Hydrogen sulphide management in anaerobic digestion: a critical review on input control, process regulation, and post-treatment

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Abstract

Hydrogen sulphide (H_2S) in biogas is a problematic impurity that can inhibit methanogenesis and induce equipment corrosion. This review discusses technologies to remove H_2S during anaerobic digestion (AD) via: input control, process regulation, and post-treatment. Post-treatment technologies (e.g. biotrickling filters and scrubbers) are mature with >95% removal efficiency but they do not mitigate H_2S toxicity to methanogens within the AD. Substrate pretreatment (i.e. chemical addition) reduces sulphur input into AD via sulphur precipitation. However, available results showed <75% of H_2S removal efficiency. Microaeration to regulate the digester condition is a promising alternative for controlling H_2S formation. Microaeration, or the use of oxygen to regulate the redox potential at around -250 mV, has been demonstrated at pilot and full scale with >95% H_2S reduction, stable methane production, and low operational cost. Further adaptation of microaeration relies on a comprehensive design framework and exchange operational experience for eliminating the risk of over-aeration.

Keywords: Anaerobic digestion; Biogas desulphurisation; Hydrogen sulphide; Microaeration; Pretreatment

Highlights

- H_2S removal by post-treatment is expensive & unsuitable for a growing biogas market
- ORP regulation to prevent H_2S formation can be achieved by microaeration
- Microaeration is efficient, inexpensive, & retrofittable to existing biogas plants
- Over-aeration risk can be alleviated by sharing operation & design experience

1. Introduction

Fugitive release of methane (CH_4) from organic waste and agricultural production is a major contribution to greenhouse gas emission (Kapoor et al., 2020). For thousands of years, CH_4 release from the decay of plant and animal matter was balanced by natural removal processes (Nisbet et al., 2020). In recent years, intensifying agricultural and industrial activities have outpaced the capacity of these natural processes to remove excess CH_4, resulting in elevated atmospheric concentration of this high potent greenhouse gas. The global warming effect of CH_4 is 25 times higher than that of carbon dioxide (CO_2) (Gerber et al., 2013; McCauley et al., 2020). On the other hand, when biogenic CH_4 can be collected, it is a valuable fuel and a renewable source of raw chemicals for the industry.

In the absence of oxygen, organics are broken down by a consortium of microorganisms (hydrolytic and fermentative bacteria, acetogens, and methanogens) to produce a mixture of CH_4 and CO_2, commonly called biogas. Anaerobic digestion is essentially an engineering process to convert organic wastes to collectable biogenic CH_4 for beneficial usage (Kapoor et al., 2020; Nguyen et al., 2021). In addition to CH_4 and CO_2, biogas contains a trace amount of hydrogen sulphide (H_2S). Direct utilisation of biogas for cooking and heating at household is a common practice in some developing countries without or with minimal monitoring of H_2S impacts. However, a more beneficial use of biogas is for electricity generation or upgrading to biomethane, which can be used as transport fuel, town gas replacement, or feedstock to the chemical industry (Nguyen et al., 2021). H_2S removal from biogas is essential for these applications.

H_2S formation during anaerobic digestion is a vexing problem in biogas. H_2S is the product of sulphur reduction by sulphur-reducing bacteria. H_2S concentration in biogas varies from 100 to 10,000 ppmv depending on the feedstock's sulphur content (e.g. 115 mg S/kg

sewage sludge and 600 mg S/kg cattle manure) (Chen et al., 2020; Choudhury et al., 2019). During anaerobic digestion, sulphate-reducing bacteria can inhibit methanogenesis due to the competition for a wide variety of organic and inorganic substrate (e.g. acetate, butyrate, fatty acids, hydrogen and propionate) (Chen et al., 2008; Song et al., 2018a). The generated H_2S is toxic to methanogens in the range of 50 to 220 mg S/L at pH 7-8, thus, further suppressing CH_4 production (Dykstra & Pavlostathis, 2021). There is also a threshold concentration of H_2S in biogas for most applications (e.g. 3-4 ppmv H_2S for natural gas replacement and <100 ppmv H_2S for power generation) (Nguyen et al., 2021; Scholz et al., 2013).

Post-treatment technologies are widely used for H_2S removal from biogas. They are based on biotrickling filtration or physical-chemical (e.g. absorption and adsorption) scrubbing. These technologies can achieve good and reliable H_2S removal (Almenglo et al., 2016; Gabriel & Deshusses, 2003) but are not cost-effective and can generate significant volume of acidic wastewater (Dobslaw & Ortlinghaus, 2020; Ren et al., 2019). While post-treatment can be conveniently added to existing anaerobic digestion facilities, it incurs significant capital and ongoing operational costs. More than 50% of the operating and maintenance cost was attributed to the H_2S adsorption unit to purify 86 m^3/day of biogas (Pipatmanomai et al., 2009). Post-treatment also has high energy and chemical consumption, and requires regular replacement and disposal of adsorbent materials (Huynh Nhut et al., 2020; Nguyen et al., 2021). In addition, post-treatment processes do not address the issue of H_2S inhibition that can reduce the efficiency of biogas production.

Recent interest in biogas as a major source of renewable energy to displace fossil fuel has spurred the development of efficient and sustainable H_2S removal technologies. Promising strategies with a high level of technology readiness include pre-treatment and in-situ process regulation.

Pretreatment is a simple and potentially low cost strategy for reducing H_2S formation during anaerobic digestion. Prior to anaerobic digestion, sulphur in the substrate is removed by precipitation followed by liquid-solid separation and the suppression of sulphate-reducing bacteria. Examples of substrate pretreatment for sulphur removal are alkaline treatment, oxidation and chemical precipitation (Dhar et al., 2011a; Zhen et al., 2013).

In-situ process regulation is achieved by either controlling a specific operating parameter or chemical addition. In-situ treatment can be achieved by adding iron salts or oxidative chemicals into the digester to facilitate sulphide precipitation or oxidise H_2S to elementary sulphur for removal via the digestate. A more elegant strategy is to regulate key operational parameters (e.g. pH, temperature and redox potential) towards an unfavourable condition for sulphate-reducing bacteria to restrict or even eliminate H_2S formation (Rathnayake et al., 2021; Yan et al., 2018). Reducing H_2S formation during anaerobic digestion can also eliminate H_2S toxicity to methanogens to enhance CH_4 production (Yan et al., 2018). Among the operational parameters, redox potential appears to be easily regulated for the purpose of H_2S removal. Changing redox potential affects the reducing or oxidising capacity of anaerobic digestion. To eliminate H_2S, a small amount of air or oxygen can be injected into the digester to increase the oxidising capacity of the system, thus inhibiting sulphate-reducing bacteria activity and promoting sulphide oxidation. This technique is referred to as microaeration. Microaeration is an attractive H_2S removal technique owing to its high efficiency, ease to retrofit and low operational cost (Chen et al., 2020; Nghiem et al., 2014).

Most of the available reviews on H_2S in the literature focus only on post-treatments, lacking a viewpoint on emerging H_2S removal strategies such as pretreatment and in-situ process regulation. This review critically assesses recent development in the removal of H_2S from biogas with a focus on economic viability and a holistic H_2S management during

anaerobic digestion. Mechanisms responsible for H_2S formation and biogas production are discussed to highlight the underlying principles for managing H_2S during anaerobic digestion. Then a systematic comparison is provided by considering treatment cost, technology maturity, operability and removal efficiency. This review provides researchers and practitioners with state-of-the-art knowledge on H_2S in anaerobic digestion and assistance upon their selection of suitable H_2S removal technologies.

2. Hydrogen sulphide in anaerobic digestion

2.1. Formation of hydrogen sulphide during anaerobic digestion

Organic substrates or feedstocks used in anaerobic digestion always contain sulphur-bearing compounds. Methionine and cysteine are common sulphur-containing amino acids in proteins. The high protein levels of some manures (e.g. poultry and swine) used as feedstock can result in a high sulphur input for anaerobic digestion. Sulphur also occurs in a variety of food such as egg (1.8 mg S/g), garlic (5.6 mg S/g), and onion (0.5 mg S/g) (Doleman et al., 2017).

During anaerobic digestion, organic and inorganic sulphur (e.g. SO_4^{2-}) are transformed and reduced to H_2S (Hao et al., 2014; Okoro & Sun, 2019). These transformations occur concurrently with the conversion of organic carbon to biogas via the dissimilatory pathway. *Desulfomicrobium*, *Desulfocurvus*, and *Lentimicrobium* were identified as bacteria responsible for SO_4^{2-} reduction (Li et al., 2020). Organic and inorganic sulphur can also be reduced to H_2S via the dissimilation pathway supported by the metabolic activity of anaerobic sulphate-reducing bacteria such as *Desulfotomaculum solfataricum* and *Desulfotomaculum thermosapovorans (Li et al., 2020; Okoro & Sun, 2019)*.

Sulphate-reducing bacteria in anaerobic digestion play a key role in the formation of H_2S and may influence the CH_4 production. During anaerobic digestion, ubiquitous sulphate-

reducing bacteria transform SO_4^{2-} into H_2S via the assimilation and dissimilation pathways (Fig. 1). The generated H_2S is inhibitory or toxic to methanogens, thus reducing the rate of CH_4 production (Chen et al., 2014). Furthermore, sulphate-reducing bacteria and methanogens compete for the energy source (e.g. acetic acid). This competition can affect the stability of anaerobic digestion process and decrease the quantity of CH_4 produced (Chen et al., 2014). Key mechanisms of H_2S inhibition to methanogenesis is discussed further in section 2.3.

Anaerobic sulphur cycle includes the disproportionation of inorganic sulphur intermediates to H_2S and SO_4^{2-}, and the potential of H_2S oxidation to elemental sulphur (Figure 1). Sulphur disproportionation is a microbiologically catalysed process in which partially oxidised sulphur compounds (e.g. elemental sulphur, thiosulphate, and sulphite) serve as both electron donor and acceptor, and are transformed into a more reduced (H_2S) or more oxidised (SO_4^{2-}) sulphur species (Finster, 2008; Poser et al., 2013). The ability to disproportionate sulphur can be found in the members of the *Desulfobulbaceae* and *Desulfovibrionaceae*. Most of these bacteria are phylogenetically similar to sulphate-reducing bacteria and possess the genes required for dissimilatory sulphate reduction (Finster, 2008).

Sulphur-oxidising bacteria are ubiquitious in anaerobic digestion. They are responsible for chemolithotrophic oxidation of H_2S to elemental sulphur. This implies a possible pathway for eliminating H_2S in anaerobic digestion. The application of sulphur-oxidising bacteria in H_2S removal will be discussed in section 3.2.4.

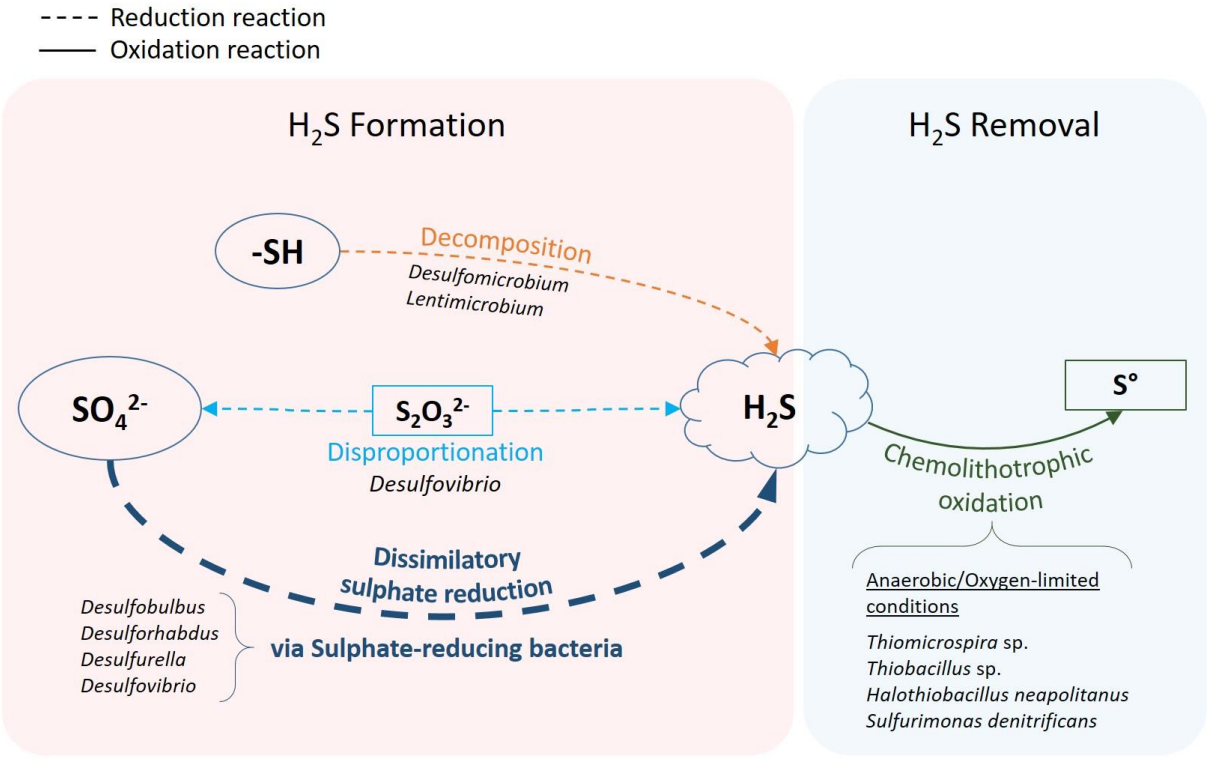

Figure 1: Sulphur transformative pathways to H_2S and H_2S removal pathway in anaerobic digestion. Dissimilatory sulphate reduction (thickened dotted blue line) represents the main pathway for H_2S formation.

2.2. Problems associated with H_2S in biogas

H_2S reduces economic value and limits beneficial applications of biogas. Biogas generated from anaerobic digestion of sewage sludge typically contains 500 to 2500 ppmv H_2S (Nguyen et al., 2021). High sulphur–content substrates such as organic waste from livestocking, slaughterhouse, and dairy farming can produce biogas with a much higher H_2S content at up to 10,000 ppmv. H_2S itself is a toxic gas. In an internal combustion engine, H_2S in biogas is oxidised to SO_2 or SO_3, which are extremely corrosive to pipeline, instruments, equipment, and any metal surface. Trace level of H_2S in biogas can also poison the ion

exchange membrane in fuel cell used to convert biogas to electricity. Therefore, H_2S must be removed before biogas utilisation (Nghiem et al., 2014).

Technical specifications of H_2S in biogas for beneficial applications have been progressively developed in recent years, given the significant role of biogas in the renewable energy mix. As the frontrunners in biogas commercialisation, several countries have developed standards and technical guidelines for safe biogas utilisation. H_2S limit in biomethane for natural gas replacement or transport fuel is set at 4 ppmv or less (Table 1). For stationary power generation, most engine manufactures also specify an H_2S limit of 100 ppmv in biogas as part of the guarantee condition (Table 1).

Table 1: Specifications for H_2S in biogas for different uses

	Regulatory body	**H_2S limit (ppmv)**	**Application**	**Ref.**
Standards	Austria	3	Natural gas replacement	(Scholz et al., 2013)
	Germany	4	Natural gas replacement	(Scholz et al., 2013)
	US	3.7	Natural gas replacement	(Foss & Head, 2004)
	EU	3.6	Automotive fuel	(EBA, 2017)
Guidelines	Engine manufacturer	100	Power generation	(Nguyen et al., 2021)
	Fuel cell manufacturer	5	Power generation	(Admed & Papadias, 2012)

2.3. Mechanisms of hydrogen sulphide toxicity/inhibition

Competition for energy source is a major inhibiting mechanism to methanogenesis by H_2S formation. In anaerobic digestion, H_2S and CH_4 generation can simultaneously occur using the same energy source such as acetic acid and hydrogen (Shi et al., 2020). SO_4^{2-} reduction (Eq. 1) by H_2 has higher Gibbs free energy (ΔG) (i.e. more energy is released) than CO_2 reduction (Eq. 2) by H_2 (Chen et al., 2014). In other words, SO_4^{2-} reduction is more

thermodynamically favourable than CO_2 reduction by H_2. Similarly, SO_4^{2-} reduction by acetic acid as the electron donor is also more favourable than the methanogenesis of acetic acid itself (Eq. 3-4). Sulphate-reducing bacteria can outcompete methanogens when SO_4^{2-} is abundant (Dar et al., 2008; Song et al., 2018b). As a result, the rate of methanogenesis and CH_4 production are suppressed at high SO_4^{2-} content (i.e. COD/ SO_4^{2-} ration below 1.7) (Lens et al., 1998; Piccolo et al., 2021; Song et al., 2018b).

$$SO_4^{2-} + 4H_2 = H_2S + 4H_2O + 2OH^- \quad (\Delta G = -154 \text{ kJ/mol}) \quad (1)$$

$$CO_2 + 4H_2 = CH_4 + 2H_2O \quad (\Delta G = -135 \text{ kJ/mol}) \quad (2)$$

$$SO_4^{2-} + CH_3COOH = H_2S + 2HCO_3^- \quad (\Delta G = -43 \text{ kJ/mol}) \quad (3)$$

$$CH_3COOH = CH_4 + CO_2 \quad (\Delta G = -28.5 \text{ kJ/mol}) \quad (4)$$

Secondary inhibition of methanogenesis is caused by H_2S toxicity to methanogens. The anaerobic digester is at near neutral pH, where sulphide occurs in the unprotonated form of H_2S. As a neutral and small molecule, H_2S can diffuse through the cell membrane into cytoplasm and react with cellular components (O'Flaherty et al., 1998). Inside the cell, H_2S can interfere with the assimilation of sulphur and denature native proteins by forming bisulfide bridges with polypeptide chains (Chen et al., 2008). As a result, the anaerobic microbial communities can be damaged by H_2S toxicity, especially methanogens (O'Flaherty et al., 1998). The inhibition of methanogenesis is proportional to the concentration of H_2S in the substrate and the gas phase (Hilton & Oleszkiewicz, 1988). However, in practice, factors such as COD/ SO_4^{2-} ratio, pH, and sensitivity to H_2S toxicity can influence the degree of H_2S inhibition and competition with other anaerobic microbes (Chen et al., 2008). Reported H_2S inhibitory concentrations to methanogens vary with values ranging from 50 to 220 mg S/L at pH 7-8 (Dykstra & Pavlostathis, 2021).

3. Technologies to control and manage H_2S formation

Commercial or near commercial ready technologies to manage H_2S in biogas can be categorised in three groups namely post-treatment, pretreatment, and process regulation (Figure 2). To date, post-treatment of biogas is still the most widely used strategy to remove H_2S. Biogas cleaning and upgrading processes have been used at commercial scale to ensure safe biogas or CH_4 utilisation. However, post-treatment does not solve the issue of H_2S toxicity to methanogens. On the other hand, H_2S toxicity to methanogenesis can be mitigated through the other two strategies that are extensively reviewed here namely i) pretreatment of substrates to reduce sulphur loading, and ii) regulating the anaerobic digestion process to inhibit the activity of sulphate-reducing bacteria.

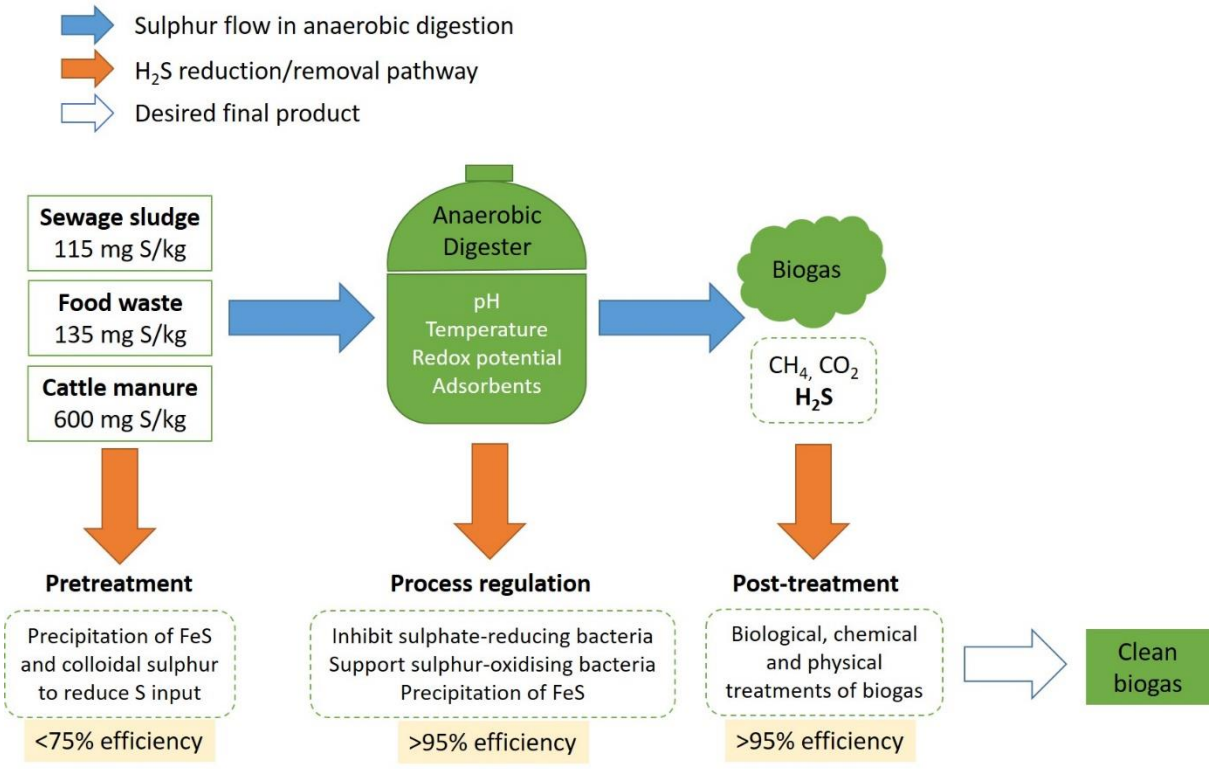

Figure 2: Approaches to H_2S management during anaerobic digestion process including influent, effluent, and operational control.

3.1. Post-treatment

Post-treatment technologies to remove H_2S from biogas can be categorised into biological desulphurisation (i.e. biofiltration) and physical-chemical scrubbing. Although both technologies have been applied at full-scale, they entail high capital and operational cost. The high cost of post-treatment is inherent as further discussed below.

3.1.1. Biofiltration

Biofiltration utilises the sulphide oxidative capabilities of specific microorganisms to convert H_2S to elementary sulphur or sulphate for removal from the gas phase (Okoro & Sun, 2019). Biofiltration technologies include biotrickling filters and or a simpler configuration known as biofilters.

Biotrickling filtration for H_2S removal is a mature technology. Comprehensive reviews on the performance of biotrickling filters are widely available (Bu et al., 2021; Huynh Nhut et al., 2020; Vikrant et al., 2018). The filter beds are usually made up of chemically inert packing materials to immobilise sulphide-oxidising microorganisms (Barbusiński & Kalemba, 2016; López et al., 2016). The operation of biotrickling filters involves the passing of biogas through the wet filter bed (Fernández et al., 2013; Huynh Nhut et al., 2020) to enable the dissolution and diffusion of H_2S to the microbial biofilm, where H_2S oxidation to elemental sulphur or SO_4^{2-} occurs via microbial activity. The condition of biotrickling filter can be either aerobic or anoxic depending on whether oxygen or nitrate is used as the electron acceptor. The anoxic system has some advantages over the aerobic counterpart such as reduced risk of explosion and no biogas dilution. However, the additional cost to supply nitrate to anoxic biotrickling filters is a major disadvantage of anoxic biotrickling filters (Fernández et al., 2013; Huynh Nhut et al., 2020). Biotrickling filters have shown high H_2S removal efficiencies of $\geq$ 95% for inlet H_2S load of up to 4,000 ppmv when employed at pilot

(Almenglo et al., 2016; Nagendranatha Reddy et al., 2019) and full scale (Gabriel & Deshusses, 2003; Shelford et al., 2019). Biotrickling filters are also effective for treating low H_2S concentration biogas (200 ppmv), achieving >93% removal efficiency (Zhuo et al., 2019).

In practice, biotrickling filter is primarily used to remove H_2S for odour control rather than biogas utilisation. This is because the high treatment cost (about US\$1.5/m^3 biogas (Okoro & Sun, 2019)), well above the economic value of biogas. The high cost of biotrickling filter over other technologies (e.g. in-situ treatment in section 3.3) is due to operational expenses such as energy consumption, nutrients for microbial growth, replacement of packing material and microorganism (Huynh Nhut et al., 2020). In addition, biogas dilution and biogas clogging due to sulphur accumulation are inherent and unavoidable in biotrickling filters (Huynh Nhut et al., 2020).

3.1.2. Physical-chemical scrubbing

Physical-chemical scrubbing can effectively remove H_2S from biogas. Most commonly used technologies include wet scrubbing using water, caustic solution, and organic solvents as H_2S absorbent, adsorption using solid adsorbents (e.g. activated carbon and zeolites) and membrane separation. There have been several comprehensive reviews of these technologies (Georgiadis et al., 2020; Okoro & Sun, 2019; Xiao et al., 2017). Absorption technologies rely on the solubility of H_2S in wash solution (i.e. water or organic solvents). They have shown up to 98% H_2S removal efficiency at pilot-scale operations (Krischan et al., 2012; Schiavon Maia et al., 2017). Adsorption can reduce H_2S content in biogas to below 1 ppmv (Okoro & Sun, 2019). Selection of adsorbing material with high H_2S adsorption capacity, low adsorption temperature and high regeneration ability is necessary to increase the scalability of this technology (Georgiadis et al., 2020). On the other hand, membrane separation has made

significant techno-economic progress in biogas cleaning applications (Nguyen et al., 2021). High H_2S removal efficiency of 99% has been achieved in a pilot two-stage membrane biofilter (Rolewicz-Kalińska et al., 2021).

Scrubbing technologies increase the cost of biogas production due to their requirements for equipment, chemicals, and waste disposal (Okoro & Sun, 2019). The costs of absorption using NaOH and adsorption were estimated to be US$2.38/$m^3$ and US$1.23/$m^3$ biogas, respectively (Okoro & Sun, 2019). These values exceeded the estimated cost of using biotrickling filter by two times, and the costs of in-situ chemical addition and microaeroation by 200 times. Recent progresses in materials engineering and understanding of the process are expected to reduce the treatment cost by scrubbing technologies. However, such reduction is incremental and post-treatment technologies for biogas desulphurisation should be used as the last resort.

3.2. Substrate pretreatment

Compared to post-treatment, substrate pretreatment has a lower level of technical maturity. The principle of sulphur removal via substrate pretreatment revolves around precipitating soluble sulphur forms (e.g. S^{2-} and SO_4^{2-}). Reported concentrations of soluble sulphur in cattle manure, sewage sludge and slaughterhouse sludge are 400, 70 and 3 mg/L, respectively (Fontaine et al., 2021; Forouzanmehr et al., 2021; Yan et al., 2018). Once the precipitated sulphur is formed, it is removed from the substrate via a liquid-solid separation process before feeding the substrate to the digester. Dhar et al. (2011a) and Dhar et al. (2011b) combined iron salt ($FeCl_2$) and hydrogen peroxide (H_2O_2) to pretreat waste activated sludge (WAS) and reported sulphur removal via ferrous sulphide (FeS) and elementary sulphur precipitation. WAS pretreatment by iron salt addition can achieve 75% reduction in H_2S formation during anaerobic digestion compared to untreated WAS (Table 2). This lower

292 removal efficiency compared to post-treatment (>90%) is due to the fact that pretreatment
293 can only target soluble sulphur fraction of the substrate. WAS may contain sulphur-bearing
294 compounds that are only released during hydrolysis and acidogenesis, thus not being
295 removed via pretreatment. This sulphur fraction contributes to H_2S formation during
296 anaerobic digestion. Lime (e.g. CaO or $Ca(OH)_2$) addition is another technique for SO_4^{2-}
297 precipitation (i.e. $CaSO_4$) and has resulted in 98% H_2S reduction for pretreated levulinic acid
298 wastewater (Yang et al., 2019). In addition, alkaline treatment of WAS using $Ca(OH)_2$ prior
299 to anaerobic digestion showed considerable H_2S reduction and biogas production compared
300 to the untreated sample (Table 2). Dai et al. (2017a) attributed this process improvement to
301 reduced abundance of sulphate-reducing bacteria and restricted activity of sulphite reductase.

302 Pretreatment to remove sulphur from the substrate before the digester can also increase
303 the efficiency of anaerobic digestion. Lowering the concentrations of sulphur minimises
304 sulphur reduction to H_2S during the anaerobic digestion. This can prevent the competition
305 between sulphate-reducing bacteria and methanogens, thus increasing CH_4 production in
306 some cases by up to 50% (Table 2). Pretreatment of substrates with high sulphur loading can
307 assist in maintaining a COD/SO_4^{2-} ratio greater than 10, which has been shown to alleviate
308 the inhibitory effect of H_2S on methanogens (Song et al., 2018b). Anaerobic digestion of
309 pretreated substrates (e.g. wastewater and waste activated sludge) has resulted in improved
310 CH_4 generation (Table 2) (Dai et al., 2017a; Dhar et al., 2011a; Dhar et al., 2011b).

311 Removal of sulphur precipitate from the substrate before anaerobic digestion is a
312 critical step. Thus, pretreatment is restricted to liquid substrates (e.g. industrial wastewater)
313 that allow for cost effective sulphur precipitate removal sedimentation. To date, pretreatment
314 for sulphur removal has only been investigated at lab scale level. Further research is
315 necessary to quantify the cost of chemical addition and disposal of sulphur precipitates prior
316 to full scale implementation.

317 **Table 2**: Selected examples of substrate pretreatment and substrate management to minimise H_2S formation in anaerobic digestion.

Pretreatment	**Substrate**	**Operation design for pretreatment**	**Sulphur removal mechanism**	**H_2S reduction (%)**	**Increase in biogas production (%)**	**Ref.**
Thermo-oxidative pretreatment	Waste activated sludge	0.6 mg H_2O_2 + 1.5 mg $FeCl_2$/mg S^{2-} at 60 ℃ for 30 min	FeS and colloidal sulphur precipitation	75	20	(Dhar et al., 2011a)
Combined depressurisation and chemical treatment	Waste activated sludge	5.1 atm for 30 min 0.6 mg H_2O_2 + 1.5 mg $FeCl_2$/mg S^{2-} for 30 min	Hydrogen peroxide and iron salt react with dissolved sulphide to form FeS, elemental sulphur and sulphates	47	8	(Dhar et al., 2011b)
High dose iron-mediated persulfate oxidation	Waste activated sludge	0.8 mmol $S_2O_8^{2-}$ + 1.0 mmol Fe(II)/g VSS 300 rpm for 15 min	Lower activity of sulphate-reducing bacteria Lower concentration of bound protein for H_2S formation due to oxidation FeS and colloidal sulphur precipitation	60	No data	(Zhen et al., 2013)
Calcium hydroxide pretreatment	Levulinic acid wastewater	$Ca(OH)_2$ is added at Ca^{2+}/SO_4^{2-} = 1.75 200 rpm for 3 h	$CaSO_4$ precipitation	98	No data	(Yang et al., 2019)
Alkaline fermentation	Waste activated sludge	Anaerobic condition pH 10 by addition of 4 M $Ca(OH)_2$ 8 d HRT	Reduce the abundance of sulphate-reducing bacteria Restrict the activity of sulfite reductase (i.e. inhibiting H_2S formation)	54	50	(Dai et al., 2017a)

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3.3. Regulate the anaerobic digestion to reduce H_2S formation

Regulating the anaerobic digestion process to inhibit or reduce H_2S formation has recently emerged as a very cost effective technology to improve biogas quality. The methods often involve suspension of sulphate-reducing bacteria proliferation and functions. This approach requires careful regulation of pH, temperature, and/or oxygen reduction potential (ORP) to limit the formation of H_2S while continue to facilitate biogas production. Sulphate-reducing bacteria are more resilient than methanogens. They can proliferate in a wider pH (5-8), temperature (15-70 °C), and ORP (-150 to -500 mV) range compared to methanogens (Jones & Ingle, 2005; Liu et al., 2018). The optimal growth conditions for methanogens (i.e. pH = 6.8 – 7.2, temp = 37-70 °C and ORP = -200 to – 500 mV) are within the optimal growth conditions of sulphate-reducing bacteria (Chen & Chang, 2020; Varol & Ugurlu, 2017). Thus, there is only small window to shift the anaerobic digestion parameters away from the favourable conditions for sulphate-reducing bacteria without affecting methanogens for H_2S reduction. To-date results in reducing H_2S via pH, temperature, and ORP regulation during anaerobic digestion are outlined in the following sections.

3.3.1. pH

pH conditions govern H_2S formation by suppressing the activity of sulphate-reducing bacteria and regulating the speciation of free sulphide in anaerobic digestion. In general, at low pH (i.e. acidic conditions), the activity of sulphate-reducing bacteria is high and free sulphide dominates in the H_2S form (O'Flaherty et al., 1998). Increasing the pH can shift the dominating sulphide form to sulphide ions (S^{2-} and HS^-), which are less toxic to bacteria than H_2S (Tran et al., 2021b). The activity of sulphate-reducing bacteria is less favourable at pH > 8 (i.e. lower proton concentration) since SO_4^{2-} reduction is a proton consuming process (Tran et al., 2021a). These behaviours have been widely used to control H_2S in the sewer network

by alkaline addition for pH increment (Rathnayake et al., 2021). Thus, increasing the pH can reduce the rate of SO_4^{2-} reduction and mitigate H_2S formation during anaerobic digestion. At the same time, H_2S inhibition and toxicity on methanogens can be relieved.

Previous studies have documented the inhibitory effect of alkaline condition on H_2S formation during anaerobic digestion. Yan et al. (2018) demonstrated that the high initial alkaline condition at pH 8 led to a 45% decrease in H_2S content of biogas during mesophilic anaerobic digestion of slaughterhouse wastewater sludge. More SO_4^{2-} and organic sulphur were transferred into the liquid and solid as soluble and precipitated sulphides at pH 8, thus less H_2S was formed. Although Yan et al. (2018) have only examined the initial pH value, they reported significant improvement in both quantity (i.e. 10% increase) and quality of biogas production (i.e. 64% higher CH_4 yield) (Yan et al., 2018). Dai et al. (2017b) observed a similar result during anaerobic digestion of sewage sludge. By raising the system to pH 8-8.5, they reported 90% lower H_2S content with no discernible impact on biogas production. Dai et al. (2017b) suggested that the high ammonia-pH system reduced the abundance of sulphate-reducing bacteria while increasing the abundance of methanogens. Nevertheless, it is clear that the number of studies on pH regulation for H_2S control is small and limited to lab-scale investigation. With this method, other factors such as SO_4^{2-} concentration and temperature should also be taken into consideration to induce a synergistic effect.

3.3.2. Temperature

Sulphate-reducing bacteria can tolerate a wide range of temperature. Thus, temperature regulation can only reduce but cannot completely eliminate H_2S formation during anaerobic digestion. In fact, sulphate-reducing bacteria can thrive in a wider range of temperature (15-70 °C) than methanogens (35-70 °C) (Chen & Chang, 2020; Liu et al., 2018). Both mesophilic and thermophilic sulphate-reducing bacterial strains have been identified in wastewater sludge. A comprehensive list of the strains and their properties is available in the

368 literature (Liu et al., 2018). Sulphate-reducing bacteria are less sensitive to temperature than
369 methanogens (Shin et al., 1996; Vallero et al., 2004; Visser et al., 1993). In other words,
370 while thermophilic digestion resulted in significantly higher biogas production than
371 mesophilic condition (Jeong et al., 2014; Labatut et al., 2014; Li et al., 2013), temperature
372 impact on sulphate-reducing bacteria is negligible (Colleran & Pender, 2002; Tang et al.,
373 2004; Vallero et al., 2004). As a result, H_2S concentration per biogas volume in thermophilic
374 digestion is lower than mesophilic digestion due to the dilution effect (although the amount of
375 H_2S remains the same).

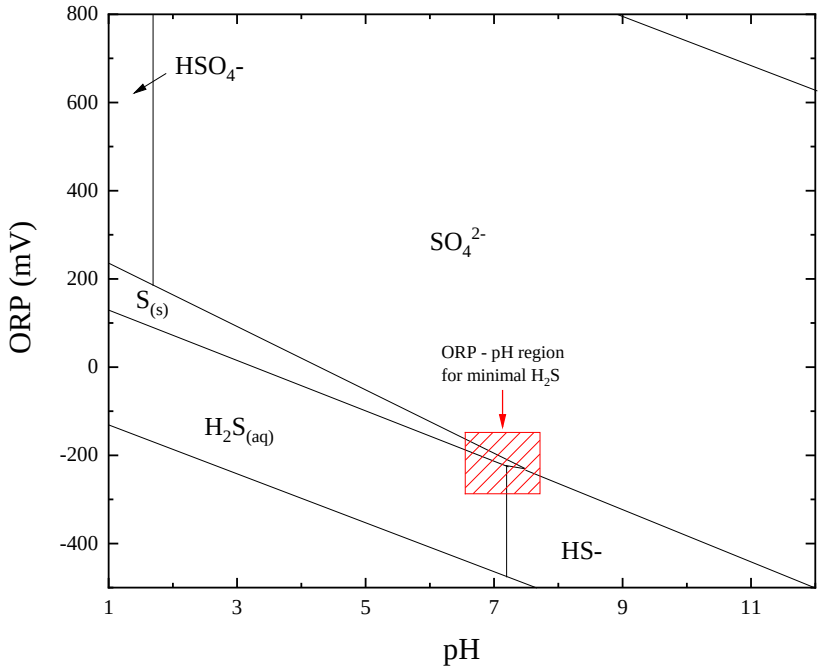
376 3.3.3. Redox potential

377 The redox potential is a measurement of the overall reducing or oxidising condition in
378 the digester. Negative redox potential defines a reducing environment. Anaerobic digestion is
379 an example of such environment, with redox potential below -200 mV. Effect of changing
380 redox potential on the microbial communities of complex anaerobic systems has been
381 established (Chen et al., 2020; Liu et al., 2013). Regulating the redox potential has emerged
382 as a cost-effective technique to direct the materials and energy to the production of desirable
383 products (e.g. CH_4) and at the same time inhibiting unwanted chemical reactions (e.g. H_2S
384 formation).

385 The redox potential can be monitored in real time via oxidation-reduction potential
386 (ORP) measurement. Using real time data from an ORP probe, the redox potential can be
387 regulated by precisely injecting a small volume of oxygen (O_2) or air to the digester. This is
388 known as microaeration. Optimal H_2S removal via microaeration occurs at the O_2/S^{2-} ratio of
389 0.5 to 1.0 (Duangmanee, 2009). Oxygen acts as an electron acceptor to facilitate the oxidation
390 of H_2S in both aqueous and gaseous phases to elementary sulphur and some thiosulfate (Díaz
391 et al., 2011). H_2S oxidation is promoted by a consortium of sulphide-oxidising bacteria such

as *Thiobacillus* sp. They are ubiquitous in the anaerobic digester and use carbon dioxide and organic matter as carbon and energy source (Wellinger & Lindberg, 1999). Thus, sulphide-oxidising bacteria can potentially enhance the biogas production rate and composition of anaerobic digestion (Nghiem et al., 2014). Previous investigations have reported 90 to 99% H_2S removal by microaeration in anaerobic digestion at lab- (Andreides et al., 2021), pilot- (Díaz et al., 2011; Huertas et al., 2020), and full-scale (Díaz et al., 2015; Nghiem et al., 2014).

The theoretical basis of microaeration to control H_2S formation in biogas can be explained by the relationship between the redox potential, pH and the speciation of sulphur in the digester (Figure 3). There is a small window at the vicinity of -250 mV and near neutral pH where elementary sulphur (rather than H_2S) is the final product of sulphur reaction (Figure 3). As discussed in section 2.1, by introducing a small amount of oxygen (or electron acceptor) to the digester, H_2S can be converted to elemental sulphur via the chemolithotrophic pathway by sulphide-oxidising microorganisms that are naturally available in the digesters (Wellinger & Lindberg, 1999). Methanogenesis is not inhibited under this anaerobic condition (Table 3). Previous works have conclusively demonstrated ORP as the governing parameter to control the formation of H_2S during anaerobic digestion. Indeed, effective H_2S removal of 99% has been achieved through maintaining a desired ORP window without compromising the CH_4 production and the process stability of anaerobic digestion (Khanal & Huang, 2006; Khanal et al., 2003; Nghiem et al., 2014). It is noteworthy that the ORP set points of these studies (from -320 to -270 mV) deviated slightly from the theoretical set point in Figure 3. The underlying reason for this deviation is still unclear.



414

415 **Figure 3**: ORP – pH diagram for sulphur. The red box highlights the optimal Eh – pH
416 region to achieve minimal H_2S formation during anaerobic digestion.

417 The small ORP - pH window for microaeration (Figure 3) is a major operational risk
418 factor. Anaerobic microbes cannot survive in the presence of O_2. In other word, the injected
419 O_2 must be immediately consumed so that an anaerobic condition is maintained in the
420 digester. Thus, uneven or over aeration is detrimental to the digester and can cause significant
421 disruption. Excessive injection of air or O_2 is an also a major safety risk as the O_2 and CH_4
422 may eventually reach the explosive threshold.

423 Recent pilot and full scale trial data has demonstrated microaeration as a very
424 cost–effective technology for H_2S removal. Apart from the cost of minor equipment (e.g.
425 ORP probe, valves, and compressor or O_2 cylinder) and parasitic power demand, there is very
426 little operational cost and no other chemical consumption. Díaz et al. (2015) conducted an
427 economic analysis of three microaerobic scenarios to remove H_2S from full-scale anaerobic
428 digesters. These scenarios include supply of pure 100% O_2, technical grade 95%

O_2 generated by pressure swing adsorption, and air. Technical grade O_2 treatment showed the lowest operating cost of US\$0.0022/m^3 of biogas, followed by air (US\$0.0032/m^3) and pure O_2 (US\$0.0045/m^3) (Díaz et al., 2015). These results are consistent with a more recent study by Okoro and Sun (2019) who compared the cost of microaeration to other H_2S removal technologies. The analysis by Okoro and Sun (2019) involved a review of costing data in combination with inherent data uncertainties to provide a basis for quantitative comparison of the desulphurisation strategies. The estimated cost of microaeration is US\$0.015/m^3 biogas, which is about 200 times lower compared to post-treatment by biotrickling filters or physical-chemical scrubbing (Okoro & Sun, 2019).

3.3.4. In-situ chemical addition

Weak and highly soluble oxidising agents such as ferric iron (Fe^{3+}), peroxide (H_2O_2), and potassium permanganate ($KMnO_4$) can be used to regulate the digester redox potential and reduce the risk of uneven and over aeration. In addition to the oxidisation of sulphide to elementary sulphur, chemical addition can also remove H_2S via metal sulphide precipitation (Lupitskyy et al., 2018; Zhang et al., 2008). Fe^{3+} addition directly to the digester to remove dissolved sulphide has been demonstrated (Lin et al., 2017; McFarland & Jewell, 1989; Zhou et al., 2016). Fe^{3+} can oxidise sulphide it to elemental sulphur (Eq. 5) and the produced ferrous (Fe^{2+}) can subsequently form FeS precipitate with the remaining sulphide in the system (Eq. 6).

$$2Fe^{3+} + HS^- \rightarrow 2Fe^{2+} + S^0 + H^+ \qquad (\Delta G: -160.9\ kJ/mol) \qquad (5)$$

$$Fe^{2+} + HS^- \rightarrow FeS + H^+ \qquad (\Delta G: -21.0\ kJ/mol) \qquad (6)$$

Other oxidising chemicals can also be added to the anaerobic digester to prevent H_2S formation. Examples of such chemicals include H_2O_2 and potassium permanganate ($KMnO_4$). They can oxidise dissolved sulphide to sulphur and liberate oxygen during their

decomposition, thus keeping the digester less anaerobic. This may lead to an increase in the system ORP to the favourable conditions for H_2S removal as discussed in section 3.2.4. The drawback of these oxidising agents is their short lifetime and fast reaction time, which necessitates an automatic, intermittent dosing system (Zhang et al., 2008).

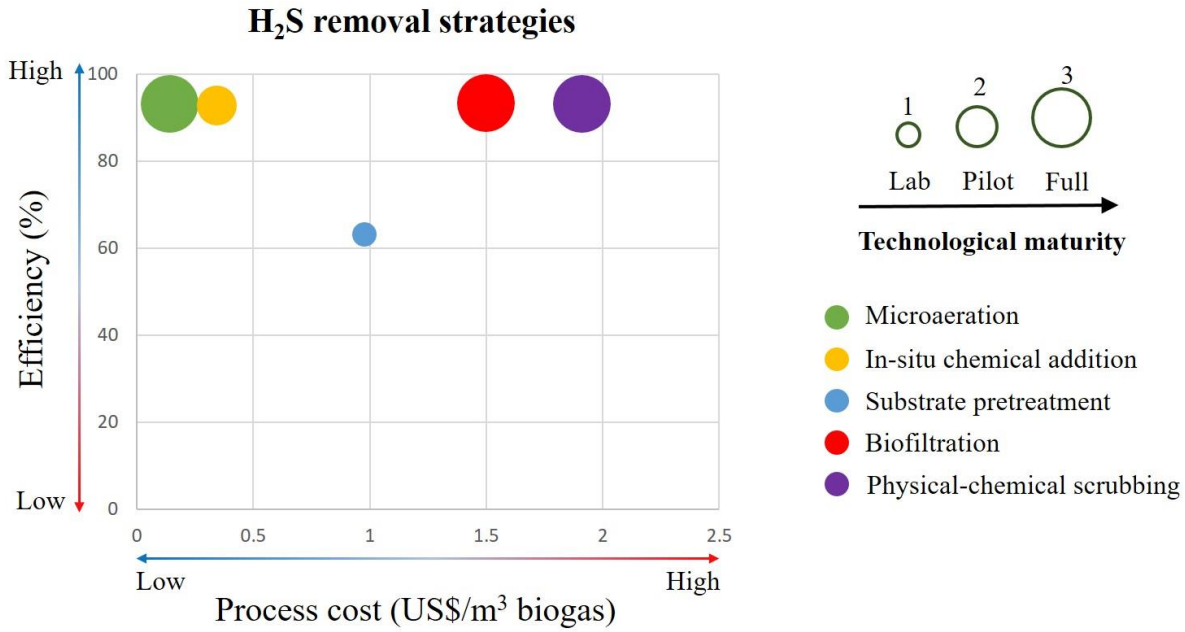
In-situ chemical removal of H_2S in anaerobic digestion is highly efficient, but the chemical cost is a major disadvantage. Oxidising agents such as Fe^{3+} and H_2O_2 are expensive (Zhang et al., 2008; Zhou et al., 2016). When they are used in large quantity for in-situ H_2S removal, it translates to a rather high treatment cost of US$5.04–9.81 kg^{-1} S to achieve 88–100% H_2S removal (iron to sulphide ratio of 1.2-2.5:1 w/w) (Zhang et al., 2008). Assuming 90% H_2S removal at an initial 1650 ppmv H_2S/m^3 biogas (i.e. similar to the study of microaeration cost by Díaz et al. (2015)), the cost of in-situ chemical addition would be US$0.01–0.02/$m^3$ biogas. This is ten times higher than the cost of microaeration (Díaz et al., 2015). Natural iron ores such as limonite, which contain a high concentration of iron oxides, have been adopted as low-cost alternative sorbents for in-situ H_2S abatement (Zhou et al., 2016).

4. Future roadmap

As the focus is shifted from waste management to bioenergy production, new biogas projects have become more cost sensitive. Post-treatment technologies have gradually been superseded with newer technologies that are more cost effective for biogas desulphurisation. With the exception of substrate pre-treatment, all technologies reviewed here can offer high H_2S removal efficiency (Figure 4). They are at a similar level of technological maturity with demonstrated pilot- and full-scale operations (Table 4). Data corroborated in this review highlights treatment cost as a key factor to differentiate these technologies. Microaeration standouts as the most cost effective option. Surprisingly, despite several reports of successful

full-scale microaeration operation in the literature, the uptake of this technology is still limited.

Major hurdles to the uptake of microaeration by the biogas industry include the current lack of operational experience, design expertise, and a rigorous system for risk management. In recognition of the important contribution of biogas to energy security, these hurdles have been progressively addressed in recent years. Dedicated attempt to share microaeration operational experience is evidenced by several peer-reviewed articles to describe pilot and full scale microaeration experience (Table 4). The risk of uneven aeration can be eliminated through engineering design, for example, injecting air or O_2 to the external digestate circulation loop and with downstream ORP monitoring. The risk of over aeration can also be eliminated or significantly reduced by a safety measure such as overriding restriction on the volume of air and oxygen that can be injected to the digester. For small scale digester, using dissolved oxidising agents such as Fe^{3+} and H_2O_2 can be a viable compromise to address operational risk acknowledging that chemical addition to regulate the redox potential is more expensive than microaeration. Additional resources to support the planning of new biogas projects, engineering design, and operational training are also recommended for further uptake of microaeration.



494

495 **Figure 4**: Comparison of H_2S removal strategies for anaerobic digestion in terms of

496 process cost, removal efficiency, and technological maturity.

497 **Table 3**: Reports of pilot- and full-scale H_2S removal operation experience.

H_2S removal strategy	**Scale**	**Initial H_2S content (ppmv)**	**H_2S removal efficiency (%)**	**Reference**
Microaeration	Full	1,650	95	(Díaz et al., 2015)
Microaeration	Full	2,870	99.5	(Jeníček et al., 2017)
Biotrickling filter	Full	3,000	99	(Tomàs et al., 2009)
Bioscrubber	Full	2,200–2,500	99.3	(Haosagul et al., 2020)
Wet scrubber	Full	1,000–5.000	99	(Surita & Tansel, 2015)
SULFURIX^{TM} Wet scrubber	Full	No data	95–99	(GWE, 2021)
Microaeration	Pilot	6,000	99.5	(Nghiem et al., 2014)
Biotrickling filter	Pilot	2,000	99	(Nagendranatha Reddy et al., 2019)

Chemical absorber (Fe^{3+}) + biological treatment	Pilot	3,542	95	(Lin et al., 2013)
Chemical absorber (Fe-EDTA)	Pilot	No data	98	(Schiavon Maia et al., 2017)
Alkaline oxidative scrubber (NaOH + H_2O_2)	Pilot	3,000	97	(Krischan et al., 2012)

5. Conclusion

This review assesses the current technologies to remove or control the formation of H_2S in biogas in terms of cost, technological maturity, and adaptability to anaerobic digestion. Biotrickling filters and scrubbers are well established post-treatment technologies for large scale operations but with a high treatment cost. As the biogas market continues to grow, more cost-effective alternatives for H_2S removal have emerged in recent years. Microaeration is a simple and cost-effective alternative to post-treatment with many added benefits. Information corroborated here also highlights the need for a comprehensive design framework and sharing operational experience to eliminate the risk of over-aeration.

References

1. Admed, S., Papadias, D. 2012. Biogas impurities and cleanup for fuel cells U.S. Department of Energy

2. Almenglo, F., Bezerra, T., Lafuente, J., Gabriel, D., Ramírez, M., Cantero, D. 2016. Effect of gas-liquid flow pattern and microbial diversity analysis of a pilot-scale biotrickling filter for anoxic biogas desulfurization. *Chemosphere*, **157**, 215-223.

3. Andreides, M., Pokorná-Krayzelová, L., Říhová Ambrožová, J., Volcke, E.I.P., Bartáček, J. 2021. Key parameters influencing hydrogen sulfide removal in microaerobic sequencing batch reactor. *Biochemical Engineering Journal*, **168**, 107951.

4. Barbusiński, K., Kalemba, K. 2016. Use of biological methods for removal of H_2S from biogas in wastewater treatment plants - a review. *Architecture Civ. Eng. Environ.*, **9**, 103-112.

5. Bu, H., Carvalho, G., Yuan, Z., Bond, P., Jiang, G. 2021. Biotrickling filter for the removal of volatile sulfur compounds from sewers: A review. *Chemosphere*, **277**, 130333.

6. Chen, H., Chang, S. 2020. Dissecting methanogenesis for temperature-phased anaerobic digestion: Impact of temperature on community structure, correlation, and fate of methanogens. *Bioresour. Technol.*, **306**, 123104.

7. Chen, J.L., Ortiz, R., Steele, T.W.J., Stuckey, D.C. 2014. Toxicants inhibiting anaerobic digestion: A review. *Biotechnol. Adv.*, **32**(8), 1523-1534.

8. Chen, Q., Wu, W., Qi, D., Ding, Y., Zhao, Z. 2020. Review on microaeration-based anaerobic digestion: State of the art, challenges, and prospectives. *Sci. Total Environ.*, **710**, 136388.

9. Chen, Y., Cheng, J.J., Creamer, K.S. 2008. Inhibition of anaerobic digestion process: A review. *Bioresour. Technol.*, **99**(10), 4044-4064.

10. Choudhury, A., Shelford, T., Felton, G., Gooch, C., Lansing, S. 2019. Evaluation of Hydrogen Sulfide Scrubbing Systems for Anaerobic Digesters on Two U.S. Dairy Farms. *Energies*, **12**(24), 4605.

11. Colleran, S., Pender, S. 2002. Mesophilic and thermophilic anaerobic digestion of sulphate-containing wastewaters. *Water Sci. Tech.*, **45**(10), 231-235.

12. Dai, X., Hu, C., Zhang, D., Chen, Y. 2017a. A new method for the simultaneous enhancement of methane yield and reduction of hydrogen sulfide production in the anaerobic digestion of waste activated sludge. *Bioresour. Technol.*, **243**, 914-921.

13. Dai, X., Hu, C., Zhang, D., Dai, L., Duan, N. 2017b. Impact of a high ammonia-ammonium-pH system on methane-producing archaea and sulfate-reducing bacteria in mesophilic anaerobic digestion. *Bioresour. Technol.*, **245**, 598-605.

14. Dar, S.A., Kleerebezem, R., Stams, A.J.M., Kuenen, J.G., Muyzer, G. 2008. Competition and coexistence of sulfate-reducing bacteria, acetogens and methanogens in a lab-scale anaerobic bioreactor as affected by changing substrate to sulfate ratio. *Appl. Microbiol. Biotechnol.*, **78**(6), 1045-1055.

15. Dhar, B.R., Elbeshbishy, E., Hafez, H., Nakhla, G., Ray, M.B. 2011a. Thermo-oxidative pretreatment of municipal waste activated sludge for volatile sulfur compounds removal and enhanced anaerobic digestion. *Chem. Eng. J.*, **174**(1), 166-174.

549 16. Dhar, B.R., Youssef, E., Nakhla, G., Ray, M.B. 2011b. Pretreatment of municipal waste
550 activated sludge for volatile sulfur compounds control in anaerobic digestion. *Bioresour.*
551 *Technol.*, **102**(4), 3776-3782.

552 17. Díaz, I., Lopes, A.C., Pérez, S.I., Fdz-Polanco, M. 2011. Determination of the optimal
553 rate for the microaerobic treatment of several H2S concentrations in biogas from sludge
554 digesters. *Water Sci. Tech.*, **64**(1), 233-238.

555 18. Díaz, I., Ramos, I., Fdz-Polanco, M. 2015. Economic analysis of microaerobic removal of
556 H2S from biogas in full-scale sludge digesters. *Bioresour. Technol.*, **192**, 280-286.

557 19. Dobslaw, D., Ortlinghaus, O. 2020. Biological Waste Air and Waste Gas Treatment:
558 Overview, Challenges, Operational Efficiency, and Current Trends. *Sustainability*, **12**(20),
559 8577.

560 20. Doleman, J.F., Grisar, K., Van Liedekerke, L., Saha, S., Roe, M., Tapp, H.S., Mithen,
561 R.F. 2017. The contribution of alliaceous and cruciferous vegetables to dietary sulphur
562 intake. *Food Chemistry*, **234**, 38-45.

563 21. Duangmanee, T. 2009. Microaeration for hydrogen sulfide removal from biogas. in: *Civil*
564 *and Environmental Engineering*, Vol. Doctor of Philosophy, Iowa State University.

565 22. Dykstra, C.M., Pavlostathis, S.G. 2021. Hydrogen sulfide affects the performance of a
566 methanogenic bioelectrochemical system used for biogas upgrading. *Water Res.*, **200**,
567 117268.

568 23. EBA, E.B.A. 2017. Natural gas and biomethane for use in transport and biomethane for
569 injection in the natural gas network. in: *Part 2: Automotive fuel specifications (EN 16723 –*
570 *Part 2)*.

571 24. Fernández, M., Ramírez, M., Pérez, R.M., Gómez, J.M., Cantero, D. 2013. Hydrogen
572 sulphide removal from biogas by an anoxic biotrickling filter packed with Pall rings. *Chem.*
573 *Eng. J.*, **225**, 456-463.

574 25. Finster, K. 2008. Microbiological disproportionation of inorganic sulfur compounds. *J.*
575 *Sulphur Chem.*, **29**(3-4), 281-292.

576 26. Fontaine, D., Eriksen, J., Sørensen, P. 2021. Sulfur from biogas desulfurization: Fate of S
577 during storage in manure and after application to plants. *Sci. Total Environ.*, **754**, 142180.

578 27. Forouzanmehr, F., Solon, K., Maisonnave, V., Daniel, O., Volcke, E.I.P., Gillot, S.,
579 Buffiere, P. 2021. Sulfur transformations during two-stage anaerobic digestion and
580 intermediate thermal hydrolysis. *Sci. Total Environ.*, 151247.

581 28. Foss, M.M., Head, C. 2004. Interstate natural gas–quality specifications &
582 interchangeability. *Center for Energy Economics, Bureau of Economic Geology, University*
583 *of Texas at Austin*.

584 29. Gabriel, D., Deshusses, M.A. 2003. Performance of a full-scale biotrickling filter treating
585 H2S at a gas contact time of 1.6 to 2.2 seconds. *Environ. Prog.*, **22**(2), 111-118.

586 30. Georgiadis, A.G., Charisiou, N.D., Goula, M.A. 2020. Removal of Hydrogen Sulfide
587 From Various Industrial Gases: A Review of The Most Promising Adsorbing Materials.
588 *Catalysts*, **10**(5), 521.

589 31. Gerber, P.J., Steinfeld, H., Henderson, B., Mottet, A., Opio, C., Dijkman, J., Falcucci, A.,
590 Tempio, G. 2013. *Tackling climate change through livestock: a global assessment of*
591 *emissions and mitigation opportunities*. Food and Agriculture Organization of the United
592 Nations (FAO).

32. GWE. 2021. The SULFURIX™ Wet Biogas Scrubber for hydrogen sulfide removal, Global Water & Energy

33. Hao, T.-w., Xiang, P.-y., Mackey, H.R., Chi, K., Lu, H., Chui, H.-k., van Loosdrecht, M.C.M., Chen, G.-H. 2014. A review of biological sulfate conversions in wastewater treatment. *Water Res.*, **65**, 1-21.

34. Haosagul, S., Prommeenate, P., Hobbs, G., Pisutpaisal, N. 2020. Sulfide-oxidizing bacteria community in full-scale bioscrubber treating H2S in biogas from swine anaerobic digester. *Renew. Energy*, **150**, 973-980.

35. Hilton, B.L., Oleszkiewicz, J.A. 1988. Sulfide-Induced Inhibition of Anaerobic Digestion. *J. Environ. Eng.*, **114**(6), 1377-1391.

36. Huertas, J.K., Quipuzco, L., Hassanein, A., Lansing, S. 2020. Comparing Hydrogen Sulfide Removal Efficiency in a Field-Scale Digester Using Microaeration and Iron Filters. *Energies*, **13**(18), 4793.

37. Huynh Nhut, H., Le Thi Thanh, V., Tran Le, L. 2020. Removal of H2S in biogas using biotrickling filter: Recent development. *Process Saf. Environ. Prot.*, **144**, 297-309.

38. Jeníček, P., Horejš, J., Pokorná-Krayzelová, L., Bindzar, J., Bartáček, J. 2017. Simple biogas desulfurization by microaeration – Full scale experience. *Anaerobe*, **46**, 41-45.

39. Jeong, J.-Y., Son, S.-M., Pyon, J.-H., Park, J.-Y. 2014. Performance comparison between mesophilic and thermophilic anaerobic reactors for treatment of palm oil mill effluent. *Bioresour. Technol.*, **165**, 122-128.

40. Jones, B.D., Ingle, J.D. 2005. Evaluation of redox indicators for determining sulfate-reducing and dechlorinating conditions. *Water Res.*, **39**(18), 4343-4354.

41. Kapoor, R., Ghosh, P., Kumar, M., Sengupta, S., Gupta, A., Kumar, S.S., Vijay, V., Kumar, V., Kumar Vijay, V., Pant, D. 2020. Valorization of agricultural waste for biogas based circular economy in India: A research outlook. *Bioresour. Technol.*, **304**, 123036.

42. Khanal, S.K., Huang, J.-C. 2006. Online Oxygen Control for Sulfide Oxidation in Anaerobic Treatment of High-Sulfate Wastewater. *Water Environment Research*, **78**(4), 397-408.

43. Khanal, S.K., Shang, C., Huang, J.-C. 2003. Use of ORP (oxidation-reduction potential) to control oxygen dosing for online sulfide oxidation in anaerobic treatment of high sulfate wastewater. *Water Science and Technology*, **47**(12), 183-189.

44. Krischan, J., Makaruk, A., Harasek, M. 2012. Design and scale-up of an oxidative scrubbing process for the selective removal of hydrogen sulfide from biogas. *J. Hazard. Mater.*, **215-216**, 49-56.

45. Labatut, R.A., Angenent, L.T., Scott, N.R. 2014. Conventional mesophilic vs. thermophilic anaerobic digestion: A trade-off between performance and stability? *Water Res.*, **53**, 249-258.

46. Lens, P.N.L., Visser, A., Janssen, A.J.H., Pol, L.W.H., Lettinga, G. 1998. Biotechnological Treatment of Sulfate-Rich Wastewaters. *Critical Reviews in Environmental Science and Technology*, **28**(1), 41-88.

47. Li, C., Champagne, P., Anderson, B.C. 2013. Biogas production performance of mesophilic and thermophilic anaerobic co-digestion with fat, oil, and grease in semi-continuous flow digesters: effects of temperature, hydraulic retention time, and organic loading rate. *Environ. Tech.*, **34**(13-14), 2125-2133.

637 48. Li, J., Liang, Y., Miao, Y., Wang, D., Jia, S., Liu, C.-H. 2020. Metagenomic insights into
638 aniline effects on microbial community and biological sulfate reduction pathways during
639 anaerobic treatment of high-sulfate wastewater. *Sci. Total Environ.*, **742**, 140537.

640 49. Lin, H., King, A., Williams, N., Hu, B. 2017. Hydrogen sulfide removal via appropriate
641 metal ions dosing in anaerobic digestion. *Environmental Progress & Sustainable Energy*,
642 **36**(5), 1405-1416.

643 50. Lin, W.-C., Chen, Y.-P., Tseng, C.-P. 2013. Pilot-scale chemical–biological system for
644 efficient H2S removal from biogas. *Bioresour. Technol.*, **135**, 283-291.

645 51. Liu, C.-G., Xue, C., Lin, Y.-H., Bai, F.-W. 2013. Redox potential control and applications
646 in microaerobic and anaerobic fermentations. *Biotechnol. Adv.*, **31**(2), 257-265.

647 52. Liu, Z.-h., Yin, H., Lin, Z., Dang, Z. 2018. Sulfate-reducing bacteria in anaerobic
648 bioprocesses: basic properties of pure isolates, molecular quantification, and controlling
649 strategies. *Environ. Technol. Rev.*, **7**(1), 46-72.

650 53. López, L.R., Dorado, A.D., Mora, M., Gamisans, X., Lafuente, J., Gabriel, D. 2016.
651 Modeling an aerobic biotrickling filter for biogas desulfurization through a multi-step
652 oxidation mechanism. *Chem. Eng. J.*, **294**, 447-457.

653 54. Lupitskyy, R., Alvarez-Fonseca, D., Herde, Z.D., Satyavolu, J. 2018. In-situ prevention of
654 hydrogen sulfide formation during anaerobic digestion using zinc oxide nanowires. *J.*
655 *Environ. Chem. Eng.*, **6**(1), 110-118.

656 55. McCauley, J.I., Labeeuw, L., Jaramillo-Madrid, A.C., Nguyen, L.N., Nghiem, L.D.,
657 Chaves, A.V., Ralph, P.J. 2020. Management of Enteric Methanogenesis in Ruminants by
658 Algal-Derived Feed Additives. *Current Pollution Reports*, **6**(3), 188-205.

659 56. McFarland, M.J., Jewell, W.J. 1989. In situ control of sulfide emissions during the
660 thermophilic (55°C) anaerobic digestion process. *Water Res.*, **23**(12), 1571-1577.

661 57. Nagendranatha Reddy, C., Bae, S., Min, B. 2019. Biological removal of H2S gas in a
662 semi-pilot scale biotrickling filter: Optimization of various parameters for efficient removal
663 at high loading rates and low pH conditions. *Bioresour. Technol.*, **285**, 121328.

664 58. Nghiem, L.D., Manassa, P., Dawson, M., Fitzgerald, S.K. 2014. Oxidation reduction
665 potential as a parameter to regulate micro-oxygen injection into anaerobic digester for
666 reducing hydrogen sulphide concentration in biogas. *Bioresour. Technol.*, **173**, 443-447.

667 59. Nguyen, L.N., Kumar, J., Vu, M.T., Mohammed, J.A.H., Pathak, N., Commault, A.S.,
668 Sutherland, D., Zdarta, J., Tyagi, V.K., Nghiem, L.D. 2021. Biomethane production from
669 anaerobic co-digestion at wastewater treatment plants: A critical review on development and
670 innovations in biogas upgrading techniques. *Sci. Total Environ.*, **765**, 142753.

671 60. Nisbet, E.G., Fisher, R.E., Lowry, D., France, J.L., Allen, G., Bakkaloglu, S., Broderick,
672 T.J., Cain, M., Coleman, M., Fernandez, J., Forster, G., Griffiths, P.T., Iverach, C.P., Kelly,
673 B.F.J., Manning, M.R., Nisbet-Jones, P.B.R., Pyle, J.A., Townsend-Small, A., al-Shalaan, A.,
674 Warwick, N., Zazzeri, G. 2020. Methane Mitigation: Methods to Reduce Emissions, on the
675 Path to the Paris Agreement. *Rev. Geophys.*, **58**(1), e2019RG000675.

676 61. O'Flaherty, V., Mahony, T., O'Kennedy, R., Colleran, E. 1998. Effect of pH on growth
677 kinetics and sulphide toxicity thresholds of a range of methanogenic, syntrophic and
678 sulphate-reducing bacteria. *Process Biochem.*, **33**(5), 555-569.

679 62. Okoro, O.V., Sun, Z. 2019. Desulphurisation of Biogas: A Systematic Qualitative and
680 Economic-Based Quantitative Review of Alternative Strategies. *ChemEngineering*, **3**(3), 76.

681 63. Piccolo, N., Goel, R., Snowling, S., Kim, Y. 2021. Modeling the anaerobic digestion of
682 wastewater sludge under sulfate-rich conditions. *Water Environ. Res.*, **93**(10), 2084-2096.

683 64. Pipatmanomai, S., Kaewluan, S., Vitidsant, T. 2009. Economic assessment of biogas-to-
684 electricity generation system with H2S removal by activated carbon in small pig farm.
685 *Applied Energy*, **86**(5), 669-674.

686 65. Poser, A., Lohmayer, R., Vogt, C., Knoeller, K., Planer-Friedrich, B., Sorokin, D.,
687 Richnow, H.-H., Finster, K. 2013. Disproportionation of elemental sulfur by haloalkaliphilic
688 bacteria from soda lakes. *Extremophiles*, **17**(6), 1003-1012.

689 66. Rathnayake, D., Bal Krishna, K.C., Kastl, G., Sathasivan, A. 2021. The role of pH on
690 sewer corrosion processes and control methods: A review. *Sci. Total Environ.*, **782**, 146616.

691 67. Ren, B., Zhao, Y., Lyczko, N., Nzihou, A. 2019. Current Status and Outlook of Odor
692 Removal Technologies in Wastewater Treatment Plant. *Waste and Biomass Valorization*,
693 **10**(6), 1443-1458.

694 68. Rolewicz-Kalińska, A., Lelicińska-Serafin, K., Manczarski, P. 2021. Volatile organic
695 compounds, ammonia and hydrogen sulphide removal using a two-stage membrane
696 biofiltration process. *Chem. Eng. Res. Des.*, **165**, 69-80.

697 69. Schiavon Maia, D.C., Niklevicz, R.R., Arioli, R., Frare, L.M., Arroyo, P.A., Gimenes,
698 M.L., Pereira, N.C. 2017. Removal of H2S and CO2 from biogas in bench scale and the pilot
699 scale using a regenerable Fe-EDTA solution. *Renew. Energy*, **109**, 188-194.

700 70. Scholz, M., Melin, T., Wessling, M. 2013. Transforming biogas into biomethane using
701 membrane technology. *Renew. Sust. Energ. Rev.*, **17**, 199-212.

702 71. Shelford, T.J., Gooch, C.A., Lansing, S.A. 2019. Performance and Economic Results for
703 Two Full-scale Biotrickling Filters to Remove H2S from Dairy Manure-derived Biogas.
704 *Appl. Eng. Agric.*, **35**(3), 283-291.

705 72. Shi, X., Gao, G., Tian, J., Wang, X.C., Jin, X., Jin, P. 2020. Symbiosis of sulfate-reducing
706 bacteria and methanogenic archaea in sewer systems. *Environ. Int.*, **143**, 105923.

707 73. Shin, H.S., Oh, S.E., Bae, B.U. 1996. Competition between SRB and MPB According to
708 Temperature Change in the Anaerobic Treatment of Tannery Wastes Containing High
709 Sulfate. *Environ. Tech.*, **17**(4), 361-370.

710 74. Song, X., Luo, W., Hai, F.I., Price, W.E., Guo, W., Ngo, H.H., Nghiem, L.D. 2018a.
711 Resource recovery from wastewater by anaerobic membrane bioreactors: Opportunities and
712 challenges. *Bioresour. Technol.*, **270**, 669-677.

713 75. Song, X., Luo, W., McDonald, J., Khan, S.J., Hai, F.I., Guo, W., Ngo, H.H., Nghiem,
714 L.D. 2018b. Effects of sulphur on the performance of an anaerobic membrane bioreactor:
715 Biological stability, trace organic contaminant removal, and membrane fouling. *Bioresour.*
716 *Technol.*, **250**, 171-177.

717 76. Surita, S.C., Tansel, B. 2015. Evaluation of a Full-Scale Water-Based Scrubber for
718 Removing Siloxanes from Digester Gas: A Case Study. *Water Environ. Res.*, **87**(5), 444-449.

719 77. Tang, Y., Shigematsu, T., Ikbal, Morimura, S., Kida, K. 2004. The effects of micro-
720 aeration on the phylogenetic diversity of microorganisms in a thermophilic anaerobic
721 municipal solid-waste digester. *Water Res.*, **38**(10), 2537-2550.

722 78. Tomàs, M., Fortuny, M., Lao, C., Gabriel, D., Lafuente, J., Gamisans, X. 2009. Technical
723 and economical study of a full-scale biotrickling filter for H2S removal from biogas. *Water*
724 *Pract. Technol.*, **4**(2).

79. Tran, T.T.T., Kannoorpatti, K., Padovan, A., Thennadil, S. 2021a. Effect of pH regulation by sulfate-reducing bacteria on corrosion behaviour of duplex stainless steel 2205 in acidic artificial seawater. *R. Soc. Open Sci.*, **8**(1), 200639.

80. Tran, T.T.T., Kannoorpatti, K., Padovan, A., Thennadil, S. 2021b. Sulphate-Reducing Bacteria's Response to Extreme pH Environments and the Effect of Their Activities on Microbial Corrosion. *Appl. Sci.*, **11**(5), 2201.

81. Vallero, M.V.G., Camarero, E., Lettinga, G., Lens, P.N.L. 2004. Thermophilic (55–65 °C) and Extreme Thermophilic (70–80 °C) Sulfate Reduction in Methanol and Formate-Fed UASB Reactors. *Biotechnol. Prog.*, **20**(5), 1382-1392.

82. Varol, A., Ugurlu, A. 2017. Comparative evaluation of biogas production from dairy manure and co digestion with maize silage by CSTR and new anaerobic hybrid reactor. *Eng. Life Sci.*, **17**.

83. Vikrant, K., Kailasa, S.K., Tsang, D.C.W., Lee, S.S., Kumar, P., Giri, B.S., Singh, R.S., Kim, K.-H. 2018. Biofiltration of hydrogen sulfide: Trends and challenges. *J. Clean. Prod.*, **187**, 131-147.

84. Visser, A., Gao, Y., Lettinga, G. 1993. Effects of short-term temperature increases on the mesophilic anaerobic breakdown of sulfate containing synthetic wastewater. *Water Res.*, **27**(4), 541-550.

85. Wellinger, A., Lindberg, A. 1999. Biogas upgrading and utilization. *IEA bioenergy task*. pp. 3-19.

86. Xiao, C., Ma, Y., Ji, D., Zang, L. 2017. Review of desulfurization process for biogas purification. *IOP Conference Series: Earth and Environmental Science*, **100**, 012177.

87. Yan, L., Ye, J., Zhang, P., Xu, D., Wu, Y., Liu, J., Zhang, H., Fang, W., Wang, B., Zeng, G. 2018. Hydrogen sulfide formation control and microbial competition in batch anaerobic digestion of slaughterhouse wastewater sludge: Effect of initial sludge pH. *Bioresour. Technol.*, **259**, 67-74.

88. Yang, F., Bai, L., Li, P., Li, Q., Luo, L., Li, W. 2019. Improved methane production and sulfate removal by anaerobic co-digestion corn stalk and levulinic acid wastewater pretreated by calcium hydroxide. *Sci. Total Environ.*, **691**, 499-505.

89. Zhang, L., De Schryver, P., De Gusseme, B., De Muynck, W., Boon, N., Verstraete, W. 2008. Chemical and biological technologies for hydrogen sulfide emission control in sewer systems: A review. *Water Res.*, **42**(1), 1-12.

90. Zhen, G., Lu, X., Niu, J., Su, L., Chai, X., Zhao, Y., Li, Y.-Y., Song, Y., Niu, D. 2013. Inhibitory effects of a shock load of Fe(II)-mediated persulfate oxidation on waste activated sludge anaerobic digestion. *Chem. Eng. J.*, **233**, 274-281.

91. Zhou, Q., Jiang, X., Li, X., Jiang, W. 2016. The control of H2S in biogas using iron ores as in situ desulfurizers during anaerobic digestion process. *Appl. Microbiol. Biotechnol.*, **100**(18), 8179-8189.

92. Zhuo, Y., Han, Y., Qu, Q., Li, J., Zhong, C., Peng, D. 2019. Characteristics of low H2S concentration biogas desulfurization using a biotrickling filter: Performance and modeling analysis. *Bioresour. Technol.*, **280**, 143-150.