure drop due to excess biomass and bed compaction decreases the biofilter efficiency, which represents the major drawback of biofiltration. The large footprint required for biofiltration is also considered an issue for practical applications.

In biotrickling filters, a bed of inert packing materials is continuously sprayed by a liquid phase circulating from the bottom to the top of the column (Figure 2). The packing materials (random or structured) present specific surface areas ranging from 100 to 300 m^{-1} and up to 1,000 m^{-1} for polyurethane-based beds [4]. Biotrickling filters are usually inoculated with activated sludge from wastewater treatment plants but pure cultures can also be used in order to shorten the bacterial lag phase [12]. The biomass is fixed onto the packing material and the gas phase (G) and the liquid phase (L) can move either counter-currently or co-currently. The mode of operation has no significant influence on performance [8, 11]. A flowing liquid phase presents several advantages: temperature control, pH control (the highest removal efficiencies are reached for pH close to neutral), substrate and oxygen transport

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from the gas phase to the biofilm, nutrient addition, and removal of accumulated metabolites generated by biodegradation. It is usually reported that the liquid flow rate has no influence on the removal efficiency [12-14] although a significant influence at high gas velocity has been described [13]. The major drawback of these bioreactors is the accumulation of excess biomass in the packing material, which causes clogging and increases the pressure drops [15]. The most efficient technique to solve this problem is washing the packed bed with water [8].

Bioscrubbers involve a two-stage process (Figure 3). The pollutant is first transferred from the gas phase to the liquid phase by absorption in a packed column filled with inert material. In most applications, the gaseous and the aqueous phases move counter-currently. Once solubilized, the pollutant is oxidized in a biological reactor containing the appropriate microbial strains and nutrients. The packing materials filling the column must be selected to enhance the mass transfer between the gas and the liquid. However, as for the biotrickling filters, the packed bed has to be cleaned frequently in order to avoid clogging.

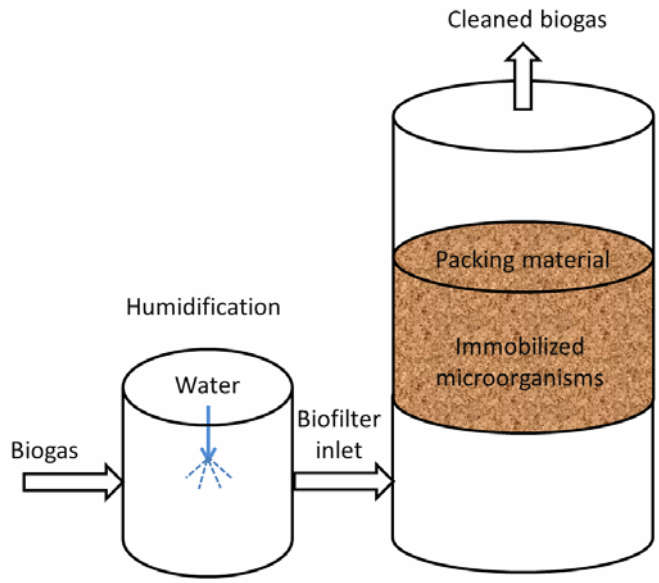

Figure 1. Schematic representation of a biofilter

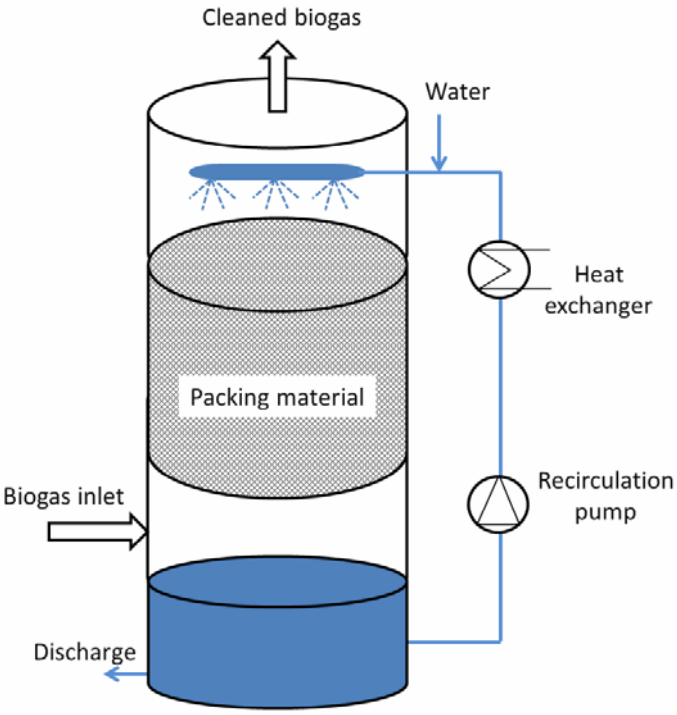

Figure 2. Schematic diagram of the DMT biotrickling filter

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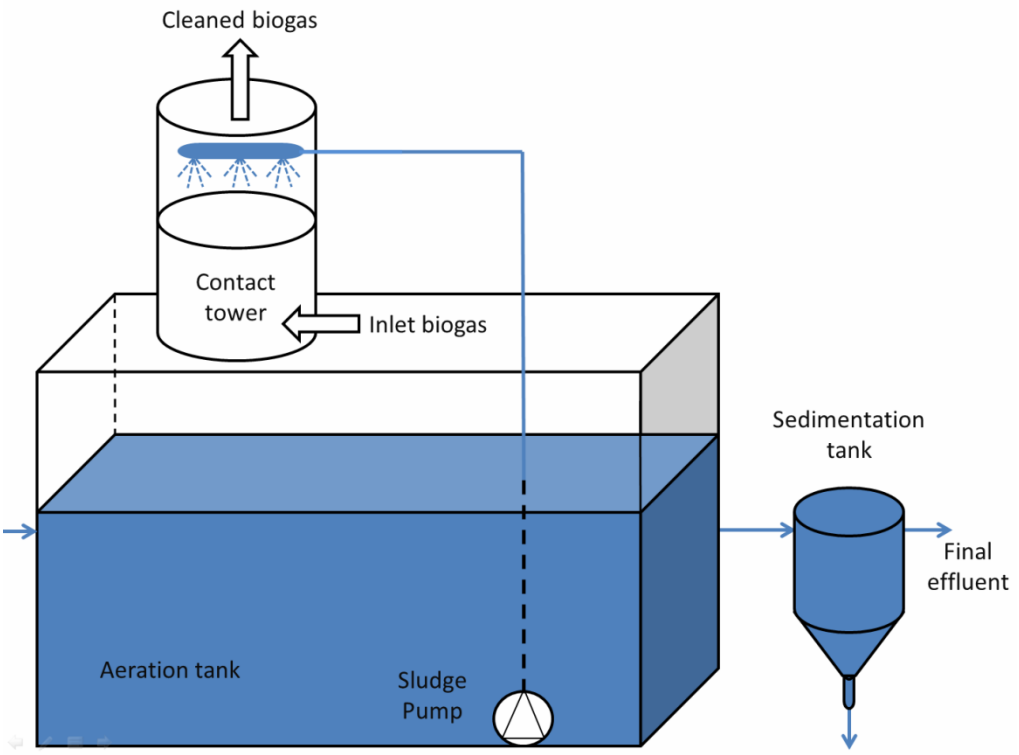

Figure 3. Schematic diagram of a biological sulfur removal process [16]

The operational parameters generally used to compare bioreactor performance are the Loading Rate (LR = (Q/V) C_{in}; g m^{-3} h^{-1}), the Elimination Capacity (EC = (Q/V) (C_{in} - C_{out}); g m^{-3} h^{-1}), the Removal Efficiency (RE = 100 (C_{in} - C_{out})/C_{in}; %) and the Empty Bed Residence Time (EBRT = V/Q; s^{-1} or min^{-1}). Q is the gas flow rate (m^3 h^{-1}), V is the packed bed volume (m^3), and C_{in} and C_{out} are the inlet and outlet pollutant concentrations, respectively (g m^{-3}). The performances of bioprocesses are characterized by the curve given in Figure 4. At low loading rates, bioreactors can reach 100% removal efficiency, whereas at high loading rates, the removal efficiency decreases because either H_2S molecules do not have time to diffuse inside the biofilm, or the biofilm cannot fully degrade the pollutant. At higher loading rates, the elimination capacity tends towards a plateau corresponding to the maximum elimination capacity (EC_{max}). The critical EC value and the EC_{max} value depend on the EBRT value. For a given bioreactor, a significant decrease in the EBRT (due to an increased gas flow rate) reduces the critical removal capacity.

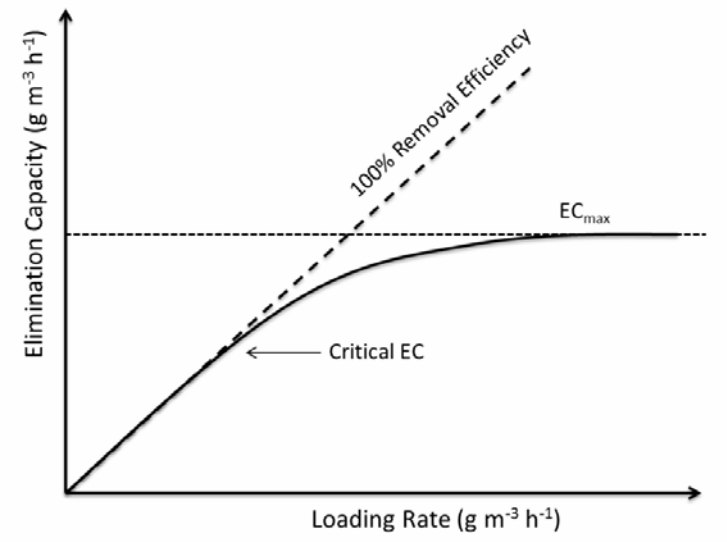

Figure 4. Typical curve describing bioprocess performance

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In air treatment, bioreactor operation is based on the natural presence of oxygen, which is necessary for degradation of the pollutant (oxygen acts as an electron acceptor). In biogas treatment, aerobic H_2S degradation requires a small addition of air, which represents a clear drawback for the following reasons. Firstly, there is a safety problem due to potentially explosive oxygen/methane mixtures during uncontrolled air addition (the lower and upper explosive limits for methane in air are 5% and 15%, respectively). Secondly, air addition leads to biogas dilution due to the presence of nitrogen in air. This second point can nonetheless be avoided by the addition of pure oxygen. Although air addition represents a major issue for biogas treatment, many studies have been carried out in aerobic conditions and innovative processes have been developed. Biodegradation of H_2S in biogas by bacteria can also occur in bioreactors under anoxic conditions [17-21], with alternative electron acceptors such as nitrates (NO_3^-). Such conditions solve the problem due to air addition and thus new studies carried out under anoxic conditions are in progress. As a result, this paper is in two main parts. The first is devoted to H_2S treatment under aerobic conditions, while the second considers the treatment under anoxic conditions. For each part, the bioprocesses are presented, the operating conditions affecting performance are summarized, the state of the art of research studies is described and commercial applications are given.

2. Aerobic processes

In such bioprocesses, H_2S must be transferred from the biogas to an aqueous phase where it is degraded by microorganisms. The performance for gas treatment can be either by mass transfer or kinetically controlled, but the determination of the rate-limiting step always remains a challenge. Once transferred from the gas phase to an aqueous phase, and in the presence of oxygen, H_2S is oxidized by the aerobic microorganisms [22]:

$$H_2S+0.5O_2 \rightarrow S^0+H_2O \quad (1)$$

$$H_2S+2O_2 \rightarrow SO_4^{2-}+2H^+ \quad (2)$$

Under oxygen-limiting conditions, H_2S oxidation leads to a deposit of elemental sulfur (S^0) which can be recovered. With excess amounts of oxygen, H_2S oxidation produces sulfuric acid (H_2SO_4) which contributes to acidifying the environment of the microorganisms. Various microbial communities are able to oxidize H_2S [19, 20, 23-25]. Sulfide oxidizing bacteria (SOB) encompass several genera such as *Xanthomonas*, *Thiobacillus*, *Acidithiobacillus*, *Achromatium*, *Beggiatoa*, *Thiothrix*, *Thioplaca*, and *Thermotrix* [26]. The most common H_2S-oxidizing bacteria are acidophilic, such as *Thiobacillus thiooxidans* [5]. The metabolism of species such as *Thiobacillus, Beggiatoa*, *Thiothrix*, and *Thermotrix* for H_2S oxidation has been extensively studied by Syed et al. [27]. These microorganisms can be obtained from either a selected and inoculated species [23] or activated sludge from wastewater treatment. In 1987, Sublette and Sylvester through a series of publications demonstrated that *Thiobacillus denitrificans* could be readily cultured aerobically (and anaerobically) in batch or continuous reactors for the microbial degradation of H_2S from gases [19-21]. As a result, a preliminary design was completed for the treatment of a biogas from an anaerobic digester treating municipal sewage waste [17]. The bioreactor consisted of a bubble column receiving a gas feed of biogas (60% CH_4, 1,500 ppmv H_2S) plus compressed air (21% O_2). Although the composition of the treated gas at the outlet of the bubble column was 33.6% CH_4, 9.3% O_2, 22.4% CO_2 and 34.7% N_2, this first case study highlighted the feasibility of using a microbial system for the removal of H_2S from biogas.

Before presenting both laboratory and full-scale aerobic bioreactors used for H_2S removal from biogas, it should be highlighted that preventive treatments are available, such as the addition of air to the digester. Thus, the majority of on-farm anaerobic digesters include a system to maintain 4 to 6% air in the bioreactor headspace [1]. Air addition allows the development of aerobic *thiobacteria*, which oxidize H_2S into elemental sulfur and, as a result, S^0 deposits are found all over the headspace of the digester [28]. This efficient method is usually used for biogas containing high H_2S concentrations. The use of both biogas production and H_2S concentration as parameters to regulate the oxygen supply needed for biomass development is currently under study [29].

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2.1 Biotrickling filters

2.1.1 Results from laboratory-scale and pilot-scale biotrickling filters

Aerobic H_2S degradation requires a small addition of air, which represents a clear drawback. As indicated earlier, there is a safety problem due to explosive oxygen methane mixtures in case of uncontrolled air addition, and air addition leads to a biogas dilution due to the presence of nitrogen. High dilutions of biogas with air have been tested in biofilters filled with lava rock [30] and coconut fibers [31], but such methane dilutions cannot be considered for industrial applications. As a result, biotrickling filters are the main bioprocess used for aerobic treatment (Figure 2) because air addition can be controlled. For practical applications, the air supply has to be adjusted by a controller to maintain the oxygen concentration in the gas below 3%.

Using laboratory-scale biotrickling filters (Table 2), the biological treatment of H_2S has been successfully tested for H_2S concentrations up to 12,000 ppmv [32]. It should be noted that a biogas mimic (N_2 replacing CH_4) is usually used in laboratory-scale experiments for safety reasons. Moreover, methane is only sparingly soluble in water and not well degraded in biotrickling filters. As can be observed in Table 2, high EBRT values are needed. This is mainly due to the high H_2S concentrations that require an elevated contact time between H_2S and the biofilm [33]. Thus, the removal efficiency is increased from 85.6 to 94.7% when EBRT increases from 78 to 313 s [31]. Similarly, Fortuny et al. [34] have shown that an EBRT decrease from 180 to 120 s has no influence on performance (RE remains constant at 97.7% on average) whereas a decrease to under 120 s leads to a significant drop in performance (RE = 39.7% at EBRT = 30 s). According to Table 2, biogas treatment is usually studied at an EBRT of around 3 min, which is in agreement with the value given by mathematical modeling [33]. Using multiple regression analysis, Charnnock et al. [33] calculated that the highest H_2S removal is 94.7% at EBRT = 180 s. Nevertheless, this value is higher than the critical EBRT proposed by Montebello et al. for a biotrickling filter treating a synthetic biogas loaded with 2,000 ppmv of H_2S (around 55 s and 75 s for [35, 36], respectively), and by de Arespacochaga et al. [37] for a biotrickling filter treating a biogas from a WWTP (around 80 s for an H_2S concentration ranging from 2,200 to 4,350 ppmv).

Table 2. Results from laboratory-scale aerobic biotrickling filters

Gas composition	Packing material	Inlet H_2S concentration ppmv	pH	EBRT (s)	Elimination Capacity ($g\ m^{-3}\ h^{-1}$)	RE (%)	Ref.
N_2 (65%) + CO_2 (35%) H_2S (traces)	Glass Raschig rings	1,000	7	69	32.5	99	[46]
Mimic of biogas ($N_2 + CO_2 + H_2S$)	Polyurethane foam	2,500 - 12,300		167	250	84	[32]
Mimic of biogas ($N_2 + CO_2 + H_2S$)	HS Q-PAC®	900 - 10,000		180	200	84	[32]
Biogas(*) CH_4: 69% CO_2: 29% N_2: 1%	Polypropylene Pall rings	3,000	1 - 5	180	170	90	[48]
Mimic of biogas ($N_2 + H_2S$)	HD Q-PAC®	2,000 - 8,000	6.0 - 6.5	180	50 150	100 92	[60]
N_2 + Air + H_2S	HD Q-PAC®	2,000	6.0 - 6.5	120	84	97.7	[34]
Synthetic biogas ($N_2 + H_2S$ + MT)	Metallic Pall rings	2,000	6.0 - 6.5	180	100	99	[55]
Synthetic biogas	Stainless steel Pall rings	2,000	6.0 - 6.5	29 - 131	100	100	[35]
Biogas(**)	1:8 mixture plastic rings: coconut fibers	6,395 ± 2,309	0.5 - 4	100 - 180	150.3	97.3	[33]
Synthetic biogas ($N_2 + H_2S$)	Metallic Pall rings	2,000	2.50 - 2.75	75	100	95	[36]
Biogas(*)	HD Q-PAC®	2,200 - 4,350	1.5 - 2	80 - 85	169	84	[37]

(*): biogas from the anaerobic digester of a wastewater treatment plant

(**): biogas from the full-scale anaerobic digester in a concentrated rubber latex factory

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2.1.2 Sulfur management: O_2 and H_2S mass transfer

In biotrickling filters, the deposits of elemental sulfur S^0 (Eq 1) lead to the clogging of the packing material, which limits the operation of the bioreactor. As the final product of H_2S oxidation can be either S^0 or SO_4^{2-} according to the O_2/H_2S ratio (Eqs 1-2), the oxygen mass transfer from gas to water represents a major parameter of this technology [38]. From experimental results and a mathematical model, Roosta et al. [39] have shown that S^0 and SO_4^{2-} selectivity is sensitive to the concentration of dissolved oxygen. Moreover, from a sulfur mass balance analysis, de Arespacochaga et al. [37] have shown that the $SO_4^{2-}{}_{produced}/H_2S_{removed}$ ratio is 29 - 33% (i.e. 67 - 71% of H_2S is removed as S^0) even for an O_2/H_2S ratio of around 7. According to these authors, the O_2/H_2S ratio that must be taken into account is that of the biofilm, which depends on the Henry constants of O_2 and H_2S, respectively. They have calculated that the actual O_2/H_2S ratio in the biofilm is below 0.5, which corresponds to a stoichiometric ratio for partial oxidation (Eq 1). Thus, an insufficient O_2 supply can lead to treatment limitation, and there is a need to control the oxygen mass transfer accurately. Obviously, mass transfer in biotrickling filters could be improved by determining the optimal hydrodynamic conditions. Unfortunately, traditional correlations used in conventional chemical gas/liquid systems fail to characterize the mass transfer in biotrickling filters. Two main points have to be noted: (i) the mass transfer coefficients experimentally determined are markedly lower than that usually observed for conventional wet scrubbing [40, 41]; (ii) the mass transfer coefficients cannot be successfully correlated to the characteristics of the packing materials [40-42]. Although relationships between mass transfer coefficients and the gas and liquid velocities have been established, it appears that these empirical expressions are based on constants dependent on the packing materials. Nonetheless, these expressions are useful to select those packing materials that improve the mass transfer and limit pressure drops. However, even if an increase in the oxygen mass transfer could be reached, it must be pointed out that an increase in H_2S mass transfer would be concomitantly observed. As a result, given that biotrickling filter performance is mainly affected by the deposit of elemental sulfur S^0, the key parameter that has to be taken into account is the O_2/H_2S ratio, whatever the hydrodynamic conditions. This ratio depends on the physical properties of H_2S and O_2, mainly their solubility. H_2S is much more soluble in water than O_2 (4000 mg L^{-1} vs. 9.1 mg L^{-1} at 293 K, respectively) in relation to the values of their Henry's law constant ($H = C^G/C^L = 0.36$ for H_2S and 32.0 for O_2 at 293 K). Moreover, it should be noted that their diffusion coefficients are of the same order of magnitude (1.93 10^{-9} m^2 s^{-1} for H_2S [43]; 2.4 10^{-9} m^2 s^{-1} for oxygen [44]) indicating that H_2S and O_2 diffuse in the same manner near the aqueous/biomass interface or inside the biofilm. As a result, for the best conditions of oxygenation (corresponding to an oxygen concentration in the biogas limited to 3%), it can be calculated that the O_2/H_2S ratio is not favorable for complete sulfur oxidation (Eq 2) for H_2S concentrations higher than 1,300 ppmv. In other words, the limitation of the oxygen concentration in the biogas leads preferentially to the formation of elemental sulfur (S^0). Such oxygen limitation clearly represents the bottleneck of biogas treatment using aerobic biotrickling filters. Nonetheless, studies were carried out in order to try to improve the oxygen control by a direct injection of air into the recycling liquid. At industrial-scale, the conventional oxygen supply system based on direct injection of air in the liquid phase has been demonstrated ineffective, but the implementation of a jet-venturi device for oxygen supply could be a promising option [45]. However, the low oxygen mass transfer efficiencies of such systems can cause significant dilution of biogas at the outlet of the biotrickling filter [37]. To solve this problem, an alternative system, called the Profactor system, has been designed (Figure 5) [46]. The oxygen enrichment of the liquid used for H_2S treatment is carried out in a bubble column installed near the biotrickling filter. Thus, the biogas remains totally free of oxygen. The system can decrease the H_2S concentration from 1,000 ppmv to less than 3 ppmv (RE > 99%; EC = 32.5 g m^{-3} h^{-1}; Table 2). At higher H_2S inlet concentrations (2,000 ppmv), the outlet concentration ranges from 34 to 75 ppmv (RE = 93%; EC = 55 g m^{-3} h^{-1}). Unfortunately, the need to dissolve oxygen efficiently in water requires the addition of a second column, which represents a major drawback of the process.

2.1.3 Microbial diversity

The bacterial analysis of the biomass in biotrickling filters has been carried out at neutral pH and for acidic conditions. Maestre et al. [47] have investigated the bacterial composition of a laboratory-scale biotrickling filter treating a biogas mimic at neutral pH (N_2 + 2,000 ppmv H_2S). According to these authors, a major shift in the diversity of the community is observed with time. At start-up, a very diverse community exists while at steady state, a majority of sulfide oxidizing bacteria (SOB), including

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Thiothrix, *Thiobacillus* and *Sulfurimonas denitrificans*, predominates. Analyzing the bacteria of a biofilter treating biogas from a full-scale digester in a concentrated rubber latex factory containing H_2S at high concentrations (6,395 ± 2,309 ppmv) under acidic conditions (pH from 4 to 0.5), Charnnok et al. [33] have shown that SOB *Acidithiobacillus* is the major microorganism group. As a result, the pH transition, from neutral to acid, significantly reduces the microbial diversity. Nonetheless, the specialization of the SOB community has no negative effect on the removal capacity [35]. The same analysis has been carried out by de Arespacochaga et al. [37] who specified that the optimum temperature for aerobic H_2S removal in extremely acidic conditions by *Acidithiobacillus* is around 30 °C. Further research, involving the isolation of pure cultures and their metabolic characterization, needs to be carried out in order to fill the current gaps in our knowledge about the relationships between phylogeny, function and environmental conditions inside biotrickling filters [47].

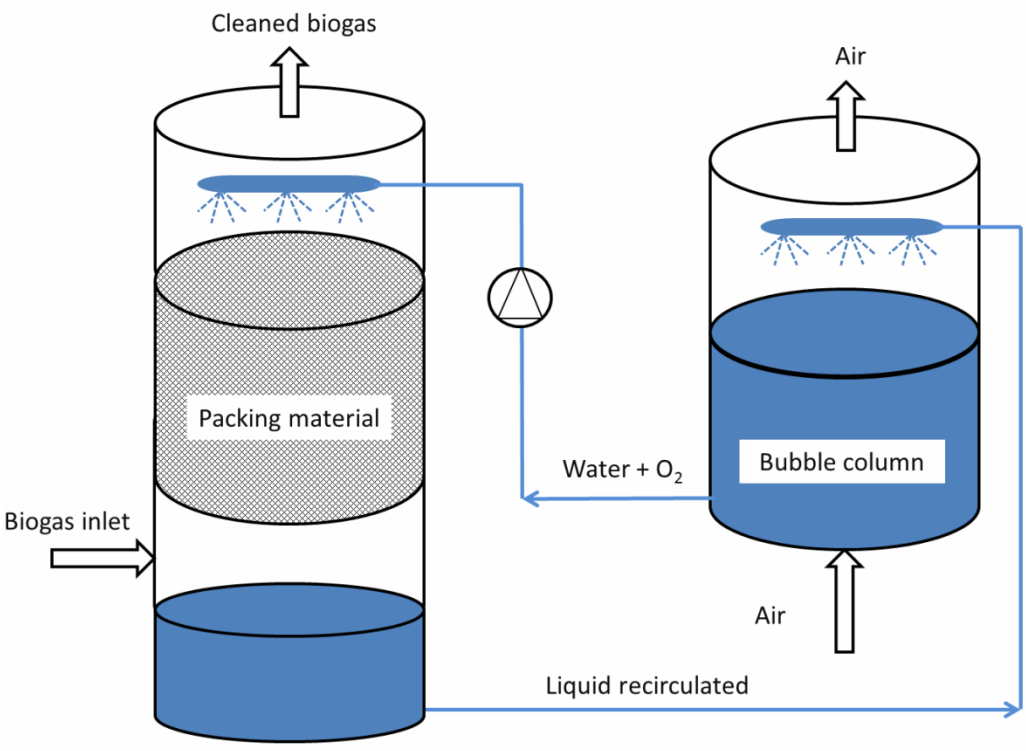

Figure 5. Schematic diagram of the Profactor system

2.1.4 Economic aspects

An economic study, based on a full-scale biotrickling filter treating the biogas from a municipal wastewater treatment plant, has shown that the cost of one kg of H_2S removed is 3.2 € against 5.8 € for a chemical alternative [48]. Tomas et al. [48] have calculated that the cost of one m^3 of biogas treated is 0.013 € against 0.024 € for a chemical alternative, which demonstrates the economic viability of biotrickling filters for biogas treatment [38].

Another economic analysis has been carried out to calculate the cost of H_2S removal based on operational data obtained from experimental pilot plant trials [49]. Three cases have been compared: (i) raw biogas directly treated by a "polishing system" based on adsorption, including a regenerable iron-based adsorbent, a biogas drying unit and an activated carbon unit; (ii) raw biogas first treated by a biotrickling filter down to H_2S concentrations of 650 ppmv before the "polishing system"; (iii) raw biogas first treated by a biotrickling filter down to H_2S concentrations of 200 ppmv before the "polishing system". The different systems were operated to achieve a biogas quality required for a Solid Oxide Fuel Cell (SOFC) i.e. 0.1 – 0.5 ppmv at the anode. The costs, including both capital and operational expenses, were 9.6, 4.8 and 3.7 € Nm^{-3} for the three cases, respectively. This result highlights that the use of a low-cost desulfurization technology, such as aerobic biotrickling filters before an adsorption system, reduces the overall treatment cost by a factor of 3 [37].

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2.1.5 Simultaneous removal of other compounds in biogas

As indicated earlier, apart from the main pollutant H_2S, biogas can contain siloxanes and other reduced sulfur compounds such as methanethiol (MT), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS). Studies devoted to the simultaneous removal of reduced sulfur compounds in biogas using bioprocesses are very scarce. Based on the literature data concerning air treatment, it can be concluded that the pH of the aqueous phase has a great impact on the abatement of other reduced sulfur compounds like MT, DMS and DMDS [50, 51]. Whereas the abatement of H_2S is complete, whatever the pH level from 7 to 1, the total elimination of other reduced sulfur compounds requires a pH level close to neutrality. Moreover, the literature based on air treatment highlights that H_2S and MT have a negative effect on DMS and DMDS removal, whereas DMS and DMDS do not affect the removal of H_2S and MT [43]. The order of degradation is H_2S > MT > DMDS > DMS [52-54]. Regarding biogas treatment, a recent study compared the efficiencies of aerobic and anoxic biotrickling filters treating a mixture of H_2S and MT at neutral pH [55]. These authors reported a negative influence on the elimination capacity of MT by a high H_2S loading rate. Competition for the dissolved oxygen could explain this result [56]. However, the presence of MT could also have a beneficial effect on the performance of the bioreactors due to the chemical reaction with S^0. Nevertheless, even if the effect of H_2S on the biological oxidation of other reduced sulfur compounds should be investigated from an academic point of view, it has to be kept in mind that (i) the concentrations of MT, DMS and DMDS are relatively low in comparison with the concentration of H_2S; (ii) maintaining a pH close to neutrality requires a large amount of costly chemical reactants, which is difficult to justify for the treatment of secondary and minority pollutants. As a result, if priorities need to be set, efforts should focus rather on the search for the relevant conditions to treat H_2S over a long period.

Conversely, the presence of siloxanes has to be taken into account due to their adverse effect on the use on biogas (abrasion of engine parts). Recent studies have investigated the feasibility of using aerobic and anoxic biotrickling filters for the removal of siloxanes [57-59]. However, removal efficiencies are limited even at EBRT higher than those used for H_2S treatment (i.e. > 3 min). The low solubility of these compounds has been put forward to explain these unconvincing results. In conclusion, although the degradation of siloxanes is biologically possible, it seems that bioprocesses are not a relevant choice for their treatment. Overall, the simultaneous removal of H_2S and siloxanes in the same biotrickling filter does not appear technically feasible.

2.1.6 Conclusion

To sum up, from the literature data, it can be concluded that the feasibility of using aerobic biotrickling filters for the removal of H_2S from biogas has been technically demonstrated at laboratory and pilot scales. Moreover, economic studies have highlighted that biotrickling filters could be an interesting solution to limit the treatment cost. Nonetheless, the need to control the oxygen mass transfer accurately remains a key issue for the development of aerobic processes at full-scale. Even if the biotrickling filters could be technically improved, while remaining economically viable, the need to limit the concentration of oxygen in the biogas means that such bioprocesses are probably not the most suitable technology for the treatment of biogas highly loaded with H_2S.

2.2 Other bioprocesses

Based on our current knowledge, there are few references in the literature describing other aerobic bioprocesses for biogas cleaning.

2.2.1 Full-scale bioscrubber

A conventional full-scale bioscrubber has been tested to treat biogas (40 m^3 h^{-1}) produced from potato processing wastewater [16]. In order to transfer H_2S from the gas phase to the liquid phase, the biogas is introduced into a tray column (3 m^3) in which it is contacted with activated sludge liquor from an aeration tank (550 m^3; Figure 3). The sludge liquor is then returned to the aeration tank where H_2S is oxidized by sulfur-oxidizing bacteria. Using this configuration for a biogas loaded with 2,000 ppmv of H_2S, the removal efficiency is more than 99%. After six months of continuous operation, the authors indicated that there was no corrosion or clogging problems in the contact tower. Despite this success, it seems that such a full-scale bioscrubber was not applied to other industries.

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2.2.2 Two-phase bioreactor

A two-phase bioreactor has also been investigated in order to avoid biogas dilution with air (Figure 6). This system includes an anaerobic absorption column treating biogas, an aerobic biofilter treating air, and a liquid recirculation system between both columns [61]. The two columns are packed with polyurethane foam inoculated with *A. thiooxidans*. The dissolved oxygen concentrations are maintained at 2 and 8 mg L^{-1} in the anaerobic column and biofilter, respectively. H_2S is degraded in both columns and the overall removal efficiency is around 97% for H_2S concentrations up to 400 ppmv. Although this process is not sufficiently described in [61] to understand the H_2S degradation occurring in both columns (no nitrate addition in the anaerobic column treating biogas, contrary to the conventional anoxic processes described in part 3), it could be an attractive alternative to conventional biotrickling filters. However, further studies are needed to test the efficiency of this two-phase bioreactor under severe operating conditions.

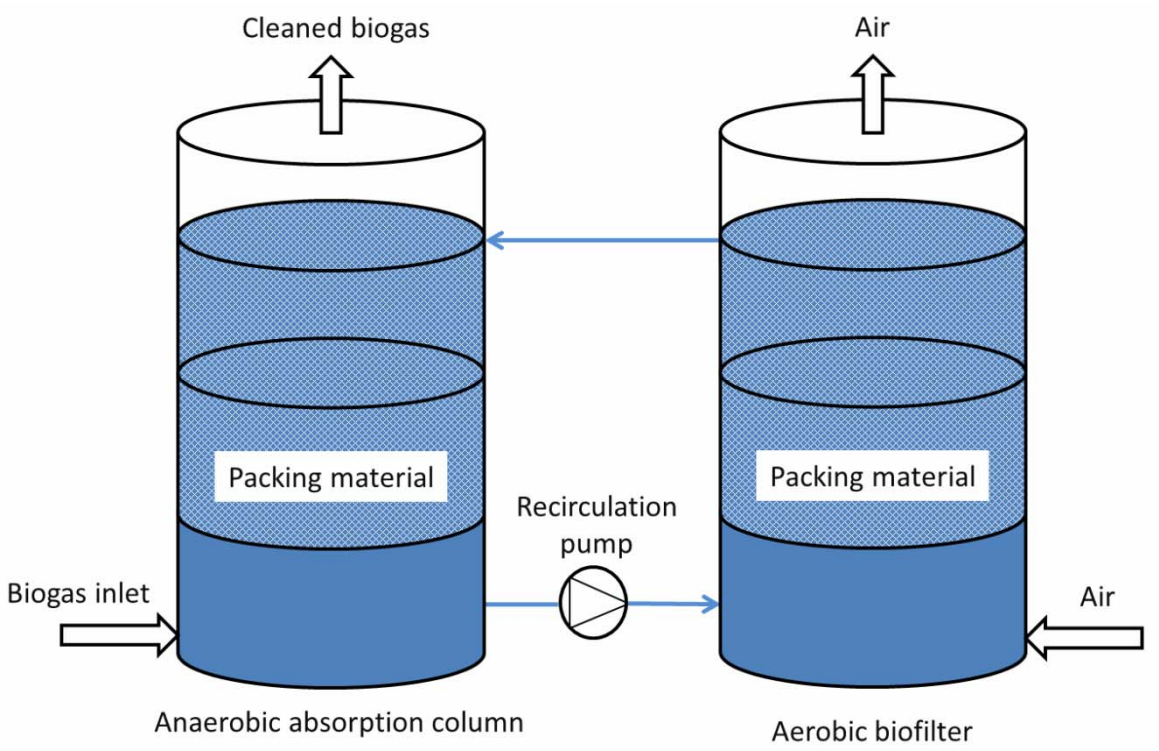

Figure 6. Schematic diagram of the two-phase bioreactor

2.2.3 Combined chemical and biological processes

A combined system using an Fe^{3+} solution reacting with H_2S can be used [62-65] (Figure 7). In the first stage, H_2S is converted into elemental sulfur according to the reaction:

$$H_2S+2Fe^{3+}+2OH^- \rightarrow S^0+2Fe^{2+}+2H_2O \quad (3)$$

In the second stage, the liquid is regenerated. The elemental sulfur is removed and the Fe^{2+} produced is then biologically oxidized using *Thiobacillus ferrooxidans*:

$$2Fe^{2+}+H_2O+0.5O_2 \rightarrow 2Fe^{3+}+2OH^- \quad (4)$$

This process was first studied with the name of BIO-SR [65] and it is close to the commercial SulFerox® process (a Shell Iron Redox process), in which Fe^{2+} is converted to Fe^{3+} by oxidation with air. According to Pagella et al. [64], the optimum pH for the growth of *T. ferrooxidans* is around 2.2. At these low pH values, the ferric ion precipitation is avoided. Owing to the two stages (chemical and biological), the process can treat aerobic or anaerobic gases loaded with high H_2S concentrations. Moreover, the iron ions are continuously recycled in the system. From experiments carried out at pilot-scale at EBRT = 120

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s, Ho et al. [66] have shown that this combined system can efficiently treat biogas with H_2S inlet concentrations ranging from 890 to 2,250 ppmv (RE = 96%). A removal capacity of 62 g m^{-3} h^{-1} is obtained for Fe^{2+} and Fe^{3+} concentrations fixed at 10 g L^{-1}. Similar results have been reported by Lin et al. [67] for the treatment of biogas from a swine farm digester (average H_2S concentration: 3,452 ppmv). A removal efficiency of 95% was achieved at EBRT = 288 s. Although this attractive process has been studied at laboratory-scale for various reactor configurations [68], it seems that it has failed to develop at a large scale. The conversion of a laboratory- or pilot-scale process to a full-size operation thus remains a challenge.

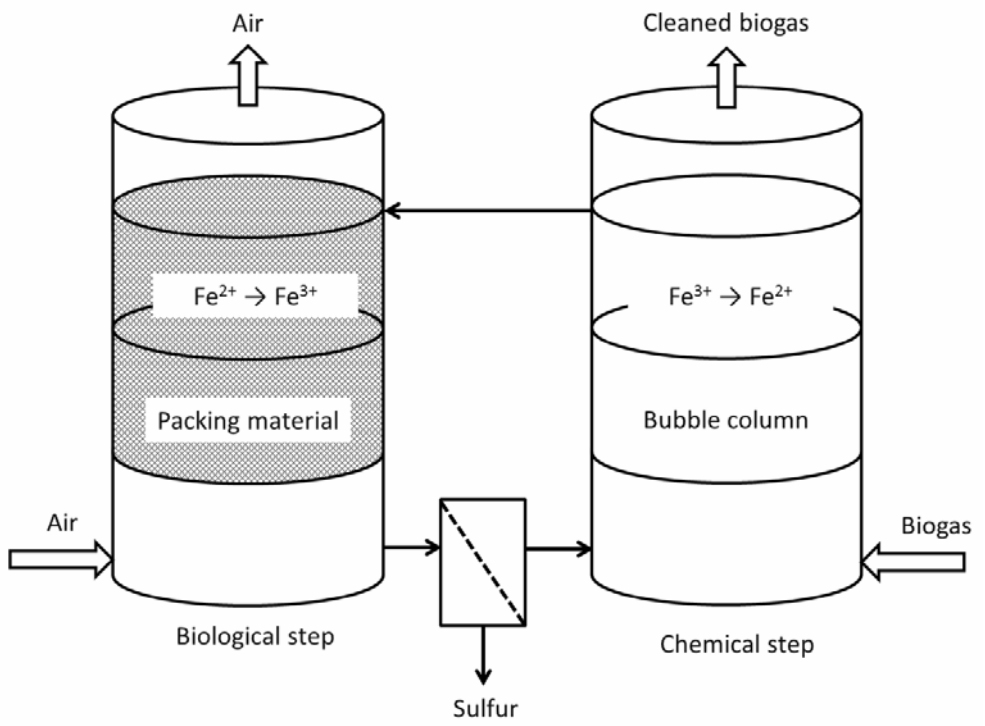

Figure 7. Schematic diagram of the iron bioprocess

2.3 Commercial bioprocesses

The traditional chemical H_2S removal processes are very expensive because of high chemical and energy requirements, and thus economic costs. As a result, biological treatment methods have been developed and commercial processes are available. Nonetheless, most of them combine a chemical step, in which H_2S is contacted with a reacting liquid to give another dissolved sulfide-containing component, with a biological step.

The THIOPAQ® technology, developed in the Netherlands by Paques BioSystems, is designed to remove H_2S from biogas efficiently. The first commercial unit was built in 1993 in the Netherlands [22]. The system (http://en.paques.nl/products/featured/thiopaq) leads to the production of elemental sulfur. A variation of this technology is the Shell-Paques® system, which includes system components that can process natural gas under pressure. Most applications are used for the treatment of biogas originating from anaerobic wastewater treatment facilities and landfill sites (around 80 installations worldwide; [69] but full-scale plants are also used for natural gas cleaning. This process combines a chemical and a biological step. H_2S is first removed in a chemical scrubber by absorption into a sodium carbonate/bicarbonate solution (pH 8.0 – 8.5). Then, the scrubbing liquid containing the sulfide produced is biologically converted into elemental sulfur in the bioreactor. H_2S in the treated gas is guaranteed to be below 4 ppmv. This process claims to be suitable for a flow ranging from 200 to 2,500 Nm^3 h^{-1} with an H_2S removal efficiency of up to 100% [1]. However, Gonzalez-Sanchez et al. [70] highlight that the sodium carbonate/bicarbonate solution can precipitate at high CO_2 partial pressure, which represents a drawback of the system.

Similarly, the BIOPURIC™ process (Veolia Company) involves a chemical scrubber combined with a biotrickling filter. Sulfur oxidizing microorganisms metabolize the H_2S into elemental sulfur S^0 and

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sulfuric acid H_2S0_4. It is claimed that this technology can remove 90-98% of the H_2S contained in biogas with H_2S concentrations ranging from 1,000 ppmv to 15,000 ppmv.
Biogas can also be cleaned using the DMT-BioSulfurex® process [71]. H_2S is converted into H_2S0_4 and S^0 in an aerobic biotrickling filter at a pH range from 0.5 to 2. Elimination capacities ranging from 40 to 90 g m^{-3} h^{-1} are obtained in full-scale installations with Pall rings as packing material. According to Van der Kloet et al. [72], elimination capacities should not be higher than 90 g m^{-3} h^{-1} in order to prevent clogging due to elemental sulfur deposits. This value, which can be considered a technical limit in industrial conditions, is significantly lower than those obtained in laboratory-scale experiments of up to 250 g m^{-3} h^{-1} [32]. According to Vollenbroek et al. [73], for an H_2S concentration of around 2,000 ppmv, the oxygen concentration must be kept between 2 and 3%. In such conditions, H_2S is converted into sulfuric acid (80%) and elemental sulfur (20%). Although these percentages may be questioned (see section 2.1.2), this 20% of S^0 produced is sufficient to promote the formation of a deposit of hard material that can clog the bottom of the biotrickling filter. Once the packing material is clogged, the removal of the accumulated mixture of S^0 and biomass is difficult [72]. Mechanical and chemical cleaning methods have been tested, the best of which are based on water and air cleaning since these do not harm the biological activity [73]. Currently, preventive cleaning intervals have to be chosen. Nevertheless, efforts are being made to develop new structured packing materials to avoid the accumulation of S^0 deposits and biomass at the bottom of the column. To the best of our knowledge, the DMT-BioSulfurex® is the only process that removes H_2S from biogas without addition of chemical products (except nutrients). However, in order to overcome the clogging problem, a chemical scrubbing step using NaOH can be included in the biotrickling filter. As a result, this system (called BioSulfurex®HSC) requires a minimum amount of chemical products to limit the accumulation of S^0 deposits [71].

2.4 Conclusion

The information available about H_2S removal from biogas using aerobic bioprocesses has been reviewed critically. In comparison with conventional chemical technologies, aerobic bioprocesses are expected to lead to substantial savings in energy and chemical products. However, the biological processes used alone (without any chemical steps) have yet to demonstrate that they are technically and commercially viable. The efficiency of bioprocesses is determined by the biogas flow rate and the amount of H_2S to be removed. Bioprocesses could be competitive for low flow rates loaded with low and medium H_2S concentrations but for the removal of large amounts of H_2S, chemical processes (or a combination of chemical scrubber and bioreactor) have to be preferred. The main drawback of aerobic bioprocesses is the limitation of the concentration of oxygen in the biogas (for safety reasons and in order to avoid biogas dilution). As a result, the need to limit this oxygen concentration leads mainly to the formation of elemental sulfur, which is the bottleneck of aerobic bioprocesses. In other words, these processes are technically limited by the clogging due to S^0 deposits and do not seem the most relevant choice for the treatment of biogas highly loaded with H_2S.

3. Anoxic processes

Contrary to aerobic systems, the addition of air is unnecessary for anoxic systems, which has several advantages: (i) no safety problem because there is no formation of potentially explosive mixtures of CH_4/O_2; (ii) no biogas dilution with nitrogen; (iii) no gas liquid mass transfer limitation because oxygen is already dissolved in the liquid medium in nitrate form (NO_3^-). As a result, anoxic bioprocesses could be a suitable solution to overcome the drawbacks of aerobic bioprocesses. In recent years, advances in the field of biogas cleaning have stimulated the development of anoxic bioprocesses. Nonetheless, in the eighties, several investigations were conducted to evaluate the anaerobic removal of H_2S using microbial processes. For example, the use of photosynthetic bacteria to metabolize H_2S effectively was developed [24, 74, 75]. However, the main advantages of this process (simplicity, no need for aeration or chemical additives) were not sufficient to offset its disadvantages, mainly the radiant energy needed. Removal of H_2S using chemoautotrophic bacteria was also studied using dissolved oxygen [17, 76] or nitrates [19-21] as electron acceptors. At the time, and even though concerns linked to biogas dilution and the potential explosion of CH_4/O_2 mixtures were expressed, oxygen from air was considered more economical than nitrates. To date, studies devoted to anoxic processes are mainly based on the addition of nitrates rather than dissolved oxygen.

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3.1 Nitrate sources

Nitrates added to the liquid phase can come from different sources: calcium nitrate $Ca(NO_3)_2.4H_2O$, sodium nitrate $NaNO_3$ and potassium nitrate KNO_3. Addition of calcium nitrate has to be avoided because the calcium salts that can be formed by reaction with other components in the recirculating liquid have a low solubility (such as gypsum $CaSO_4 \cdot 2H_2O$), and can thus precipitate in the packed bed [77]. Sodium nitrate or potassium nitrate can be used, but the former is recommended because it is cheaper. Considering the high concentrations of H_2S and the biogas flow rates that must be treated, the amount of nitrate required can be very large. Nonetheless, in cases where biogas is produced by on-farm anaerobic digesters, the simultaneous biological removal of H_2S from biogas and nitrates from wastewater could be coupled [78, 79]. Although the denitrification process using nitrates or nitrites in wastewater as electron acceptors to remove H_2S is feasible [80], it has been paid little attention for biogas cleaning. To date, biogas desulfurization integrated with autotrophic denitrification is an interesting option since nitrates and nitrites are available in most wastewater treatment plants [81].

3.2 N/S ratio

Under anoxic conditions, various bacteria use nitrates as electron acceptors to oxidize H_2S. Sulfide degradation leads to the formation of sulfur, sulfate and nitrites (NO_2^-) or nitrogen (N_2) according to the following equations [79].

$$5H_2S+8NO_3^- \rightarrow 5SO_4^{2-}+4N_2+4H_2O+2H^+ \quad (5)$$

i.e. complete denitrification vs. complete H_2S oxidation (ratio N/S = 1.6)

$$5H_2S+2NO_3^- \rightarrow 5S^0+N_2+4H_2O+2OH^- \quad (6)$$

i.e. complete denitrification vs. partial H_2S oxidation(ratio N/S = 0.4)

$$H_2S+4NO_3^- \rightarrow SO_4^{2-}+4NO_2^-+2H^+ \quad (7)$$

i.e. partial denitrification vs. complete H_2S oxidation (ratio N/S = 4)

$$H_2S+NO_3^- \rightarrow S^0+NO_2^-+H_2O \quad (8)$$

i.e. partial denitrification vs. partial H_2S oxidation (ratio N/S = 1)

$$\text{Overall equation: } 15NO_3^-+12H_2S \rightarrow 9H_2O+6S^0+6SO_4^{2-}+5NO_2^-+5N_2+20H^-+4H^+ \quad (9)$$

Thiobacillus denitrificans and *Thiomicrospira denitrificans* can reduce nitrate to nitrogen for complete denitrification (Equations 5-6) whereas a few species such as *Thiobacillus thioparus* can reduce nitrates to nitrites (Equations 7-8). These sulfur bacteria grow at pH values ranging from 1 to 9 with an optimum around 7.5 [82] and in temperature conditions from 4 to 90 °C [83] with an optimum around 30 °C [77]. In order to avoid nitrite accumulation in the liquid phase and to improve biotrickling filter efficiency, a complete denitrification has to be reached. In this case, partial H_2S oxidation to elemental sulfur S^0 is achieved for an N/S stoichiometric ratio of 0.4 mol mol^{-1} (Equation 6) whereas complete H_2S oxidation to sulfate requires an N/S ratio of 1.6 mol mol^{-1} (Equation 5). As for aerobic biotrickling filters, the production of elemental sulfur S^0 has to be limited in order to avoid clogging effects. Moreover, the inhibitory effects due to the accumulation of sulfates and nitrites in the liquid phase have to be considered. As a result, the N/S ratio and the pH value are the main parameters that must be taken into account to control the performance of H_2S removal. The influence of the N/S ratio on the H_2S oxidation has been investigated in biotrickling filters [55, 77, 84, 85]. These studies demonstrated that it is possible to control the oxidation of H_2S by altering the N/S ratio. For instance, Soreanu et al. [79] and Montebello et al. [55] reported an elemental sulfur production of 25.1% at an N/S ratio of 1.52 mol mol^{-1} and 14% at an N/S ratio of 1.46 mol mol^{-1}, respectively. However, sulfate production due to a high N/S ratio can present disadvantages by decreasing the pH of the liquid phase. At acidic pH, the reduction of NO_3^- to N_2 can be affected due to the progressive inhibition of nitrous oxide reductase activity, which causes an accumulation of N_2O that is very toxic to denitrifying bacteria [86]. Moreover, N_2O is a major

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greenhouse gas and air pollutant whose production must be avoided. According to Thomsen et al. [86], a pH of 8.5 represents a favorable condition to convert NO_3^- to N_2 without the accumulation of N_2O. Since nitrates are reduced faster than nitrites [87], the latter can accumulate in the liquid phase (Equations 7-8). As the inhibitory effect due to the accumulation of nitrites has been confirmed [88], a controlled regime of nitrate addition can be carried out in order to avoid this problem. At steady state, Soreanu et al. [79] have experimentally determined that the nitrate consumption is 0.32 $mg_{N\text{-}NO3}$ $g^{-1}_{H2S\ removed}$. Consequently, levels of nitrates around 20 $mg_{N\text{-}NO3}$ L^{-1} should be sufficient to maintain the H_2S removal efficiency at its maximum value. In addition, Fernandez et al. [84] have highlighted that a nitrate consumption rate of 6 $mg_{N\text{-}NO3}$ L^{-1} h^{-1} allows a high biomass activity to be reached. When the nitrate source is limited, H_2S degradation mostly leads to the formation of sulfates, which accumulate to reach a constant concentration of approximately 2,500 mg L^{-1}, after which, elemental sulfur becomes the primary reaction product [85]. The accumulation of sulfates in the liquid phase could also reduce the removal efficiency of the bioreactor. Fernandez et al. [77] indicated that a sulfate concentration higher than 33 g L^{-1} must be avoided, but its actual influence on RE has to be investigated in order to confirm this value. When the nitrate source is not the limiting factor, the biogas flow rate and H_2S concentration are the most significant factors controlling the performance of the bioreactor [85]. As a result, it can be highlighted that the interactions between the denitrification process and sulfide oxidation are complex and there is a need to carry out experiments in order to determine the optimal conditions for H_2S removal. The main parameters to be taken into account for H_2S degradation in an anoxic biotrickling filter are: the biogas flow rate and the inlet H_2S concentration, the EBRT, the pH, the liquid flow rate (and the hydrodynamic conditions), the N/S ratio, and the concentrations of sulfates, nitrates and nitrites in the liquid phase. Although some experimental studies have been carried out to explore the performance of biotrickling filters for H_2S treatment (see below), it seems that a mathematical description of such bioreactors, accounting for the latest experimental findings reported in the literature, is required. A comprehensive description of the complex phenomena occurring in a biotrickling filter should be provided. Thus, model simulations and a sensitivity analysis would be useful to define the best experiments to carry out. It has to be noted that an attempt at empirical modeling was made by Soreanu et al. [89]. Using a mathematical analysis of the performance of a biotrickling filter, these authors indicated that the key factors controlling performance are the biogas flow rate and H_2S concentration. They concluded that the influence of H_2S concentration on removal efficiency is more significant and, as a result, biotrickling filters could be installed in series to treat biogas flows with elevated H_2S levels. Clearly, this modeling approach should be continued and improved.

3.3 Bioreactor performance

In anoxic conditions, the critical H_2S removal capacities of biotrickling filters reported in the literature (Table 3) are around 100 g m^{-3} h^{-1} at EBRT ranging from 144 to 240 s [55, 77, 84]. Such a value is nonetheless significantly higher than the results obtained by Soreanu et al. [90] who reported 10 g m^{-3} h^{-1} at EBRT = 1,080 s.

Montebello et al. [55], studying the critical EBRT value, have reported that their bioreactor is able to treat a loading rate as high as 100 g m^{-3} h^{-1} at EBRT = 120 s (RE = 100%). At EBRT = 90 s, a slight decrease in the removal efficiency (95%) is reported for LR = 100 g m^{-3} h^{-1} suggesting a mass transfer limitation.

The influence of the liquid flow rate on RE has also been studied at constant EBRT = 144 s [84]. According to Fernandez et al. [84], the liquid flow rate has no influence on RE at low H_2S concentrations, i.e. for a loading rate lower than 78 g m^{-3} h^{-1}. However, for a higher loading rate (i.e. 201 g m^{-3} h^{-1}), a decrease in RE is observed for a liquid velocity lower than 15 m h^{-1}, falling to less than 80% for a liquid velocity of 2.3 m h^{-1}. As a result, Fernandez et al. [84] propose a minimum value of 15 m h^{-1} for the liquid velocity circulating in the biotrickling filter.

3.4 Anoxic vs. aerobic bioprocesses

The efficiencies of biotrickling filters operating in aerobic and anoxic conditions have been compared [55]. As indicated in Tables 2, 3, both systems show the same performance, even though the operating conditions were different (packing materials, EBRT and pH). Moreover, as for the aerobic systems, the risk of clogging the packing material by deposits of elemental sulfur represents a major drawback for the stable and long-term operation of anoxic biotrickling filters. As a result, there is a need to carry out experiments in order to determine the optimal conditions for H_2S removal avoiding the risk of clogging.

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Given that the anoxic processes are not oxygen-limited, it seems that the prevention of clogging should be easier to obtain with these than with aerobic bioprocesses.

Table 3. Results from laboratory-scale anaerobic biotrickling filters

Gas composition	Packing material	Inlet H_2S concentration (ppm)	Nitrate sources	pH	EBRT (s)	EC (g m^{-3} h^{-1})	RE (%)	Ref.
N_2 (65%) + CO_2 (35%)	Plastic fibers	2,000	$NaNO_3$	6.3	1,080	10	100	[79]
CH_4 + CO_2 + H_2S + MT	Polyure-thane foam	2,000		7.4-7.5	240	100	99	[55]
Biogas from UASB(*) CH_4: 68 ± 3% CO_2: 26 ± 2%	Polypro-pylene Pall rings	1,400 - 14,600	$NaNO_3$	7.0	144	120	99	[84]
CH_4: 68 ± 3% CO_2: 26 ± 2%	Polyure-thane foam		$Ca(NO_3)_2$. $4H_2O$ $NaNO_3$ KNO_3	7.0	144	130	99	[77]

(*): Upflow Anaerobic Sludge Blanket
MT: Methanethiol (CH_4S)

4. Conclusion

For H_2S biogas cleaning, aerobic and anoxic bioprocesses have been studied but only aerobic bioprocesses, usually combined with a chemical step, have been developed at industrial-scale. Nevertheless, the anoxic systems could be a promising option because they avoid biogas dilution and safety problems due to adding oxygen to methane. Whatever their operating mode, aerobic or anoxic, biological processes are effective for biogas cleaning and offer the same performance. Although elimination capacities determined at laboratory-scale can be very high, EC should not be higher than 90 g m^{-3} h^{-1} at industrial-scale in order to limit clogging effects. The clogging of the packed bed due to the deposit of elemental sulfur S^0 and biomass accumulation clearly represents the main drawback of bioprocesses.

In aerobic conditions, the mass transfer limitation of oxygen negatively affects the biotrickling filter performance. In order to avoid partial oxidation to elemental sulfur S^0 and clogging effects, more efficient oxygen supply methods need to be investigated. However, at high H_2S concentrations (> 1,500 ppmv), the limitation of the concentration of oxygen in the biogas at 3% (for safety reasons and to avoid biogas dilution) leads preferentially to the production of elemental sulfur S^0, which is clearly the bottleneck of these bioprocesses. For biogas loaded with H_2S concentrations of up to 3,000 ppmv, a preventive washing of the packing material may be required to maintain the performance of the bioprocesses. Although the development of new packing materials avoiding biomass accumulation at the bottom of the column and preventing the deposit of elemental sulfur is in progress, it can be concluded that aerobic processes alone are probably not the most suitable for the treatment of biogas highly loaded with H_2S. Besides, to date, industrial applications are based on aerobic systems coupled with a chemical step.

Anoxic H_2S removal integrated with a denitrification process is probably the most interesting option. Thus, anoxic bioprocesses using nitrate as an electron acceptor should be developed. Since the amount of nitrates required for the treatment of high H_2S concentrations can be very large, the use of wastewater from treatment plants, which constitutes a cheap source of nitrates, could represent an interesting challenge. As a result, efforts should be made to develop an innovative bioprocess enabling the simultaneous removal of H_2S from biogas and nitrates from wastewater. Such a biological process should be efficient at large scale under severe operating conditions. However, the interactions between the denitrification process and sulfide oxidation are complex and there are many challenges to overcome before achieving the development of an industrial-scale pilot. The biogas flow rate, the inlet H_2S concentration, the EBRT, the pH, the liquid flow rate, the N/S ratio, as well as the sulfate, nitrate and

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nitrite concentrations in the liquid phase all have to be taken into account in order to determine the optimal conditions for H_2S removal. Although some experimental studies are needed to explore the performance of the bioprocess, a preliminary mathematical modeling of the complex phenomena occurring in such bioreactors should be carried out to target the main parameters to be studied.

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